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Insight of Weathering Processes Based on Monitoring Surface Characteristic of Tropical Wood Species

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Abstract: The main aim of the presented research was to compare the influence of selected ageing factors, such as UV radiation and complex artificial weathering methods, on the colour, wettability and roughness changes in garapa, tatajuba, courbaril and massaranduba from South America—tropical wood species that are popular for external usage in European countries. Both processes caused wood surfaces to become darker and turn to shades of brown. The highest total colour changes were shown in courbaril wood (wood with the highest extractives content). The wood surface roughness demonstrated variation, depending on the wood section and measurement direction, and increased after ageing treatments. Changes in surface contact angle were significant after the inclusion of water and drying in the weathering process (wettability decreased). Anatomical analyses of the tested tropical woods revealed structural changes after used artificial weathering treatments (distortion between cell elements, degradation of the middle lamella, micro-cracks in cell walls, thinning and degradation of parenchyma cells, cracks along pits within vessels). As a result of desorption tension, the changes caused by UV irradiation were much smaller than those caused by full artificial weathering. Fourier-transform infrared spectroscopy (FTIR) analysis indicated the occurrence of lignin and hemicelluloses oxidative changes after the weathering process which resulted in the formation of carbonyl and carboxyl compounds. The depolymerisation of cellulose was also identified. The results show that the observed changes may affect the long-term durability of finishes applied over wood subjected to weathering factors for a short period before finishing.

Keywords: tropical wood; surface preservation; wood weathering; FTIR; weathered wood roughness; wood degradation

1. Introduction

During the external exposure of wood there are some key procedures which should be followed to reduce the effects of weathering. The natural weathering was defined as a process of irreversible changes to the appearance and properties of wood effected by the long-term impact of outdoor factors, such as the solar radiation, air and oxygen contained within it, and changes in the temperature and humidity (no direct influence of biotic factors should be assumed) [1–7]. This complex phenomenon is caused by solar radiation, hydrolysis, and the leaching of wood components [8–10]. The harsh outside environment makes it necessary to consider wood durability, in accordance with EN 350-2 [11]. Next, a proper construction solution is required, such as proper usage conditions. Moreover, surface treatments can be used to prolong the service life of wood [12,13].

Despite the high durability of many tropical wood species against biological factors such as fungi or insects, it is always recommended to protect wood surface during outside exposure due to weathering. On the other hand, one of the most important factors in securing sustainable development is utilization of renewable natural materials, which undoubtedly include wood [14]. In order to reduce the environmental burden, the surfaces of wooden elements are not treated with any painting and varnishing products. In addition to the traditional interior design elements, the use of non-treated wood is expanding even further to external use. According to contemporary trends, it is recommended to use untreated wood and allowing it turn grey upon exposure to weather under aboveground conditions over using non-durable wood with applied surface coatings. Many tropical species are considered to be the most durable wood. However, the use of tropical wood has several negative consequences including illegal deforestation. Hence, impacting significant climate changes. Pronounced through net carbon emissions, deforestation leads to a global warming [15]. However, as wood of tropical species is utilized in Europe, knowledge of their weathering characteristic is important to optimize their performance. Materials should be recognizable in terms of their surface properties. The wettability of wood is one of the most significant parameters influencing the gluing as well as the coating processes [16–19]. One of the most critical factors for extending the durability of painted wood is freshness of the wood surface and only a fresh, high-energy surface guarantees optimum adhesion conditions. The loss of coating ability and glueability due to the increasing age of a wood surface was studied over time by several researchers [20–22], who arrived at the conclusion that the changes caused by the weathering are the effect of the migration of wood extractives to wood surfaces after their preparation, which causes a decrease in wood surfaces' wettability.

It is also convenient to determine the direction and degree of colour changes in individual tropical wood species caused by external factors. The aesthetic function of wooden products used externally can be extended by selecting the most resistant wood species in terms of its surface properties stability. Some knowledge about changes occurring in tropical wood species was gained, but mainly during colour testing wood subjected to different weathering treatments [23,24]. This paper is a part of an extensive study determining the influence of artificial weathering on the surface properties of several species of wood from tropical and subtropical zones. The main aim of the presented research is to compare the influence of selected ageing factors such as ultraviolet radiation and complex artificial weathering methods on the colour, wettability and surface roughness changes in garapa (*Apuleia leiocarpa* (Vogel) J.F. Macbr.), tatajuba (*Bagassa guianensis* Aubl.), courbaril (*Hymenea courbaril* L.) and massaranduba (*Manilkara bidendata* (A. DC.) A. Chev.) wood species, as these are popular for external usage in European countries.

2. Materials and Methods

The wood species used in this study are presented in Table 1. All test materials were heartwood, because the heartwood of tropical species is more commercially usable than sapwood. All species came from South America (Brazil) and wood was acquired from DLH Poland (Warsaw, Poland). The material was identified using macroscopic techniques and was deciduous diffuse-porous in all cases. Characterization of the tested wood species was supplemented with density determination, performed in accordance with the ASTM D2395 standard [25].

Wood samples were prepared for investigation and analyses by using standardized methods. To avoid differences in the tested properties caused by differences in wood anatomy, identical samples of each wood species were collected from one log. Each one was sawn to produce planks approximately 4 cm thick. The obtained planks were air-dried in a room with relative humidity up to 50% and a temperature of 21 °C for approximately 6 months before testing. Then, the defect-free planks were sized into samples for the tests. Forty samples of each wood species were prepared, each with a radial and tangential cross-section of 10 × 10 mm^2 and a length of 70 mm. Following Gardner [26] and Liptakova et al. [27], the radial-oriented or tangential-oriented surface of the wood block was planned. The aim was to make wood showing the roughness caused by the cellular structure of wood and only a negligibly small roughness caused by cutting. Moreover, the wood surface is chemically heterogeneous, and therefore does not comply with the requirements of the physicochemical theory of contact angle in a strict sense.

Table 1. Wood species used in tests.

Wood Name	Scientific Name	Plant Family	Special Features	Wood Density * (kg/m^3)
Garapa	*Apuleia leiocarpa* (Vogel) J.F.Macbr.	*Caesalpiniaceae*	Irregular fibre arrangement	739 (16)
Tatajuba	*Bagassa guianensis* Aubl.	*Moraceae*	Irregular fibre arrangement	884 (35)
Courbaril	*Hymenea courbaril* L.	*Fabaceae*	Irregular fibre arrangement, paratracheal parenchyma and in narrow bands	1038 (6)
Massaranduba	*Manilkara bidendata* (A. DC.) A. Chev.	*Sapotaceae*	Irregular fibre arrangement, parenchyma in narrow bands	1131 (18)

* means and standard deviations in parentheses.

2.1. Properties Measurements

The parameters of the colour of unmodified and modified wood were measured on the basis of the mathematical CIE (International Commission on Illumination known as the Commission Internationale de l'Elcairage) L^*C^*h colour space models. The parameter L^* represents lightness. The parameters C^* and h describe the saturation (colour intensity) and hue angle, respectively. The total colour change ΔE^* was determined in accordance with ISO 7724-3 [28]. The 3NH NH300 spectrophotometer made by X-Rite Europe GmbH (Regensdorf, Switzerland) was used to examine the colour parameters. The sensor head was 8 mm in diameter. Measurements were made using a D65 illuminate.

Surface properties can be characterized by the water contact angle (wettability). A single measurement of the water contact angle provides information on several important parameters, such as the surface free energy, contact angle and wetting coefficient or work of adhesion. To predict interactions with wetting materials such as lacquers or adhesives, the surface properties are characterized. The lower the contact angle value (θ), which is a measure of the wetting impact of the substrate by solution, the better the wettability of the material. As soon as the samples were placed in the contact angle measuring apparatus, measurements were started. The contact angle is defined as the angle between the solid surface and the tangent, drawn on the drop-surface, passing through the three-point liquid-solid atmosphere [29]. Using a contact angle analyzer, Haas Phoenix 300 Goniometer (Surface Electro Optics, Suwon City, South Korea), equipped with microscopic lenses, a digital camera connected to a computer with software—image analysis system (Image XP, Surface Electro Optics, version 5.8, Suwon City, South Korea) that provides an image of the drop on the examined wooden surfaces, the contact angles of the expanding droplets (advancing angels) were determined. To test the wettability, a re-distilled water was used as a liquid. All contact angles were measured along the grain direction followed by Gindl et al. [16]. Based on the research of Liptáková et al. [27], the measurements of the contact angle were taken 30 s after each drop of reference liquid.

The roughness was evaluated in accordance with the requirements of ISO 4287 [30]. As part of the conducted research, the arithmetic mean deviation of the assessed profile (R_a) was measured. The surface roughness was tested using the Surftest SJ-210 Series 178-Portable Surface Roughness Tester (Mitutoyo Corporation, Takatsu-ku, Japan). The parameter R_a was measured in parallel and perpendicular to the grain direction.

Properties were measured on a fresh wood surface after UV irradiation and complex artificial weathering treatment. Before and after the treatments, each of the samples were conditioned in a climatic chamber with a temperature of 21 °C and relative humidity of about 50%. Measurements were done for each tested variant 30 times. In case of roughness and wettability testing, measurements were made both on the tangential and radial cross-section.

2.2. UV Irradiation

Four fluorescent 100R's Lightech lamps of 100 W each and the spectrum 300–400 nm (90% of the radiation spectrum is a wavelength of 340–360 nm) were used for irradiating. The time of irradiation was 24 h. The source of radiation applied in this study imitated solar radiation and, in particular, the UVA component of solar radiation. This component causes the greatest changes in the appearance and structure of organic materials exposed in an outdoor environment. This is due to the fact that UVA radiation accounts for 90%–95% of the solar radiation reaching the Earth's surface [31].

2.3. Artificial Weathering

The artificial weathering method was based on the literature [10,32]. It took 30 h to complete one artificial weathering cycle. The first step of each cycle was soaking samples in water at 20 °C for 16 h. The conditions of the second step were 70 °C and 5%–10% RH for 8 h, and the third step was performed at 30 °C and 20%–25% RH with irradiation with UV rays (24 h). The tested wood species were subjected to one and four cycles of artificial weathering. That weathering method was previously used for tropical wood [33], but obtained results regarding the effect of long-term aging.

2.4. Scanning Electron Microscopy SEM

The microstructure of samples was examined using a scanning electron microscope HITACHI, model TM-3000 (Hitachi Ltd., Tokyo, Japan) with a digital image record. The samples were chosen randomly and put into the vacuum chamber. The photos at accelerating voltages equal to 5 kV were taken with 1000 magnification and the record was saved using SEM software (TM3000, Hitachi Ltd., Tokyo, Japan). The analysis was conducted at least in three repetitions for each sample.

2.5. FTIR

The spectra were recorded using an Agilent Cary 630 FTIR spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a single bounce diamond ATR unit. Scans were performed in the range of 650–4000 cm^{-1} with a resolution of 4 cm^{-1}, and 64 scans for each sample. Background correction with 32 scans was performed after each measurement. The measurements were conducted in three repetitions.

2.6. Statistical Analysis

Statistical analysis of the test results was carried out using Statistica v. 10 software (TIBCO Software Inc., Palo Alto, CA, USA). Data were analysed and provided as the mean ± standard deviation, the scatter plot of results around the median, and minimum and maximum values. To compare and determine the significance of difference between data, *t*-test was used. Analysis of variance (ANOVA) was used to determine the influence of UV irradiation, full artificial weathering process and anatomical properties, such as the direction of measurements and cross-section (tangential or radial).

3. Results and Discussion

3.1. Colour Changes

The colour of wood exposed to external conditions can rapidly change in quite a short time [23]. Due to the photodegradation (photooxidation) of lignin and extractives, wood colour usually turns yellowish or brown. During UV radiation, the surface colour changed visibly. The deviation ΔE^* in all the wood species exceeds the value of 3 (Table 2), which is considered the limit for visibility to the naked eye [34]. The Figure 1 shows the clear contrast between wood surfaces when they were fresh and after different treatments. Distinctive differences in colour can be seen. In general, wood surfaces become darker and turn to shades of brown. The previous studies conducted on softwoods [35], and tropical wood species as well [36], confirmed that the most rapid changes in Δ*E** occurred during the first stages of UV radiation. The tested wood species are rich in extractives [37]. The rapid change in the first hours of exposure could have been caused by the reaction of extractives contained within the wood to UV radiation. Pandey [38] compared the behaviour of unextracted and extractive free wood of *Acacia auriculaeformis*. The unextracted wood surface showed a rapid colour change at the initial period of exposure, which decreased upon prolonged exposure. Tests on wood (coniferous, deciduous) from moderate climates during weathering in natural external conditions did not show a wide range of changes, which can be explained by the relatively low content of extractives. The maximum value of Δ*E** was for spruce—34.1 after 12 months of weathering. In the study here and in the case of courbaril wood, Δ*E** = 51.21 was caused only after 24 h of UV radiation. Soaking wood samples in water meant that the wood dyes contained within were washed out, and accumulated on the top layers of wood, which caused wood darkening (lower values of *L**)—Table 3. The full artificial weathering process gave higher colour changes and also a response to changes in the appearance of wood surfaces in natural external conditions. In all cases of the tested wood species, wood became darker both after UV irradiation and after full weathering treatment. Conducting a higher number of artificial weathering cycles caused higher changes.

Table 2. Overall colour change (Δ*E**) during exposure.

Species	Δ*E**		
	After 24 h UV Irradiation	After 1 Cycle of Artificial Weathering	After 4 Cycles of Artificial Weathering
Garapa	4.4	6.3	8.4
Tatajuba	7.5	9.4	12.0
Courabril	52.2	58.0	58.4
Massaranduba	8.2	9.5	13.2

Table 3. Coordinates of CIE *L*C*h* colour system for individual woods (means and standard deviations in parentheses).

Species	Before Exposure			After 24 h UV Irradiation			After 1 Cycle of Artificial Weathering			After 4 Cycles of Artificial Weathering		
	*L**	*C**	*h*	*L**	*C**	*h*	*L**	*C**	*h*	*L**	*C**	*h*
Garapa	71.4 (3.1)	33.5 (2.9)	65.8 (1.3)	68.6 (0.7)	36.7 (1.3)	65.1 (2.7)	65.9 (2.5)	34.9 (1.4)	64.9 (3.4)	64.9 (2.1)	32.8 (1.5)	65.8 (2.1)
Tatajuba	58.6 (1.2)	32.8 (1.7)	69.3 (1.2)	51.8 (1.3)	35.1 (1.0)	65.6 (1.3)	49.9 (1.6)	34.0 (1.0)	63.7 (1.3)	46.9 (1.3)	32.2 (1.4)	60.9 (1.8)
Courabril	53.3 (3.7)	25.5 (1.9)	71.4 (1.3)	41.2 (1.8)	20.0 (2.1)	65.8 (2.3)	37.6 (2.2)	18.3 (1.9)	62.3 (1.5)	35.1 (1.7)	18.8 (2.0)	60.6 (1.3)
Massaranduba	50.0 (1.6)	23.9 (0.7)	42.5 (0.4)	43.8 (1.2)	21.2 (1.3)	48.1 (1.2)	43.0 (1.5)	21.9 (1.0)	49.2 (2.4)	40.3 (2.2)	18.1 (1.8)	48.8 (2.1)

In the case of wood species of a lighter colour—garapa and tatajuba—*C** and *h* values followed a similar trend: they increased after UV irradiation and decreased during the full artificial weathering process. In the case of courbaril and massaranduba wood (both of darker colour), *C** value was lower after each treatment. The different behaviours of individual wood species regarding chromatic parameters probably could have been caused by the presence of specific types of extractives in the wood. While studying the influence of extractives on discoloration, Pandey [38] found that this relation is, to a great extent, dependent on the nature and chemical composition. Both Δ*C** and Δ*h* are determined mainly by the changes in the chromophore groups in extractives and change through the lignin degradation and later leaching. Thus, it can be assumed that a higher proportion of extractives within one wood species can cause a darker colour of the wood. The test results of tropical wood discoloration caused by simulated sunlight [23] confirmed that lighter samples manifest a larger colour change due to sunlight. In the research here, the results were different. The scope of change was similar for both garapa, tatajuba of light colour and massaranduba of dark colour. Massive colour changes (total colour change ΔE^*) showed courbaril wood, known for its high extractives content [37].

According to the above, the conclusion can be frawn that wood, as a complex structure, differing between species, requires a unique approach for each individual species. Especially in the case of tropical wood, which, despite many reports, remains little known. With a large number of different wood types, the formulation of dependencies is only indicative. Due to the huge variability of properties and structure details [39], deep knowledge is necessary, especially in the context of proper wood application.

Figure 1. Visual comparison of contrast among the exposed and non-exposed surface (from left: garapa, tatajuba, courbaril and massaranduba; from top: fresh wood, after 24 h of UV irradiation, after 1 cycle of artificial weathering, after 4 cycles of artificial weathering).

3.2. Roughness Changes

The results of the surface roughness R_a of tested wood species are shown on Figures 2 and 3. Tests were performed on both the tangential and radial wood section, parallel and perpendicular to the grain. The wood roughness is a complex phenomenon because wood is an anisotropic and heterogeneous material, and several factors such as anatomical differences and the machining properties should be considered in evaluating the surface roughness of wood [40]. The roughness of the tested wood species demonstrated variation, depending on the wood section and the measurement direction (parallel or perpendicular to the grain). As can be seen from Figures 2 and 3, mostly radial sections showed higher roughness. All tested wood species are characterized with interlocked fibres, which causes variable fibre orientation. As a result, they are cut in various ways on the radial section of the wood. In general, $R_{a\perp}$ values (measured perpendicular to the wood fibres) were twice as high as those measured parallel to the grain (R_{aII}). Wood, as a non-homogeneous material, shows differences in its properties depending on the direction. The roughness perpendicular to the fibres is mostly caused by irregularities in the structural element sizes, such as the vessels' diameter.

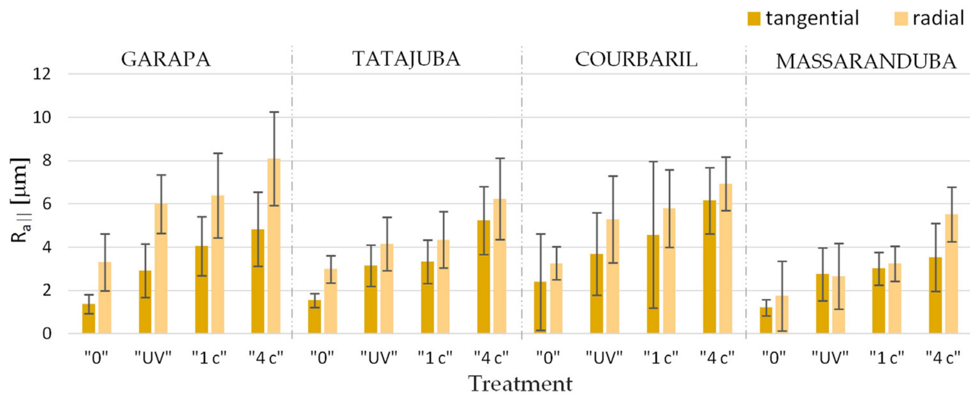

Figure 2. Roughness (R_{aII}) along the fibres of tested wood species: "O"—fresh wood, "UV"—after 24 h of UV irradiation, "1 c"—after one cycle of artificial weathering, "4 c"—after four cycles of artificial weathering.

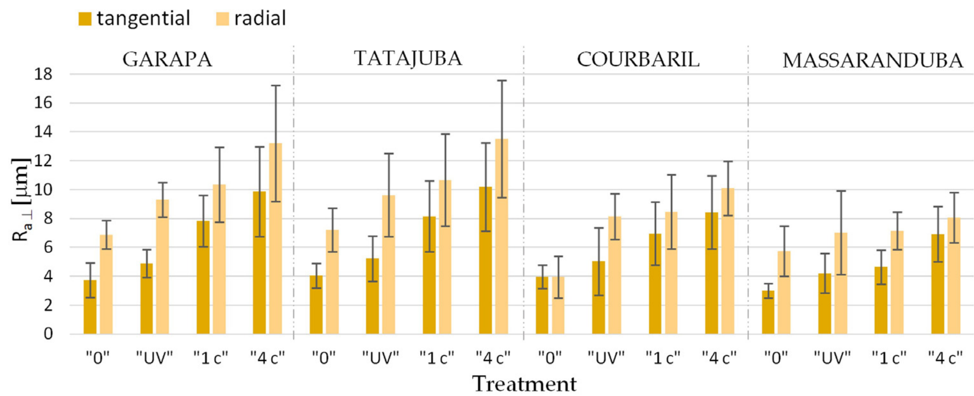

Figure 3. Roughness ($R_{a\perp}$) perpendicular to the fibres of tested wood species: "O"—fresh wood, "UV"—after 24 h of UV irradiation, "1 c"—after one cycle of artificial weathering, "4 c"—after four cycles of artificial weathering.

According to the ANOVA results (at the 0.05 confidence level), the surface roughness varied significantly depending on the examined factor (species, section, used methods of weathering) (Table 4). However, the most important influencing factors were wood section and kind of treatments used (45% and 46%, respectively).

Table 4. Statistical evaluation of the factors influencing wood surface roughness.

Feature	Factor	Sum of Squares	Mean Sum of Squares	Fisher's F-Test	Significance Level	Factor of Influence
		SS	MS	F	*p*	%
R_{aII}	Intercept	513.3754	513.3754	1365.962	0.000000 *	-
	Species	12.3166	4.1055	10.924	0.000102 *	9
	Section	19.6308	19.6308	52.233	0.000000 *	45
	Treatment	59.8475	19.9492	53.080	0.000000 *	46
	Error	9.0200	0.3758	-	-	1
$R_{a\perp}$	Intercept	1700.612	1700.612	709.3115	0.000000 *	-
	Species	27.501	9.167	3.8235	0.022689 *	12
	Section	34.875	34.875	14.5462	0.000842 *	46
	Treatment	90.381	30.127	12.5657	0.000039 *	41
	Error	57.541	2.398	-	-	4

*—significant at the 0.05 level.

Generally, the surface roughness values increased due to UV irradiation when compared with the surface roughness values of the control wood samples. The differences were statistically significant at the 0.05 confidence level in most of the cases. UV treatment initiates surface oxidation (increase in the acid/base or polar component), which leads to the introduction of functional (carboxyl) groups [15]. R_a values increased after UV irradiation at a similar level as after one cycle of artificial weathering and significantly higher after a further full weathering treatment. Exposure to UV light and water caused fewer cracks. Soaking wood in water and then drying caused the raising of wood fibres. Initial roughness was not decisive in the scope of changes.

3.3. Wettability Changes

The effects of UV irradiation on the changes in the chemistry of wood surfaces were verified using contact angles with distilled water. Results are given in Table 5. The wettability decreased (contact angle increased) for all investigated surfaces with treatment by UV radiation and the full artificial weathering process. The contact angle (θ) measurements with distilled water showed the same trend for the radial and tangential surfaces of all tested wood species. In contrast to changes in surface roughness, changes in wettability caused by exposure to UV light were not statistically significant. In general, for most of all tested wood species, UV irradiation for 24 h caused an increase in surface contact angle of 8%–15% (decrease in wettability). The inclusion of water in the weathering process resulted in a much wider range of changes. Currently, one full weathering cycle caused a change in the wettability of the surface of up to 51% (for massaranduba wood). Further ageing resulted in minor changes. Carrying out four weathering cycles resulted in slightly larger wettability changes. This can be explained by the fact that leaching of extractives with water and its accumulation on the wood surface effect decreased the degree of surface hydrophilicity [40,41]. Thus, the decrease in wetting of a wood surface is related to the chemical changes after outdoor exposure. Leaching of the extractives from the surface of weathered wood reduces water repellence, while the degradation of lignin results in a more hydrophilic surface [40]. Garapa wood has shown a different nature of change. UV exposure caused a slight decrease in the contact angle (increase in wettability). This reverse direction of change can be explained by the fact that garapa wood has the lowest density in the studied group. Thus, UV penetration of structure was more possible. The degradation of hydrophobic lignin and allowing cellulose to become more abundant on the wood surface increased the degree of surface hydrophilicity [41].

Table 5. Contact angles (θ) tested wood species before and after used weathering treatments (means and standard deviations in parentheses).

Species	Section	Before Exposure (°)	After 25 h UV Irradiation (°)	After 1 Cycle of Artificial Weathering (°)	After 4 Cycles of Artificial Weathering (°)
Garapa	tangential	66.4 (5.8)	59.5 (5.2)	70.9 (4.5)	78.0 (7.5)
	radial	49.9 (5.3)	55.3 (3.1)	65.0 (6.3)	77.0 (5.6)
Tatajuba	tangential	48.4 (6.2)	52.9 (4.7)	59.8 (5.1)	63.3 (3.7)
	radial	47.8 (6.5)	53.5 (6.0)	62.2 (4.7)	65.8 (4.6)
Courabril	tangential	49.8 (5.0)	55.8 (2.5)	68.3 (4.5)	69.3 (4.4)
	radial	45.7 (5.2)	54.1 (6.4)	66.4 (4.1)	68.2 (5.8)
Massaranduba	tangential	44.4 (4.4)	49.6 (4.5)	66.8 (3.7)	74.1 (6.9)
	radial	43.2 (4.4)	45.3 (3.6)	65.1 (8.1)	70.9 (7.5)

UV light can destruct pits, which enable coatings and adhesives to penetrate deeper into the wood surface, and therefore enhance mechanical anchoring. Each of the chemical components of wood (i.e., lignin, cellulose, hemi-cellulose or extractives) is sensitive to UV radiation with a consequential deterioration effect. Of these chemical constituents, lignin, because of its strong ultraviolet absorbing characteristic due to the phenolic nature of its molecular architecture, appears to be oxidized and degraded very rapidly by UV light [42]. This information is important in the context that, in the wood working industry, UV irradiation is usually used for the curing of coating systems and a UV source mostly exists in the production line, so it seems feasible to integrate UV-modification into the finishing process. Contrary to other activation methods, UV treatment is suitable for an online manufacturing process [16].

According to ANOVA results (at the 0.05 confidence level), the surface wettability varied significantly depending on the used methods of weathering (Table 6). It was the most important influencing factor (76%). Wood section and wood species did not have a significant influence.

Table 6. Statistical evaluation of the factors influencing wood surface wettability.

Factor	Sum of Squares	Mean Sum of Squares	Fisher's F-Test	Significance Level	Factor of Influence
	SS	MS	F	*p*	%
Intercept	117,570.1	117,570.1	6298.194	0.000000 *	-
Species	518.4	172.8	9.256	0.000300 *	18
Section	49.1	49.1	2.632	0.117806 NS	5
Treatment	2112.0	704.0	37.714	0.000000 *	76
Error	448.0	18.7	-	-	1

*—significant at the 0.05 level, NS—not significant.

3.4. Structure Changes

Microstructure changes in the wood surface properties were characterized using SEM. Most of the previous conducted studies regarded softwoods. Figure 4 presents images of wood surface before weathering, after UV irradiation and after full ageing treatment. The untreated samples indicted cell walls and some easy to recognize damages caused by splitting after mechanical preparation.

As a result of weathering, some characteristic anatomical changes occurred. Both UV irradiation and full artificial weathering treatment caused the apparent erosion of wood structure elements. This also agreed with previous studies of wood surface deterioration after exposure to sunlight or UV irradiation [43]. A number of distinctive cracks formed in the specimens after exposure to UV light. Distortion and creasing of the cells wall occurred in the longitudinal direction and resulted in the delamination of the cell walls—degradation of S1 layer [44]. The deterioration of connections between cell elements were associated with the degradation of the middle lamella. At the same time, it confirmed the degradation of lignin. The SEM micrographs revealed much more degradation in wood specimens subjected to the full weathering process. Heavy damage to the pits within vessels was observed. Most of the cracks on the pits formed transverse to the cell axis, which resulted from microfibril orientation in the S3 layer of cell walls, produced from condensing compounds of degraded lignin and hemicelluloses. In all analysed specimens, thinning of parenchyma cell walls and their shrinkage or total degradation were observed. As seen in Figure 4, deterioration was present in parenchyma cells of wood rays. Similar observations were made by Mamoňová and Reinprecht [44], who tested tropical wood species weathered in natural conditions. They stated that the highest incidence of micro-cracks after weathering is correlated with wood density.

The changes caused by UV irradiation were much smaller than those caused by full artificial weathering. Thus, this confirmed the influence of desorption tensions in structure changes that caused disruptions to wooden tissue subjected to cyclic humidity changes.

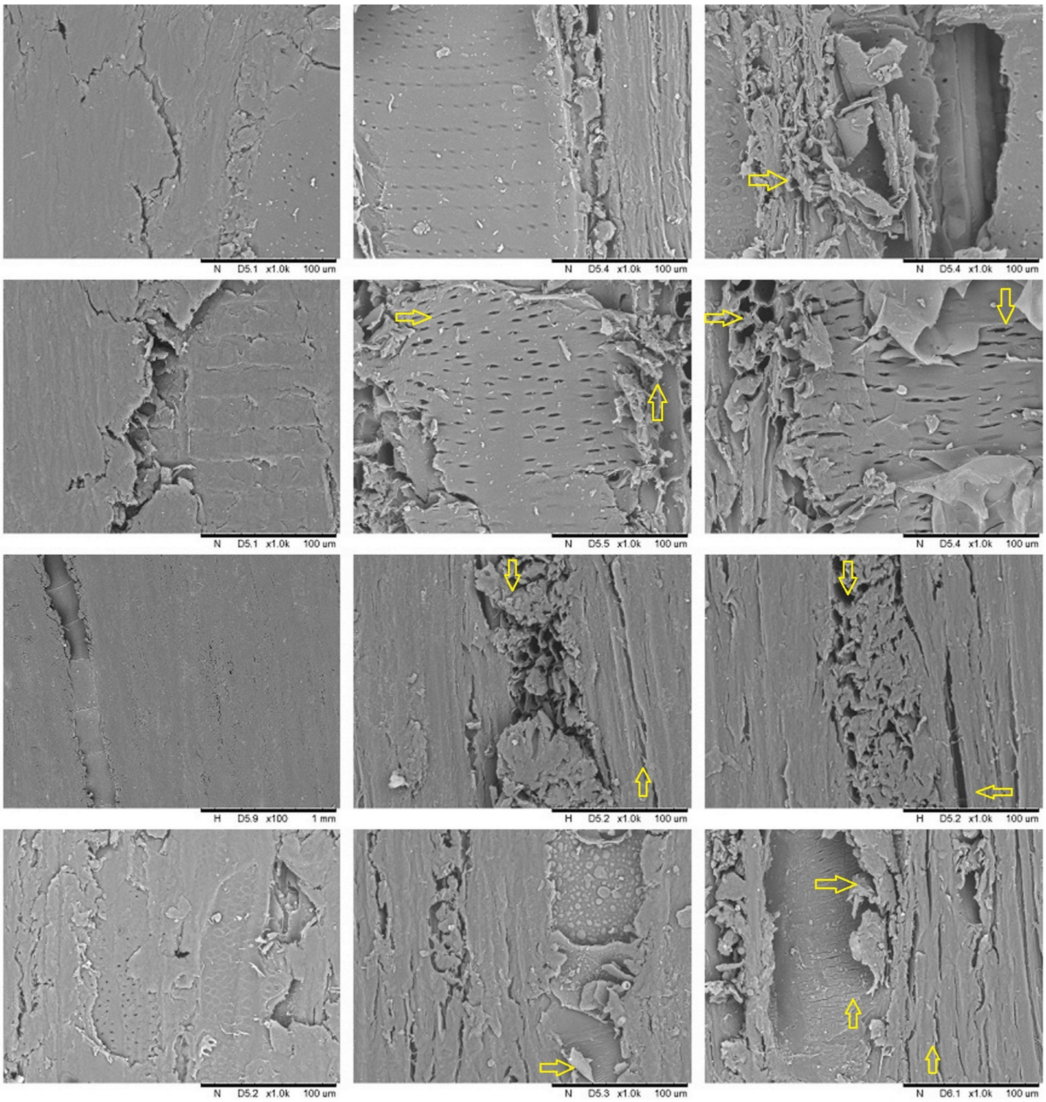

Figure 4. Comparison of microstructure exposed and non-exposed wood surface (from top: garapa, tatajuba, courbaril and massaranduba; from left: fresh wood, after 24 h of UV irradiation, after 4 cycles of artificial weathering); the described changes are marked with yellow arrows.

3.5. FTIR Analysis

The FTIR spectra of woods before and after UV irradiation and full weathering (four cycles) are shown in Figure 5. The main changes were found at 2900, 1730, 1650, 1590, 1512, 1420, 1317, 1260, 1163, and 1030 cm^{-1}. The garapa wood showed the greatest scope of changes (the highest differences in absorbance) and the smallest differences in absorbance showed massaranduba. The wood species in the studied group are characterized by the lowest and highest density. In the case of garapa and tatajuba wood, in general, the relative intensity of the bands increased more after UV treatment than after full artificial weathering. This can be explained by the fact that during the full weathering process, water-extractable compounds leached out and their accumulation on wood surfaces caused a negligible effect of weathering factors on wood. Nevertheless, the changes in the chemical structure of extractives during weathering cannot be determined by infrared spectroscopy, due to the significantly lower amount of lignin and polysaccharides [45–47]. According to the current knowledge [45–47], in the spectral range 1740–1720 cm^{-1}, various overlapping stretching vibrations of bond C=O in carbonyl and carboxyl compounds can occur. The results showed that carbonyl groups, determined at 1730 and 1650 cm^{-1}, increased more as an effect of full weathering process than after UV irradiation.

Figure 5. FTIR spectra of tested wood species before, after UV irradiation and after four full artificial weathering cycles: **a**—fresh wood, **b**—after UV irradiation, **c**—after four artificial weathering cycles.

The absorption near 1735 cm^{-1} can be attributed to vibrations in bond C=O in xylan (hemicellulose), as well as in carboxylic acids (lignin oxidation products). The occurrence of oxidation products was confirmed by the changes in intensity band, reaching 1650 cm^{-1}. These results are in accordance with the studies of other researchers, involving one or more different species and extended for longer periods of ageing [33,38,45,46]. This absorption was due to C=O carbonyl stretching in aromatic compounds, which can suggest the carbonyl compounds' formation, and the highest changes were observed in the case of garapa wood. The relative intensity of band at 1512 cm^{-1} decreased after weathering process. That peak is due to the skeletal stretching vibration of C=C in the aromatic ring of lignin [46]. The absorption at 2900 cm^{-1} was characteristic of alkane CH vibrations of methylene in cellulose, 1417 cm^{-1}—CH_2 bending crystallized, and amorphous cellulose and 1317 cm^{-1}—CH_2 wagging in crystallized cellulose [44,45]. Only in the case of massaranduba wood irradiated with UV did these peaks remain almost unchanged, which could be due to the high wood density and negligible effect of weathering factors on wood or their blocking with extractives. The peak at 1030 cm^{-1} for the C–O stretching was linked to cellulose and wood extractives [45]. The notable decrease in the relative intensity of bands at 1260 and 1230 cm^{-1} was observed after weathering. The absorbance in the range 1290–1200 cm^{-1} is characteristic for stretching C–O vibrations in lignin (guaiacyl), hemicellulose (xylans) and the conjugation of the C–O of extractives [43]. After a full weathering process, in the case of garapa and tatajuba wood, a peak at 1260 cm^{-1} was found, which might be associated with the conjugation of the C–O of extractives. Tropical woods have a relatively high number of extractives in comparison to European wood species [37]. Wood, as a complex structure, is a material for which it is difficult to formulate general conclusions. Followed by Reinprecht et al. [46], differences observed between tested wood species and changes observed on its surfaces after UV irradiation and full weathering could be explained by chemical changes taking place individually for each of them during photo-oxidation processes in the lignin-polysaccharide system, as well as extractives contained in wood. Differences between results obtained after UV treatment and full artificial weathering process might be associated with the migration of extractives such as UV-protectable extractives [45] (water-soluble extractives accumulated on the wood surfaces after full weathering process) and with the fact that extractives photooxidation products can increase the delay photodegradation of lignin [48].

4. Conclusions

Based on the results of the research into the influence of selected ageing factors such as UV irradiation and complex artificial weathering methods on the colour stability, wettability and roughness changes in garapa, tatajuba, courbaril and massaranduba, it can be concluded that:

- Regardless of ageing method, wood surfaces become darker and turn into shades of brown. The scope of changes was similar for both garapa, tatajuba of light colour and massaranduba of dark colour. Massive colour changes showed in courbaril wood, known for its high extractives content;
- The roughness of the tested wood species demonstrated variation, depending on the wood section and the measurement direction. In general, radial sections showed higher roughness due to interlocked fibres in tested wood species (fibres cut in various ways on the radial section of the wood). Roughness measured perpendicular to the wood fibres was twice as high as that measured parallel to the grain;
- The surface roughness values increased due to UV irradiation. The same time of irradiation connected with soaking wood in water and the drying caused roughness changes at a similar level, but was larger after a higher number of artificial weathering cycles;
- In contrast to changes in surface roughness, changes in wettability caused by exposure to UV light were not significant. The inclusion of water and drying in the weathering process resulted in a much wider range of changes. The wettability decreased (contact angle increased). One full weathering cycle caused a change in the surface from 24% for tatajuba wood to 51% for massaranduba wood;
- Anatomical analyses of tested tropical woods revealed structure changes after using ageing treatments. Distortion was found between cell elements associated with the degradation of the middle lamella, micro-cracks in cell walls, thinning and degradation of parenchyma cells in wood rays, and cracks along the pits in vessels formed on the S3 layer of cell walls. As a result of desorption tension, the changes caused by UV irradiation were much smaller than those caused by full artificial weathering;
- FTIR analysis indicated the occurrence of oxidative changes in lignin and hemicelluloses after the weathering process. The depolymerisation of cellulose was identified as well. The differences in FTIR results after UV treatment and full artificial weathering process must have been caused by the accumulation of water-soluble extractives on the wood surfaces.

Thus, the effect of changes caused by aging factors is the result of wood structure and its density, but also chemical composition. The results show that the observed changes may affect the long-term durability of finishes applied over wood subjected to weathering factors for a short period before finishing.

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