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Native and TMT Chestnut Extractives as Hydrophobic and Photostabylizing Additives for Wood Surfaces

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Abstract: Wood extractives have proven strong anti-oxidative properties which may be used to mitigate surface deterioration caused by photolytic effects and free radical formations. An interesting challenge regarding wood extractives is understanding how they behave in terms of treating natural wood surfaces to reduce anti-oxidative processes that arise from exposure to the main environmental factors. In this study, the possible efficacy of chestnut (*Castanea sativa* Mill.) extractives derived from native (CH) and thermally modified wood (TMT CH), as a means of protecting against UV exposure in poplar (*Populus* spp.) and spruce (*Picea abies* Karst.) wood, was evaluated. Chestnut wood was first thermally modified at 180 °C for 3 h, and the extractives were obtained by the accelerated solvent extraction technique (ASE) and subsequently used to treat wood surfaces. Samples were immersed in extractive solutions and exposed to artificial UV-weathering exposure, then contact angle and colour stability were monitored during the process. An FTIR analysis of the photo-degradation process of poplar and spruce surfaces was also executed. Extractives of TMT chestnut changed the total colour variation in both poplar and spruce wood. A much darker colour compared to the extractives of native wood was observed and an increase in ΔE^* from 9.75 to 30.76 and 6.24 to 22.97 in poplar and spruce was calculated. The stability of the colour depended both on the surface wood and the type of extractive. The initial contact angle remained almost unchanged in the poplar wood surface and only slightly increased in spruce regardless of whether they were treated with extractives from native or TMT chestnut wood. A strong reduction in contact angle after the accelerated UV exposure test was observed, especially in spruce treated with CH extractives. FTIR analysis confirmed the lower levels of chemical degradation of surfaces observed by colorimetry, where TMT CH extractives formed more stable chemical bonds than native extractives. The comparative analysis in this study clarified the complex relationships between the effects of high-temperature modification of wood and the potential protective role of TMT extractives on some wood surfaces.

Keywords: wood; chestnut; thermal modification; green extraction; extractives; artificial weathering; UV-photostability

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1. Introduction

Photodegradation of wood, although it occurs in a shallow surface layer, is a great shortcoming since the aesthetic appeal may be undesirably altered and the costs and inconvenience of maintenance measures present a problem for the end-user. As reported by El Bakali et al. [1], wood can absorb all the wavelengths of electromagnetic radiation, but only UV and low visible wavelengths cause its degradation. The penetration of light and the consequent damage of wood surfaces are related to the source and nature of light [2]. In the case of solar light discolouration and photodegradation, mainly due to the chemical breakdown of wood constituents, the predominant mechanism is lignin degradation [3]. The changes occur in a very thin (down to 0.5 mm) external layer of wood. Živković et al. [4] demonstrated that the various consequences of light exposure, recorded as discolouration, chemical changes or structural breakdown, develop dynamically in different intensities over time and through various-depth layers of wood surface.

When wood is used in adverse environments, it may be treated with chemicals to help to prevent decay, to improve its water resistance, i.e., to reduce its hygroscopicity, to reduce the effects of ultraviolet radiation or to increase its fire resistance [5]. Many of these treatments involve the use of toxic or corrosive chemicals that can be harmful to the environment. As a consequence, it is important to search for ways to reduce the use of synthetic chemical compounds in the wood industry and try to increase the use of natural compounds in order to improve the hydrophobic performance, gluing properties or paint adhesion to wood, or simply increase its colour stability.

To improve some wood properties or characteristics, different modification treatments have been developed on an industrial scale involving mainly thermal modifications, acetylation and furfurylation, all three constituting already available solutions for the market [6]. However, the colour stability of wood surface exposed to outdoor conditions is not always secured, especially not in the case of transparent coatings or thin-film finishes. The UV light may be filtered by coatings or by UV absorbers, but the problem of dark-coloured species, and also in the case of heat-modified wood, is the instability of chromophores in visible light as well [7,8].

Recently, interest in the use of natural compounds in the wood-based industry and in the chemical modification of wood has seen a renewed interest. In addition, other research in this area continues to explore and develop innovative methods for improving the performance of superhydrophobic wood by using different methods to functionalize wood surfaces. Wang et al. [9] explored the concept of superhydrophobicity, which is particularly relevant for wood, which is naturally hydrophilic and susceptible to moisture-related damage. Singh and Singh [10] in their review paper discussed the potential benefits of the use of natural products on wood and highlighted how extending the service life of wood using natural compounds as bioactive compounds can be an attractive approach for wood protection. The authors also stated that a complete replacement of synthetic and very-effective but toxic chemicals with those of natural origin would be be time-consuming. Thus, the development of new and effective formulations for wood protection and preservation is based on deep knowledge that will require investment in money and research. Among other factors, the challenging problems to be solved are linked to the following aspects:

(a) Natural compounds have been well investigated and tested and possess a wide spectrum of biological activities [9], but the enormous variability of natural compounds still remains a problem. Firstly, many of the compounds found in nature vary greatly in their composition and biocidal efficacy. Secondly, many natural compounds have still not been determined or sufficiently investigated;
(b) The bioactivity of natural compounds, in their form as they appear in wood, does not always remain effective after the process of their extraction;
(c) It is still not completely understood in which way the added extractive forms a chemical connection with the wood substrate;
(d) The extracted material is itself prone to biodegradation or photodegradation in time;
(e) The economic aspect of their use is still dubious.

Many authors have reported studies demonstrating how wood extractives may show their potential activity against fungi and insects [10–12]. However, the use of extractives, derived from native or from thermally modified wood, for wood surface protection still remains unsolved. El Bakali et al. [1] reported research on the effect of extractives derived from thermally modified wood on the durability and colour stability of various wood species. They demonstrated that the impregnation of wood by extractives derived from thermally modified wood in some cases plays a complementary role in the colour stability of wood. The authors concluded that the efficiency of impregnation depends on the nature of the extractives and the wood species used.

One of the first studies on the relationship between wood extracts and the colour stability of wood was conducted by Diouf et al. [13]. In their research, the variation in chromatic coordinates of poplar and pine wood impregnated by extracts of different species at the end of a period of exposure to a solar-type light source was reported. Among other types of extracts, those that were derived from tropical woods, such as Ipe (*Handroanthus* spp.) and Merbau (*Intsia* spp.), most efficiently contributed to the colour stability of poplar and pine wood surfaces, but, as a general statement, the authors concluded that pine and poplar surfaces, when impregnated with any type of natural wood extractives, were always more stable in their colour change than the raw surfaces of native woods.

The main benefit to be gained from the use of natural extractives for wood protection is their reduced environmental impact at the end of service life. In addition, the management of wood materials previously treated with toxic chemicals or submitted to thermal modification with liquid waste products derived from the use of a vacuum pump still remains a problem at the industrial scale, at least in the case of thermal vacuum processes. Therefore, the green extraction of secondary metabolites from wood is an environmentally friendly alternative and ensures safe and high-quality extracts, because it is a process that is able to reduce energy consumption and allows reducing the quantity of solvents. Previous studies [14,15] have highlighted how the antioxidant activity changed with the wood species, the extraction techniques and the use of solvent. Faraone et al. [16] showed some specific aspects of chestnut wood extractives, such as how to attain the highest extraction yield by using accelerated solvent extraction (ASE), the highest polyphenols content, and efficient radical-scavenging and antioxidant activity.

For the aforementioned reasons, the use of chestnut extractives is very interesting and promising for investigation from another point of view.

However, the different characteristics of wood surfaces could represent limitations for the final applications. This study highlights the wettability of poplar and spruce wood surfaces treated with natural wood extractives. The resulting colour variation and wetting behaviour are compared to the QUV weathering test, and FTIR investigations are used in an attempt to clarify the mechanisms of reaction of the extractives of chestnut.

In addition, this study proposes to achieve better solutions based on the use of wood extractives as hydrophobic additives and photodegradation-protective additives to increase resistance to aging and exposure to weathering, thus improving the durability of final wood applications.

2. Materials and Methods

2.1. Thermal Modification of Chestnut Wood

Boards of chestnut (*Castanea sativa* Mill.) with dimensions of 30 × 200 × 2000 mm (thickness × width × length, respectively) were thermally modified for three hours at 180 °C within a Thermo-Vacuum plant produced by WDE Maspell srl (Terni, Italy). Hardwood was exclusively and consistently used for the testing material. No sapwood was included. Wood was dried to 0% moisture content under a vacuum plant system (200 mbar) at 90 °C for 12 h. From an initial (pre-drying) temperature of 30 °C, the temperature was increased 5 °C each hour to 90 °C. At the end of the drying cycle, the kiln was momentarily opened, and the wood samples were quickly weighed. Then, from the cooled boards, random portions of modified and unmodified wood were split and reduced to powder by a cutting mill machine (Retsch GmbH, Haan, Germany). A drive power of 1.5 kW and rotor speed of 1500 min^{-1} guaranteed a rapid size reduction. The 40 sieve-mesh fractions of the milled wood of both modified and unmodified wood were used for the extraction. The main processes that were carried out in this study are summarized in Figure 1.

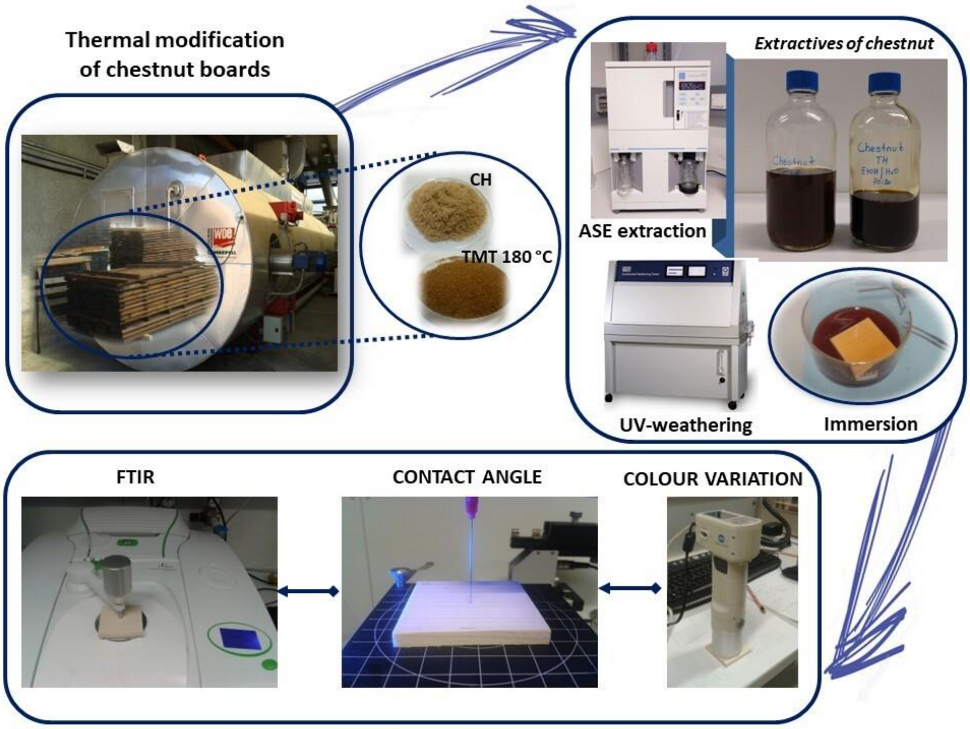

Figure 1. A visual representation of the main stages of sample preparation and analysis.

2.2. Wood Surfaces Treated with Extractives

Commercial poplar (*Populus* spp.) and spruce (*Picea abies* Karst.) tangential wood boards were used. Then, nine defect-free samples of each wood species with dimensions of 60 × 60 × 6 mm (longitudinal, tangential and radial direction, respectively) were randomly selected to form a group of samples for each surface treatment (untreated and treated with native CH and with TMT CH extractives, 3 panels per each). Poplar and spruce samples were conditioned for 4 weeks at 20 °C and 65% relative humidity. These samples were fine sanded with sanding paper of 1000 grit and their tangential faces were used as exposed and tested surfaces. Samples of each wood species were then dipped into the different solutions of chestnut extractives for about 1 min and left under a hood fume until the volatile solvent evaporated.

2.3. Accelerated Solvent Extraction (ASE)

Accelerated solvent extraction (ASE) is a method for extracting different compounds from a complex solid sample matrix, such as wood. The process uses high temperature and pressure [16], which results in an extraction that takes less time and requires less solvent than traditional methods that use less extreme physical conditions. The elevated temperature is employed to increase the extraction efficiency of the natural compounds and the elevated pressure is used to keep the solvent in a liquid state as the temperature is increased above its boiling point. For this reason, an automated ASE 150 system (Dionex Corporation, Sunnyvale, CA, USA) for the process of extraction was used. An amount of 20 ± 1 g of both kinds of chestnut (native CH and TMT CH) wood powder was used for each extraction procedure. The extraction was carried out with ethanol and water ($EtOH/H_2O$—70:30 v/v) at 110 °C and at a pressure of 100 bar for three cycles of 5 min each. For each sample, about 200 mL of the extractives solution was collected. After the extraction, the solutions obtained and needed to calculate the extraction yields were filtered and the remaining solvent was removed from the residue with a rotary evaporator at 37 °C. The other portions or quantities of extractive solutions were used as liquids for immersion treatment of poplar and spruce wood samples.

2.4. Determination of Lignin and Holocellulose Content

The classical method for the quantitative determination of lignin is based on Klason's technique involving hydrolysis with sulfuric acid. The sawdust material of each wood species was transferred to a 50 mL beaker, 15 mL of room-conditioned H_2SO_4 aqueous solution (72%) was added and the mixture was frequently stirred for 2 h at room temperature. The mixture was then diluted to 3% (w/w) with 560 mL of distilled water, heated under reflux for 4 h, filtered and washed with 500 mL of distilled water. The residue was dried to constant mass at 105 °C. In this procedure, lignin appeared as an insoluble residue and was recovered by filtration and gravimetrically determined. The holocellulose content was determined by the difference between the residue amount after extraction and the lignin content.

2.5. Colour Measurement

The colour of poplar and spruce wood surfaces before and after immersion in extractives, as well as after accelerated UV-weathering exposure, was determined on the middle spot of each specimen. One reading for each of the three replicas was taken. Colour parameters were measured by a Minolta CR-400 Spectrophotometer (Minolta Corp, Osaka, Japan), which was connected to the Color Data Software SpectraMagic NX ver. 3.31. The CIEL*a*b* colour evaluation system, created by the Commission Internationale de l'Eclairage, was used, which is characterized by the colour parameters L^* (lightness axe) and two chromaticity coordinates (a^* and b^*), which correspond respectively to the green–red and blue–yellow axes. The total colour change was calculated according to the following formula:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{1}$$

where the difference in colour coordinates, ΔL^*, Δa^* and Δb^* between native surfaces and those impregnated with extractives were first measured. Then the impregnated samples, after being exposed to the UV lamp, were compared to the impregnated samples before exposure. Three replicas were produced for each substrate species.

2.6. Contact Angle Measurement

In order to evaluate the hydrophilic surface properties of poplar and spruce, the contact angle method was used [16]. The contact angle is the angle measured as the angle of the tangent to the liquid droplet where the liquid interface meets a solid surface. It quantifies the wettability of a solid surface, via Young's equation [17,18]. Contact angle measurements in the radial surface of wood specimens, to obtain more regular results on which wide strips of earlywood or latewood of tangential surfaces may have inadequate influence, were performed by the Drop Shape Analyzer System connected to the Krüss ADVANCE software (Krüss GmbH, Hamburg, Germany). Only one liquid was used: distilled water. Five sessile drops of the distilled water of 2 µL were deposited on every single specimen. Three replicas for each wood surface were prepared and a total number of measurements of 15 drops per variable and five drops for each sample were recorded. The contact angle was continuously recorded for a time duration of 120 s at intervals of 0.05 s. The right and left angle of the droplets on the surfaces were collected and averaged with a total of 140 measurements for every droplet.

2.7. Accelerated UV-Weathering Exposure Test

An accelerated UV-weathering exposure test of the poplar and Norway spruce wood samples, not immersed and immersed into different kinds of extractive solutions, was performed using a QUV Accelerated Weathering Tester (Q-Lab Corporation, Westlake, OH, USA) equipped with UVA 340 lamps. The exposure of all wood surfaces lasted for 168 h (1 week). The exposure consisted of an initial condensation period followed by an exchange of sub-cycles of intermittent periods of water spray (lamps off) and UV-A 340 nm irradiation according to EN 927-6:2006 [19], as reported in Table 1.

Table 1. Exposure cycle of wood surfaces according to EN 927-6:2006.

Step	Action	Temperature	Duration	Condition
1	Preliminary condensation	(45 ± 3) °C	24 h	100% r.h. within chamber
2	Main exposure set	144 h = 48 cycles of 3 h intervals consisting of steps 2a and 2b	-	-
2a	UV irradiation, UV-A 340 lamps	(60 ± 3) °C	2.5 h	Irradiance set point 0.89 W/(m^2nm) at 340 nm (r.h. > 20%)
2b	Water spray		0.5 h	6 to 7 l/min·m^2, UV off, r.h. 100%

2.8. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR) Analysis

The chemical modifications caused by the immersion of both wood surfaces, poplar and spruce, into a solution of chestnut extractives, were examined by Fourier transform infrared analysis. For each type of wood sample, three spots were recorded. The resolution was set at 4 cm^{-1} and 4 scans were recorded in absorbance units with a wavenumber range from 4000 to 600 cm^{-1}. FTIR spectra were recorded on a Perkin Elmer Frontier ATR-FTIR spectrometer equipped with an attenuated total reflection (ATR) Frontier diamond/zinc selenide (ZnSe) accessory and with a 1 Reflection Top-Plate (Perkin Elmer, Waltham, MA, USA). The information from these spectra was accumulated using Spectrum software version 10.03.02. Normalisation was performed on the highest absorption band at 1016 cm^{-1}. Three replicas were examined and 9 spectra for each sample were obtained.

2.9. Statistical Analysis

The statistical analysis was performed using R Statistical Software (v4.1.2; R Core Team 2021) and MS Excel 2013 (Microsoft, Redmond, WA, USA) to calculate mean values, standard deviations and analysis of variance (ANOVA) p values of 0.05 or less were considered statistically significant.

3. Results and Discussion

3.1. Yield and Chemical Wood Component

The values of extraction yield obtained from the ASE technique, of lignin and holocellulose content, are reported in Table 2. All the measurements were performed in triplicate.

Table 2. Yield (%) of extractives, lignin and holocellulose content in native chestnut (CH) and thermally modified wood (TMT CH).

	Yield		
Type of Extractive	ASE (%)	Lignin (%)	Holocellulose (%)
CH	22.3	27.8	64.8
TMT CH 180 °C	26.2	48.1	36.2

As expected, the thermal modification increased the lignin content and decreased the holocellulose proportion. Within the organic extractives, a noticeable polarity can be expected between the extractive of unmodified and thermally modified chestnut. This is because the lignin partly becomes soluble in organic solvents after the wood samples have undergone thermal treatment [20]. Table 2 shows that the ASE extraction is very effective in extracting non-constituent material from wood, not only wood accessory chemicals but probably also the residues of thermal decomposition of basic wood constituents. During ASE extraction the temperature plays a relevant role in extraction yield. As is well known, it is important to note that the different extraction technique performances could be explained by the different acting mechanisms such as breakdown of plant tissue [21], or by diffusion or penetration processes as observed by Gironi and Piemonte [22] for chestnut wood. Generally, chestnut is a species notorious for its high natural content of extractives, between 8% and 15% of water soluble compounds. This renders the species very durable. However, the content of extractives varied in response to different parameters in which materials, solvents and extraction times play a key role [23]. On the other hand, previous experiments demonstrated that chestnut may yield much greater content of extractives after a TMT modification than other hardwoods and softwoods. Chestnut wood undergoes significant degradation during pyrolysis already at relatively low temperatures [24]. Thus, chestnut naturally has a very high content of accessories (extractives) which depends on the variety of the species, but also on the type of extraction method and intensity of extraction parameters (e.g., temperature). TMT modification of chestnut results in an ever greater content of extractives, because some residues from the breakdown of constituents are also collected by the solvent. The content of TMT extractives also depends on the technique of modification and the temperature of modification, while the amount of extractives depends on the temperature of the ASE extraction process.

As far as thermally modified wood is concerned, it possesses a higher proportion of lignin in comparison to the native source, because of the reduction in hemicelluloses, which has been demonstrated by Tjeerdsma and Militz [25] for Scots pine (*Pinus sylvestris* L.) and beech (*Fagus sylvatica* L.), and by Weiland and Guyonnet [26] for maritime pine (*Pinus pinaster*) and beech (*Fagus silvatica* L.). The content of all sugars (which form the principal constituents of hemicelluloses) is decreased during thermal modification. This can be corroborated by their high susceptibility to degradation at elevated temperatures during thermal modification, which causes the degradation of monosaccharides such as glucose, xylose and mannose [27]. In addition, the chemical changes can be related to the increase in the carbon content of thermally modified wood, which can be used as an indicator of the intensity of the thermal treatment. In fact, the increase in the carbon content reveals the loss of functional groups containing predominantly oxygen, such as carboxyl, acetyl and hydroxyl groups [20]. Consequently, all these alterations, related to the severity of the thermal process, lead to a significant increase in phenolic OH groups in comparison to unmodified wood. These results reflect the demethylation and/or demethoxylation of lignin. Therefore, the thermal degradation of lignin in *Castanea sativa* Mill., can be summarized as follows: loss of C3 side chains (reflecting depolymerisation and side-chain elimination), followed by demethylation/demethoxylation, dehydroxylation and finally incorporation into a polyaromatic network [28].

3.2. Colour Variation

Extractives are known to affect wood colour, but also contribute to the photostability and the nature of colour changes of particular species.

The deterioration of wood in the natural weathering process involves a very complex, free radical reaction sequence. However, wood appears to be a good light absorber. It was generally accepted that UV light penetrates approximately 75 μm and visible light approximately 200 μm into wood surfaces to initiate photochemical reactions, mainly in lignin, leading to photo discolouration [29]. However, Živković et al. [30] and Jirouš Rajković et al. [31] demonstrated that UV light penetrates further down than 200 μm and visible light deeper than 500 μm, causing a series of complex chemical reactions that may progress even deeper. Therefore, degradation reactions are a “surface layer”, rather than “surface” phenomenon. The free radicals generated in wood by light rapidly interact with oxygen to produce hydroperoxides which in turn are easily decomposed to produce chromophoric groups [32]. However, all chemical constituents of wood are susceptible to degradation by weathering, only at a lower rate than lignin.

Analysis of variance (ANOVA) on the total colour variation was performed to determine whether there is a significant difference between species of wood surfaces and type of extractives considering the effect of immersion only and that of the UV-weathering exposure (Figure 2).

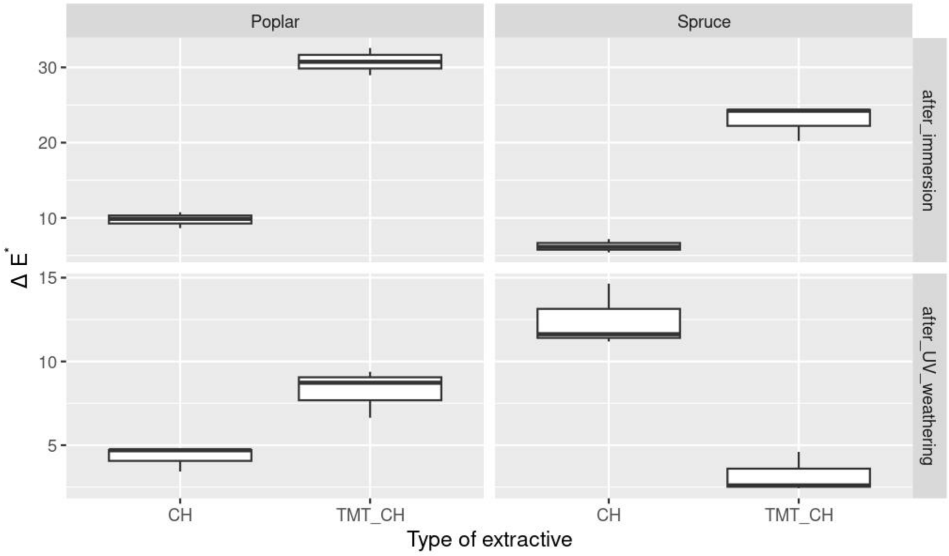

Figure 2. Box plot analysis of total colour variation (Δ*E**).

All analysed factors have a significant effect on the Δ*E** variable, as indicated by the very low *p*-values in Table 3. The immersion treatment has an exceptionally high F-value and a *p*-value that is effectively zero, indicating a profound effect on Δ*E**. This suggests that immersion treatments significantly alter the colour of wood surfaces, likely improving the aesthetics. Similar to immersion, the UV-weathering treatment also demonstrates a highly significant effect on wood surfaces. The results imply that exposure to aging significantly impacts the wood colour variation, which is critical for outdoor applications.

Table 3. Summary data of ANOVA output based on the Δ*E** variable, where df is degrees of freedom, F is F-statistic and *p*-Value is associated probability.

Treatment	df	Mean Square	F	*p*-Value	Significance
Wood surfaces	1	24.8	10,704	0.004797	Highly significant (**)
After immersion	2	362.20	156,401	3.144×10^{-11}	Extremely significant (***)
After UV-weathering	4	308.65	133,278	4.555×10^{-12}	Extremely significant (***)

3.2.1. Effect of Chestnut Wood Extractives on Poplar Wood Surfaces

Table 4 reports the *L**, *a**, *b** and Δ*E** values of the poplar wood surfaces used during the experiment before and after immersion into the solution of extractives obtained from native (CH) and thermally modified chestnut wood (TMT CH) by using ASE extraction. In addition, the results of colour measurements with poplar surfaces treated with extractives after UV-weathering were compared.

Generally, Δ*E** is considered to be a standard calculation metric which correlates with the human visual judgment of differences between two perceived colours.

The poplar wood surfaces after immersion into the extractives obtained from TMT chestnut significantly decreased in lightness and reached an *L** value of 52.69 ± 1.67, a much lower value compared to the wood surface treated with native chestnut extractives (69.94 ± 1.68). A significantly higher redness (*a**) coordinate and a somewhat lower yellow colour coordinate (*b**) were observed with TMT CH extractives than with native CH extractives. The presence of tannins within extractives of chestnut can be related to a dark colouration, because they are dark chromophores that strongly absorb light [33]. This suggests that oxygen as an oxidation factor plays an important role in the darkening of wood surfaces [34]. This effect is more pronounced with the treatment of poplar surfaces with extractives of thermally modified extractives of chestnut than with native extractives.

Table 4. Results of colour measurements of poplar wood surfaces: for reference, immersed into extractives and aged: L^*, a^*, b^* average values (standard deviations in brackets) and calculated colour differences ΔE^*. CH are extractives obtained from native chestnut wood, and TMT CH are extractives obtained from thermally modified chestnut wood at 180 °C.

Type of Wood Chestnut Extractives	CIEL*a*b* Coordinates	Type of Poplar Wood Surface		
		Reference (Before Immersion)	With Extractives (After Immersion)	With Extractives (After UV-Weathering)
CH	L^*	79.05 *(1.00)*	69.94 *(1.68)*	71.08 *(2.71)*
TMT CH		82.86 *(0.33)*	52.69 *(1.67)*	60.11 *(3.23)*
CH	a^*	3.66 *(0.22)*	5.53 *(0.37)*	7.44 *(0.77)*
TMT CH		4.13 *(0.14)*	10.07 *(0.28)*	8.64 *(0.39)*
CH	b^*	18.09 *(0.10)*	21.02 *(0.23)*	22.97 *(2.33)*
TMT CH		19.39 *(0.37)*	20.24 *(0.36)*	23.46 *(0.08)*
CH	ΔE^*	-	9.75 *(1.12)*	2.96 *(3.86)*
TMT CH			30.76 *(1.82)*	8.21 *(1.73)*

All ΔE^* values were calculated considering differences in colour coordinates measured before and after each treatment.

Macroscopically, after treatment with extractives, the effect of colouration of the surface by extractive solution on poplar wood samples was immediately pronounced as a visibly noticeable alteration. The increase in ΔE^* value became strongly pronounced when the poplar wood surfaces were treated with extractives derived from chestnut that was thermally modified at 180 °C (ΔE^* 30.76). Instead, in the case of extractives derived from unmodified chestnut wood (CH), the poplar wood surface showed a moderate but still noticeable increase of ΔE^* 9.75.

After exposure to UV-weathering, the total colour differences (ΔE^*) of the poplar wood surface, used as a reference or treated with native extractives or extractives of thermally treated chestnut wood, delivered interesting results. It should be noted that these values are calculated by comparing all the ΔE^* values (L^*, a^* and b^*) measured after weathering with those obtained after immersion in the extractive solutions.

The native poplar surface exhibited a slightly visible change to the naked eye (ΔE^* 7.37) after weathering. When extractives from native chestnut wood were applied to the poplar surfaces, a better stability of total colour after weathering was recorded (ΔE^* 2.96). In case of poplar wood immersed in extractives derived from thermally modified chestnut wood, the ΔE^* exhibited a value of 8.21, which does not present such a good stability of colour.

The values were compared to those obtained after immersion. Extractives obtained from native chestnut wood weakly changed the value of L^* in the poplar wood surface from 69.94 to 71.08 after weathering. In contrast to that, the extractives derived from thermally modified chestnut wood increased the value of L^* in poplar wood from 52.69 to 60.11, which means that the weathering caused some bleaching of the originally darkened extractive-treated surfaces. Similar behaviour was found for the a^* and b^* coordinates.

According to Esteves et al. [35], there is a strong correlation between extractives content and their composition and the lightness of wood. However, the decrease in lightness (L^*) on the poplar wood surface after immersion in a solution of extractives derived from thermally modified wood (from 82.86 to 60.11) does not imply a corresponding improvement in colour stability. In fact, the extractives from native chestnut wood seem to have conferred more colour stability to poplar wood than its surface naturally possesses, which indicates that accurate knowledge of the chemical composition of extractives and the relative photodegradation phenomena is really needed.

Natural compounds are known to affect colour stability and the flavonoids present within extractives, such as anthocyanins, can be subjected to intensive photochemical degradation. Changes in their structure and intramolecular associations are caused by elevated temperature, effect light and availability of oxygen. The rate of degradation changes according to the B-ring hydroxylation in such way that the increase in hydroxylation corresponds to a relative decrease in colour stability. Another critical element in wood photodegradation is the presence of water. It has been suggested that the principal role of water is to facilitate light penetration into the accessible regions of cell wall structures and to open non-accessible regions for light penetration [36]. However, Turkulin et al. [37] clearly indicated that moisture contributes to chemical processes involved in photolysis and in subsequent free radical reactions. This characteristic together with other factors could lead to a degradation of wood colour. However, the effects of weathering on the colour variation of poplar wood surfaces immersed into the chestnut wood extractives, in part, could also depend on the intensity of thermal modification and the relative chemical change that occurs in the extractives.

With the purpose of providing additional useful help, Figure 3 shows the colour differences between after immersion and after exposure to UV-weathering of poplar wood surfaces treated with chestnut extractives. CH extractives did not alter the original poplar colour much (ΔE^* 9.75) and underwent slight darkening after UV exposure (ΔE^* 4.28). On the contrary, the TMT CH extractives markedly changed the original poplar colour (ΔE^* 30.76) and retained dark appearance after UV exposure, but exhibited also some bleaching (ΔE^* 8.25).

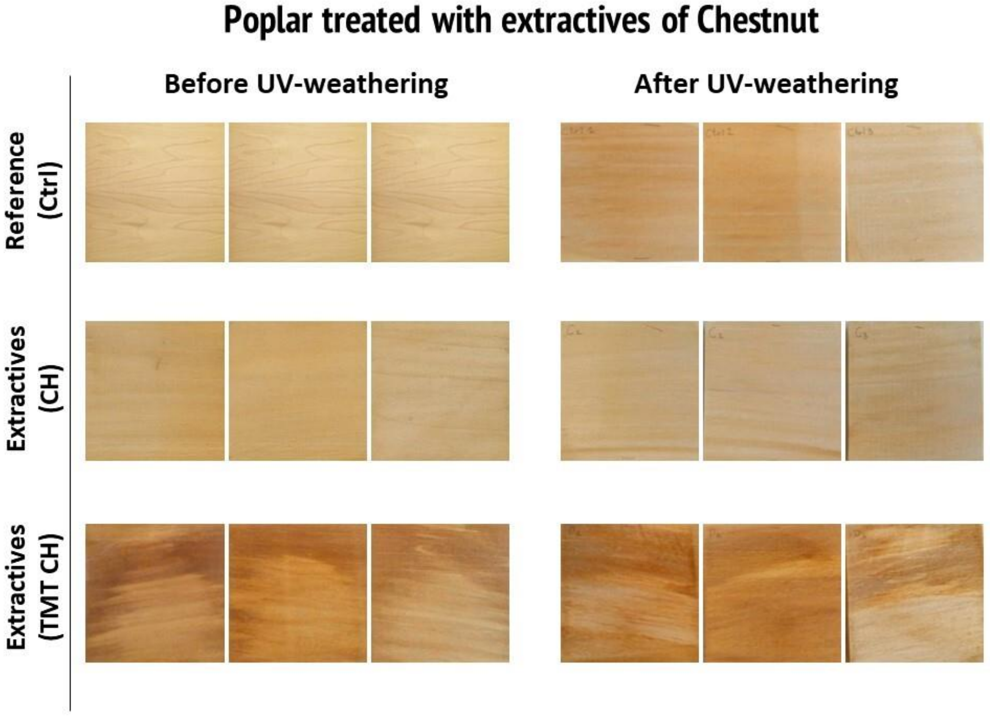

Figure 3. The visible colour changes in poplar wood surfaces treated with extractives from native chestnut wood (CH) and thermally treated wood (TMT CH) before and after artificial weathering exposure for 3 replicas.

3.2.2. Effect of Chestnut Wood Extractives on Spruce Wood Surfaces

Before any sequential treatment, the colour parameters of the spruce wood surfaces were measured as they were in the initial stage of the experiment. Table 5 reports the L^*, a^*, b^* and ΔE^* values of the spruce wood surfaces used during the experiment before and after immersion into the extractive solution derived from unmodified and thermally modified chestnut wood.

Table 5. Results of colour measurements of spruce wood surfaces: for reference, immersed into extractives and aged: L^*, a^*, b^* average values (standard deviations in brackets) and calculated colour differences ΔE^*.

Type of Wood Chestnut Extractives	CIEL*a*b* Coordinates	Type of Spruce Wood Surface		
		Reference (Before Immersion)	With Extractives (After Immersion)	With Extractives (After UV-Weathering)
CH	L^*	85.44 *(1.03)*	80.57 *(1.63)*	70.56 *(1.12)*
TMT CH		83.82 *(1.14)*	62.69 *(1.02)*	61.01 *(2.04)*
CH	a^*	3.31 *(0.09)*	4.91 *(0.37)*	10.20 *(0.41)*
TMT CH		3.91 *(0.64)*	11.13 *(0.22)*	9.82 *(0.84)*
CH	b^*	18.68 *(1.00)*	22.24 *(0.50)*	27.51 *(1.20)*
TMT CH		19.70 *(1.72)*	25.07 *(1.00)*	25.21 *(2.05)*
CH	ΔE^*	-	6.24 *(0.90)*	12.49 *(1.90)*
TMT CH			22.97 *(2.42)*	2.13 *(3.18)*

The initial immersion of spruce samples in solutions of CH or TMT CH extractives caused similar changes to those observed on poplar wood, only with somewhat lower intensities. The CH extractives changed the initial spruce colour very little (ΔE^* 6.24), whereas treatment with TMT CH extractives caused more intensive darkening (ΔE^* 22.97), although not as intensive as occurred with poplar (ΔE^* 30.76).

CH extractives caused slight darkening of the surface ($L^* = 80.57$) in comparison with natural wood ($L^* = 85.44$), but the darkening was significantly more pronounced with CH TMT extractives ($L^* = 62.69$). The b^* component changed slightly in both cases, but the red component (a^*) proved to cause the dominant change in colour (from 3.31 in native wood to 4.91 and from 3.91 to 11.13 in TMT CH extractive-treated wood). In both cases, a moderate increase in b^* was observed. A possible explanation of the increase in a^* and b^* values after weathering could be the formation of quinones and quinoid-like structures due to depolymerisation and oxidation of lignin involving free radicals [38]. Extractives obtained from native chestnut wood changed the L^* value of the spruce wood surface from 80.57 to 70.56 after UV-weathering. Instead, extractives derived from thermally modified chestnut wood conferred a better stability in the L^* value in spruce wood changing from 62.69 before exposure to 61.01 after UV-weathering. Worthy of attention is the change that occurred in the a^* coordinate. In the case of extractives derived from native chestnut wood, the spruce wood surface exhibited a significantly higher a^* value than was the case with the unexposed treated surface. This probably originated from a progressive accumulation of red chromophores on the surface of the samples during weathering. The CH extractive treatment on spruce (ΔE^* 12.49) was much less effective against UV light than with poplar (ΔE^* 4.28). On the contrary, the treatment with TMT CH extractives, which caused intensive initial darkening of both species' surfaces, helped to maintain the similar appearance of spruce after UV exposure (ΔE^* 3.21). This is different to what happened with the poplar surfaces, which were less efficiently protected from light by the TMT CH extractives (ΔE^* 8.25) (Table 5).

Many factors contribute to colour changes and the provision of high or low stability of wood surfaces, such as wood composition, light exposure, moisture and temperature, surface and coating treatments. These aspects become even more complex when other natural compounds, such as extractives, as in this case, are introduced in an attempt to reduce the photodegradation process. Concerning extractives derived from wood, one of the most relevant scientific papers is that of Diouf et al. [13], in which they tested the colour-fastness of wood surfaces impregnated with extractive solutions. They asserted that the stability of the natural colour of wood exposed to a solar-type irradiation was not directly correlated either to its global extractive content or to the total phenol content of these extractives. The stability could be improved for wood species of lower light stability if they are impregnated with extractives of durable wood species. However, according to Pandey [29], the precise mechanisms and pathways involved in the photodegradation of wood surfaces is far from being elucidated, mainly considering the anatomical differences among the wood species.

With the purpose of providing additional useful help, Figure 4 shows the colour differences before and after exposure to UV-weathering of spruce wood surfaces treated with chestnut extractives.

Figure 4. The visible colour changes of poplar wood surfaces treated with extractives from native chestnut wood (CH) and thermally treated wood (TMT CH) before and after artificial weathering exposure for 3 replicas.

The artificial UV-weathering exposure of treated spruce samples exhibited contrary behaviour with respect to the effect of different extractives and with respect to the behaviour of poplar. The untreated, original spruce wood surface showed the strongest total colour difference during weathering compared to surfaces treated with extractive solutions (Figure 4), thus highlighting the intensive and rapid photodegradation of native wood material and the need for its preservation against the effects of light and water. Different lignin contents between poplar and spruce might have contributed to the changes of the native surfaces, which were less pronounced in poplar.

3.3. Contact Angle: Influence of Chestnut Wood Extractives on the Wettability of Poplar and Spruce Wood Surfaces

The advancing contact angle obtained for the poplar wood surfaces treated with solutions of extractives of chestnut wood is presented in Figure 5. In the literature, it is often declared that the contact angle of the water droplet, deposited on the wood lateral surface, is equal to zero [39] since it changes its initial contact angle of approximately 40–60° to zero in less than 40 s. In this study, the application of extractives to the surface of poplar changed the contact angle only slightly after 120 s of measurement.

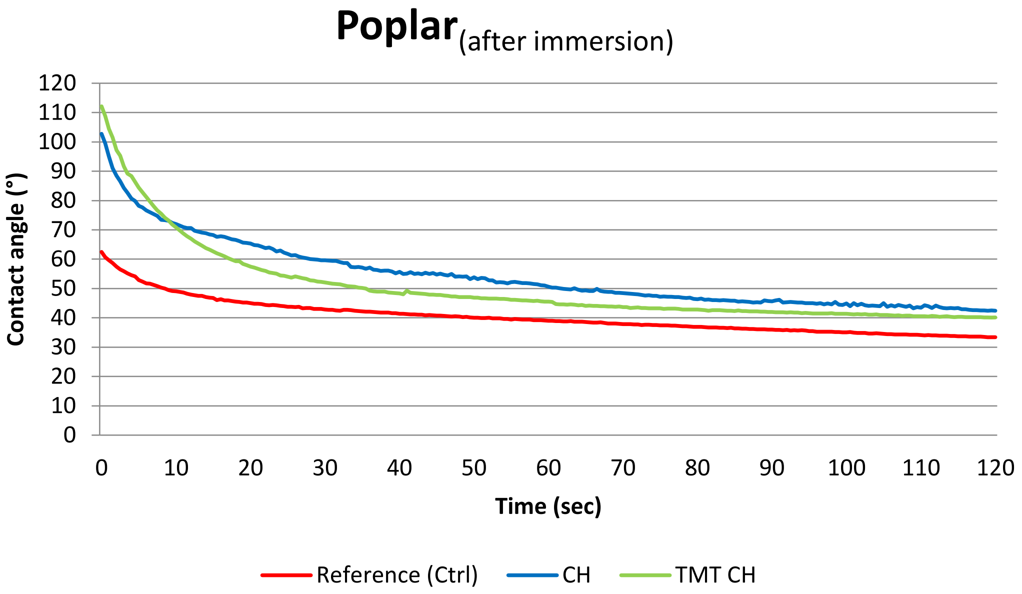

Figure 5. Contact angle recorded over a time of 120 s on poplar wood surface, where: sample wood surface with any treatment, Reference (Ctrl); sample wood surface treated with extractives of chestnut untreated, CH; sample wood surface treated with extractives of chestnut thermally treated, TMT CH.

The treatment of poplar wood surfaces with chestnut extractives seems to have little effect on the wettability. The final wettability of poplar wood surfaces immersed into extractives was only slightly improved compared to those of the poplar reference samples. Similar behaviour was observed on native spruce and its surfaces treated with native chestnut extractives (Figure 6). On the contrary, spruce wood immersed into solutions of extractives obtained from thermally modified chestnut wood demonstrated a somewhat improved hydrophobic effect, still similar to that of poplar.

It seemed that the more hydrophobic character of the surface, which appears after treatment with extractives derived from thermally modified chestnut wood, retarded to some extent the rate of sorption of water in the Norway spruce wood surface, and resulted in lower overall sorption.

Nevertheless, the different behaviour of wood wettability with particular treatments of extractive solutions, observed on the poplar and spruce surfaces, can be discussed through analysis of the results of studies on surface phenomena by several authors. The wettability of wood surfaces is regarded to be influenced by a complex set of aspects in which extractives of resinous nature may certainly play an important role [27]. The fresh wood surface is more easily wetted by water than the aged wood surface. The higher carbon percentage of the aged surface results in greater hydrophobicity than the lower carbon percentage of the fresh surface. This observation is well supported in the literature [40,41] and correlates quite well with the XPS results on aged and fresh surfaces. On the other hand, the storage of wood surface is also particularly important. In fact, a small amount of impurity such as a monolayer of an organic contaminant can significantly alter the wetting properties of a wood surface. The diffusion and adsorption of a probe liquid, like water, into the cell wall, depends on the capillarity of wood cell lumens, i.e., pores [42], as well as on the fibre orientation. In fact, as it is well known, wood is anisotropic and its properties are different in radial, tangential and axial directions. According to Kocaefe [43], the contact angles are greatest in the axial direction compared to those measured in the radial and tangential directions in untreated white ash and maple wood.

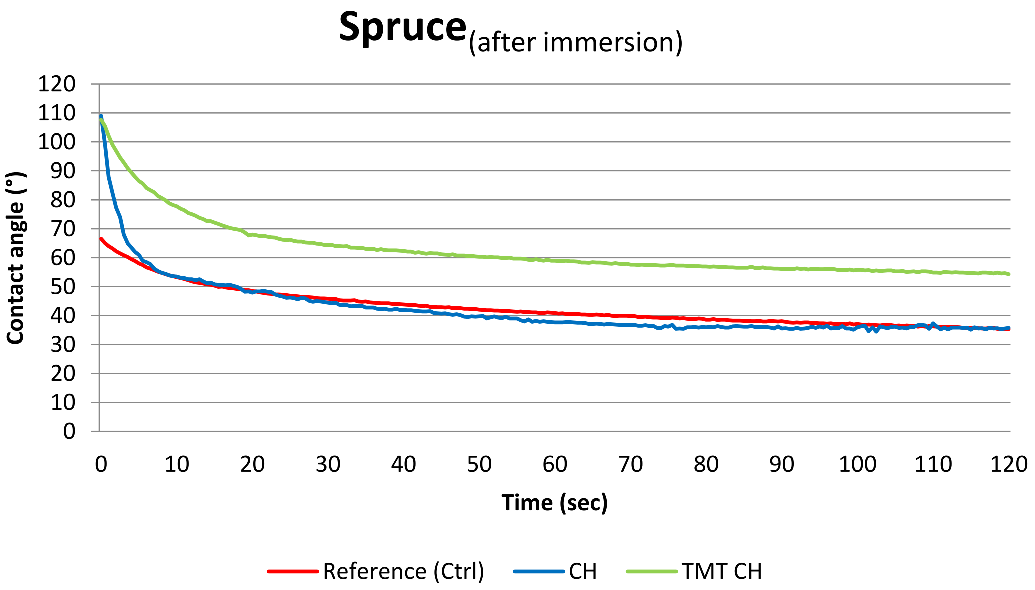

Figure 6. Contact angle recorded over a time of 120 s on spruce wood surface, where: sample wood surface with any treatment, Reference (Ctrl); sample wood surface treated with extractives of chestnut untreated, CH; sample wood surface treated with extractives of chestnut thermally treated, TMT CH.

To evaluate the variation in time of contact angle after UV exposure of the surface, the poplar and spruce wood samples were submitted again to the accelerated weathering test. Figure 7 shows a strong decrease in contact angle values in the poplar wood samples that both used chestnut extractives. Both the initial contact angle and its reduction rate indicate the greater hydrophilic nature of weathered wood, be it treated with extractives or not.

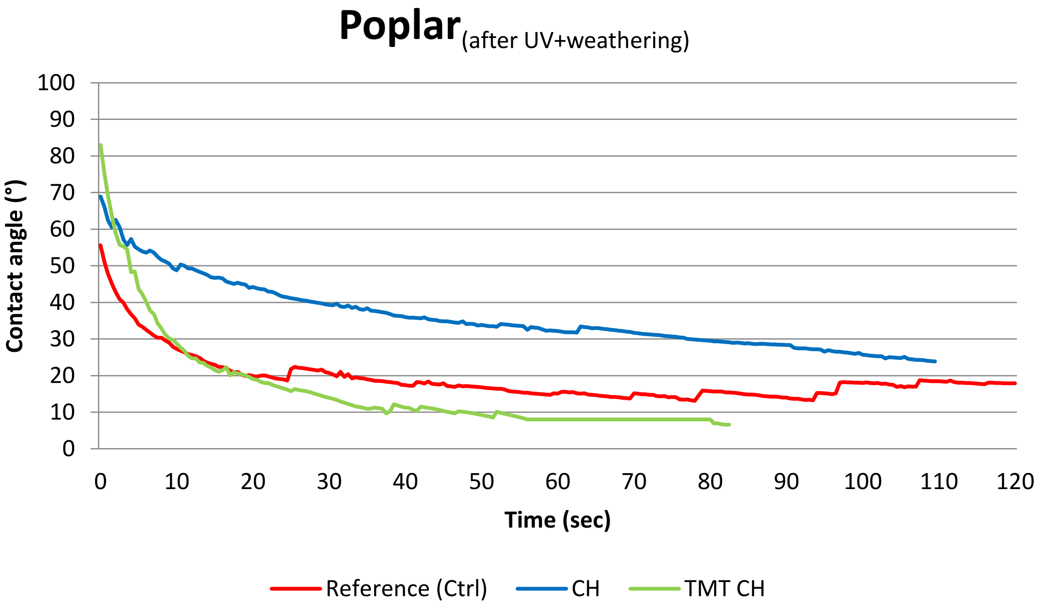

Figure 7. Variation in contact angle over 120 s of poplar wood surfaces previously treated with extractives and then submitted to accelerated weathering UV exposure test, where: sample wood surface with any treatment, Reference (Ctrl); sample wood surface treated with extractives of chestnut untreated, CH; sample wood surface treated with extractives of chestnut thermally treated, TMT CH.

Concerning the spruce wood surface, Figure 7 shows that the positive effect of the application of TMT CH extractives, noticed on unexposed wood, disappeared after weathering (Figure 8). In fact, although contact angle values for 120 s were recorded, the surfaces of spruce without extractives and with native extractives (CH) showed a higher wettability, leading to a rapid adsorption of the drop, at 30 and 20 s, respectively. The initial values of the contact angle were smaller than on the unexposed wood, and these values further decreased drastically. However, worthy of mention is the residual effect on contact angle changes conferred to the spruce wood surface by treatment with the extractives obtained from thermally modified chestnut wood, although this effect could hardly be declared as hydrophobic.

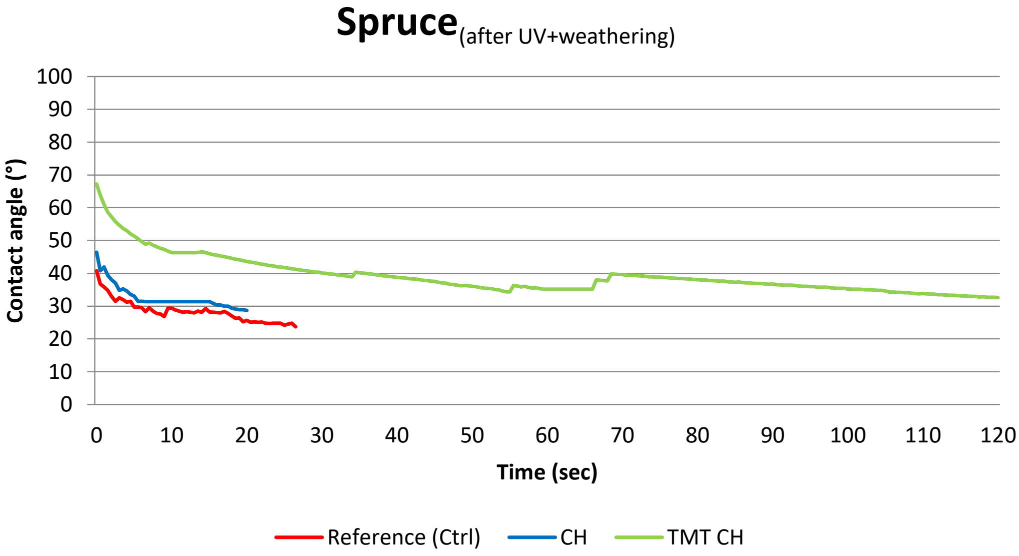

Figure 8. Variation in contact angle over 120 s of spruce wood surfaces previously treated with extractives and then submitted to accelerated weathering UV exposure test, where: sample wood surface with any treatment, Reference (Ctrl); sample wood surface treated with extractives of chestnut untreated, CH; sample wood surface treated with extractives of chestnut thermally treated, TMT CH.

Therefore, it may be concluded that all the surfaces of both wood species became hydrophilic due to UV-induced breakdown of wood constituents. Neither of the extractive treatments proved efficient in providing significant improvement in hydrophobic properties. It can be assumed that the initial reduction in wettability, observed after immersion into the extractive solutions, was caused by tannins and other chemical compounds present in the chestnut extractives. On the other hand, the decrease in contact angle on all wood surfaces with exposure was expected because accelerated weathering could be causing the breakdown of extractives and leaching out of extractives, which are organic compounds and are easily dissolved and removed by water.

The UV-weathering exposure caused not only physical alterations but also chemical changes that surely must have affected the effects of the extractives on the contact angle of both wood species, as many authors have demonstrated. Feist and Hon [32] reported that the loss of aromatic components in wood as a result of photochemical degradation, as well as of exterior weathering exposure, also change the aromatic and side-chain components of lignin to reduce their contribution to the water repellence of wood. Carbonyl, carboxyl, quinone, peroxide and hydroperoxide groups are formed in wood by photo-oxidation [44] together with the action on extractives; therefore, the weathering has the net effect of increasing the wettability of wood. Cellulose, being more resistant to weathering effects, becomes more abundant on the weathered wood surface. This increases the hydroxyl concentration on the wood surface. As a result, when a droplet of water contacts the weathered wood, greater interaction between the hydroxyl groups of wood and water undoubtedly occurs.

Artificial weathering, through the combined action of light and water, causes the gradual destruction of a wood substance on the first superficial layer of the material. As confirmed by Kalnins and Feist [45], a leached, eroded, cellulose-rich layer remains on the wood surface. The authors also suggested that liquid precipitation contributes to the photo-oxidation of extractives, which leads to the production of volatile products and to the formation of water-soluble materials and effectively removes the degradation products from the exposed surface. Rowell [46] suggested that lignin is the principal component responsible for the water repellence of wood but D'Auria et al. [47] highlighted that lignin is primarily responsible for the absorption of ultraviolet radiation, therefore its breakdown shows the first early effects of degradation caused by weathering.

3.4. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR FT-IR) Analysis

A useful tool to understand the chemical modifications and chemical bonds caused by chestnut extractives applied to both wood surfaces, poplar and spruce, is the FTIR analysis. The typical FTIR spectrum of extractives from untreated (CH) and thermally modified (TMT CH) chestnut wood is reported in Figure 9.

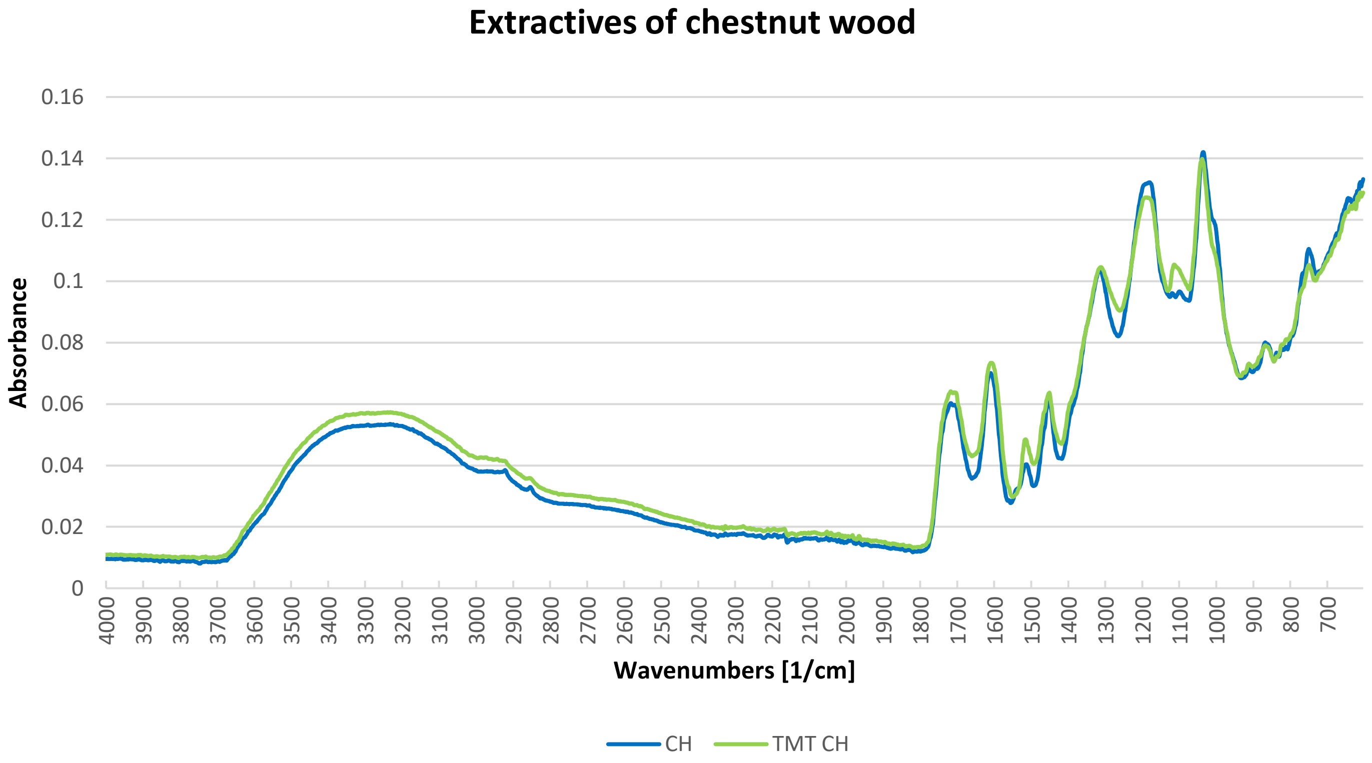

Figure 9. FTIR spectra of the two different types of extractives achieved from untreated chestnut wood (CH) and thermally treated wood at 180 °C (TMT CH).

In addition, the FTIR spectra of the different types of chestnut extractives used on the poplar wood surfaces are reported in Figure 10.

In the presence of natural chestnut extractives, an increase in the signals from the surface related to the presence of carbonyl compounds (1727 cm^{-1}) and aromatic rings (1590 cm^{-1}) was observed. Furthermore, an important increase in the peak between 1400 and 1100 cm^{-1} was observed in agreement with an increase in the presence of aromatic rings on the wood surface due to the presence of the extractive.

After UV exposure, we observed an increase in the peak at 3340 cm^{-1} due to the presence of OH groups that were not present in the reference spectrum. Furthermore, a new peak at 1639 cm^{-1} was determined. The intensity of this peak correlates with the intensity of the peak at 3340 cm^{-1} which is the OH stretching band and can therefore also be attributed to OH groups. The peak was observed neither in the reference spectrum nor on the unexposed surfaces treated with the extractives. Finally, some peaks present in the reference spectrum without extractives could not be observed after the weathering process: a peak at 1506 cm^{-1} (due to aromatic rings) and a peak at 1210 cm^{-1} due to C-O stretching are no longer present on the spectra of the weathered surface. The results suggested that the presence of extractives modifies the chemical structure of the poplar wood surfaces also after the weathering process. The use of extractives obtained from thermally modified chestnut wood gave very similar results (Figure 11).

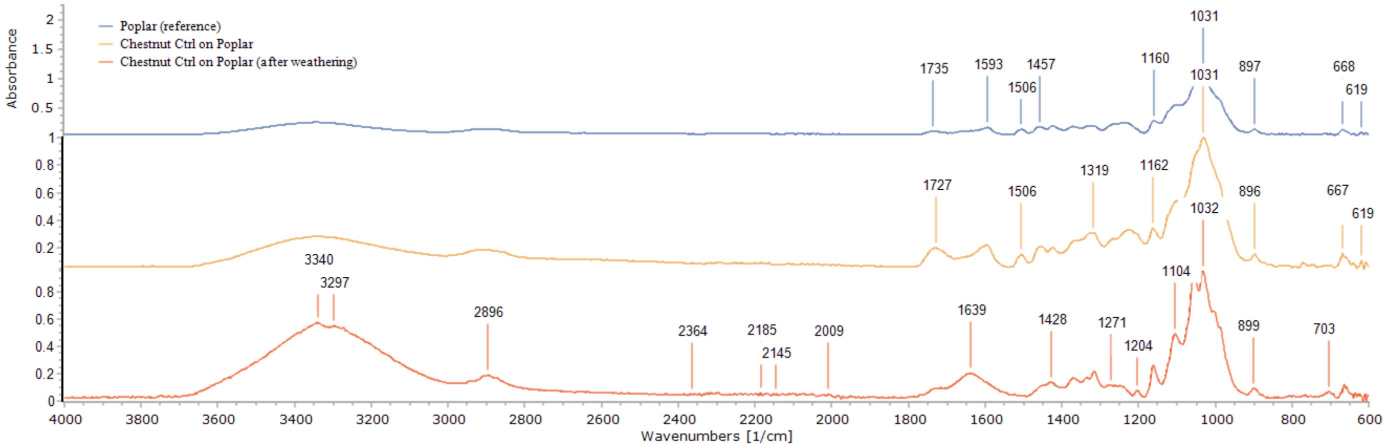

Figure 10. Comparison between FTIR spectra of poplar wood surfaces without extractives (reference), with extractives achieved from native chestnut wood and with extractives after weathering UV exposure.

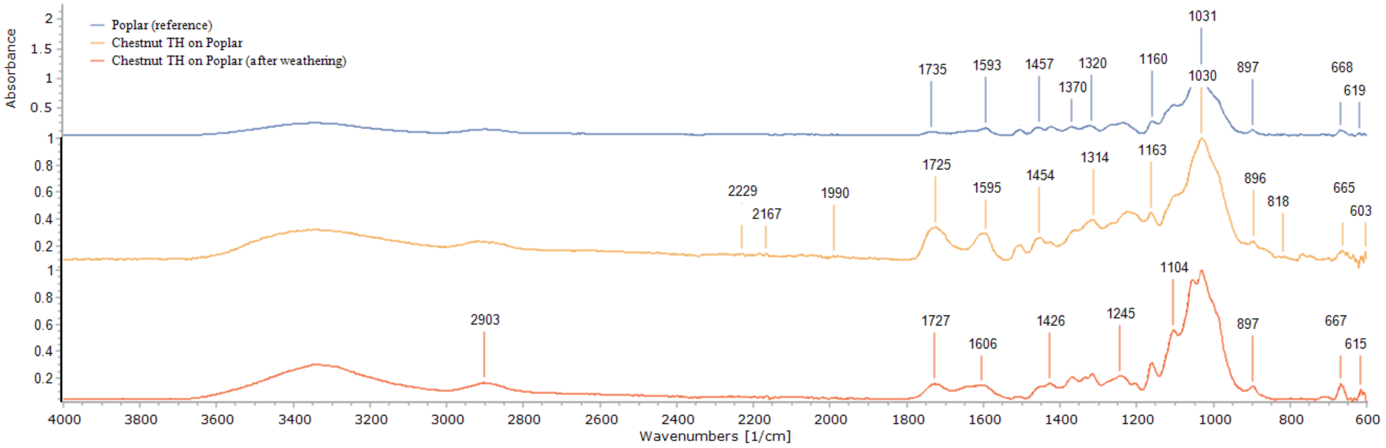

Figure 11. Comparison between FTIR spectra of poplar wood surfaces without extractives (reference), with extractives of thermally modified chestnut wood and with extractives after weathering UV exposure.

It is also underlined that, comparing the samples with extractives before and after weathering, an increase in OH stretching signal, a decrease in the carbonyl signal at 1727 cm^{-1}, an increase in the signal near 1640 cm^{-1}, and a decrease in the peak at 1506 cm^{-1} were observed after weathering. However, an increase in the signals at 1300–1400 cm^{-1} (due to phenolic OH) in the chestnut TH on poplar was observed. The same behaviour was noticed when the spruce wood surfaces were treated with extractives derived from native chestnut (Figure 12).

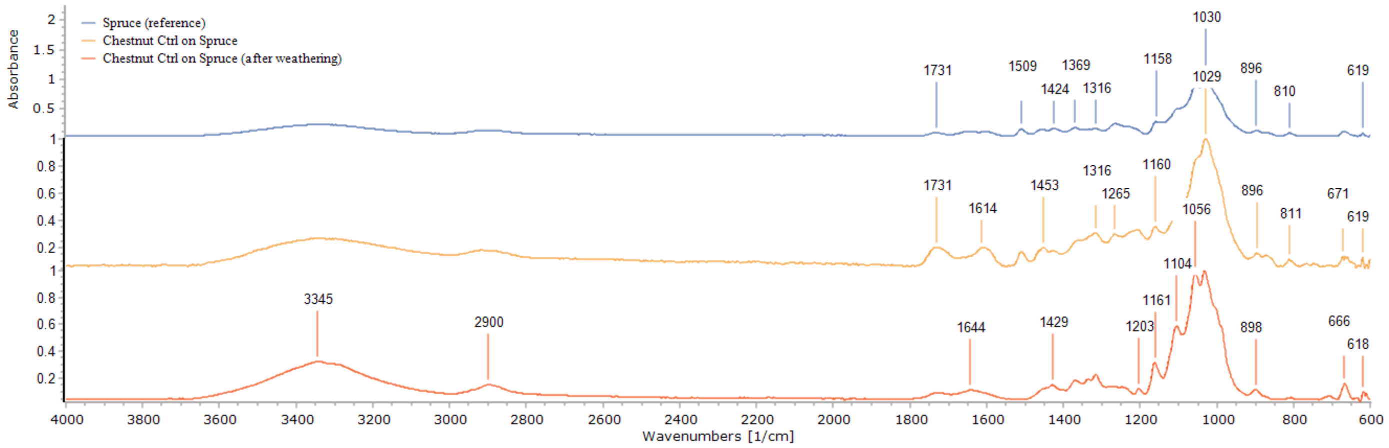

Figure 12. Comparison between FTIR spectra of spruce wood surfaces without extractives (reference), with extractives achieved from native chestnut wood and with extractives after weathering UV exposure.

Worthy of attention is the increase in the OH stretching signal, the absence of the peak at 1509 cm^{-1}, and a neat decrease in the absorption at 1265 cm^{-1} (due to guaiacyl units). Similar results to those depicted for poplar wood after weathering were observed when the spruce wood surfaces were immersed into a solution of extractives obtained from thermally modified chestnut wood (Figure 13).

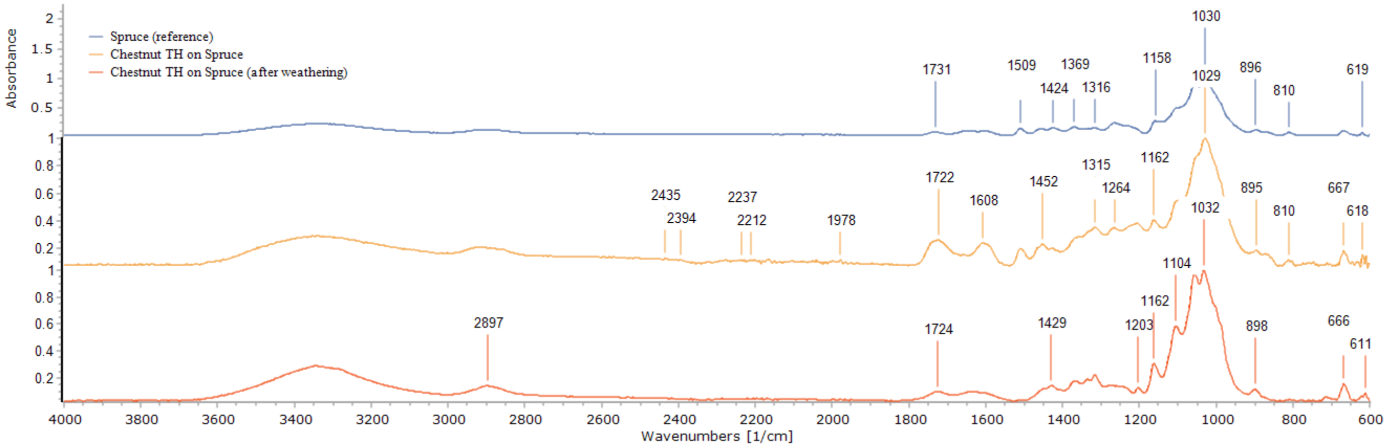

Figure 13. Comparison between FTIR spectra of spruce wood surfaces without extractives (reference), with extractives of thermally modified chestnut wood and with extractives after weathering UV exposure.

The FTIR results suggested that the degradation processes of both poplar and spruce references were related to chemical changes in basic wood constituents, mainly lignin. Chemical changes were characterized by lignin and hemicelluloses degradation. Decreases in both methoxy and carbonyl groups, cleavages of bonds in lignin and hemicelluloses, and oxidation reactions were observed.

These results clearly showed that the presence of chestnut extractives modifies both poplar and spruce wood surfaces at their application but also after the weathering process. These findings are supported by earlier studies demonstrating the beneficial role played by natural extractives in the stability of wood colour [1]. A previous study [16] on chestnut wood extractives showed a high presence of phenolic and tannin content, thus the results can be attributed to the antioxidant properties of these substances, which are able to play a protective role in the stability of colour and in the mitigation of the degradation process.

4. Conclusions

Poplar and spruce surfaces were treated with chestnut extractives to investigate the possible positive effect of natural compounds on surface photostability through their antioxidant and radical-scavenging activity and on the hydrophobicity of wood surfaces. Extractives were obtained from native chestnut wood and from thermally modified chestnut wood.

Solutions of chestnut extractives, applied on poplar and spruce surfaces through immersion, proved inefficient in changing the hygroscopic properties of surfaces as measured by the water droplet contact angle. However, extractive solutions caused a moderate change in the appearance of both species, but extractives derived from thermally modified chestnut altered the wood colour more significantly, becoming darker and more reddish. When all those surfaces were exposed to artificial UV-weathering in a QUV apparatus, a positive effect on the stability of colour was observed, particularly on the poplar specimens. Solutions of extractives acted differently on spruce and poplar, showing better stability on poplar surfaces when treated with native chestnut extractives, whereas better stability of spruce surfaces was obtained when treated with TMT chestnut extractives.

Certainly, the use of extractives presents an environmentally friendly alternative to processes involving chemical synthesis. In this research, the applied treatments proved promising since the extractives were used without protective film or a fixation agent and were exposed to water-spray leaching during exposure. Should surface modifications with extractives be physically protected by a water-repellent film, the efficacy of extractives on the photostability of light-coloured wood species would be promising. In the context of green chemistry, the role of wood extractives is expected to have a significant impact on the wood industry sector, yielding both economic and health benefits.

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