

## Article

# Modification of Shellac with Clove (*Eugenia caryophyllata*) and Thyme (*Satureja hortensis*) Essential Oils: Compatibility Issues and Effect on the UV Light Resistance of Wood Coated Surfaces

Maria Cristina Timar \*  and Emanuela Carmen Beldean

Faculty of Furniture Design and Wood Engineering, Transilvania University of Braşov, 500036 Braşov, Romania

\* Correspondence: cristinatimar@unitbv.ro

**Abstract:** Shellac (SL) is a natural resin employed for wood finishing, while clove (*Eugenia caryophyllata*) and thyme (*Satureja hortensis*) essential oils (C-EO, T-EO) are organic natural products of vegetal origin with antifungal, antimicrobial and antioxidant properties. The present paper aims at exploring the potential of modifying alcoholic shellac solutions with essential oils (C-EO, T-EO), focussing on the recurrent effects of this modification on the traditional wood finishing technique, the colour and the UV light resistance of the wood coated surfaces. The compatibility of C-EO and T-EO with ethyl alcohol and the alcoholic reference SL solution was evaluated, and modified SL solutions with a content of 5% and 10% C-EO and T-EO were prepared. Wood samples of European maple (*Acer pseudoplatanus*) and European walnut (*Juglans regia*) were finished with reference and modified SL solutions. An accelerated UV ageing test was run, and the samples were evaluated after 24, 48 and 72 h of exposure. Colour measurements in the CIELab system and FTIR–ATR investigation were employed for monitoring colour and surface chemistry changes. Coating with SL resulted in visible colour changes for both wood species ( $\Delta E$  values of 31.06 for maple and 13.00 for walnut) and increased UV resistance, reducing colour changes after 72 h UV exposure (by 83% for maple and by 59% for walnut) as compared to the uncoated controls. Modification of SL solutions with C-EO and T-EO only slightly influenced the colour of finished surfaces ( $\Delta E = 1.88$ – $5.41$  for maple,  $\Delta E = 1.36$ – $3.41$  for walnut) and their UV resistance. The colour changes ( $\Delta E$ ) of coated surfaces after 72 h exposure varied in the range 1.63–4.53 for maple and 2.39–3.58 for walnut, being generally slightly higher (by 1.7–2.9 units for maple and 0–1 unit for walnut) for the modified SL solutions. FTIR investigation highlighted only minor chemical changes of the shellac coating films after 72 h of UV exposure. A photo-induced oxidative process of eugenol seemed possible in the case of SL modified with C-EO.



**Citation:** Timar, M.C.; Beldean, E.C. Modification of Shellac with Clove (*Eugenia caryophyllata*) and Thyme (*Satureja hortensis*) Essential Oils: Compatibility Issues and Effect on the UV Light Resistance of Wood Coated Surfaces. *Coatings* **2022**, *12*, 1591. <https://doi.org/10.3390/coatings12101591>

Academic Editor: Mariaenrica Frigione

Received: 28 August 2022

Accepted: 18 October 2022

Published: 20 October 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Keywords:** shellac; essential oils; UV ageing; colour; FTIR; wood; maple; walnut

## 1. Introduction

As a natural biopolymer, shellac (SL) qualifies today as both a traditional material with a long history and a modern multifunctional material with great potential for development of greener technologies [1]. Shellac is a natural film-forming resin obtained by purification procedures of the hardened secretion of the parasite lac insects from the *Kerriidae* family (*Kerria lacca*) that mostly grow on various species of trees and bushes from South-Eastern Asian countries, especially India. Since the 17th century, shellac has become an important wood coating material in Europe, often employed to obtain exquisite, high-gloss finishes for furniture (French polish) and musical instruments (e.g., violins) [1,2]. The same material and technique are applied today for authentically restoring historic furniture/artefacts [3], as well as for the finishing of the upper-class concerto string musical instruments.

The chemical composition of shellac is complex and depends on the source of material (insects, host trees) and the purification procedures applied to remove colouring materials and waxes from the raw stick lac. Purified shellac resin is considered a complex mixture

of esters (soft resin) and polyesters (hard resin) of various poly-hydroxy carboxylic acids, the main ones being: aleuritic acid (a tri-hydroxy aliphatic linear monocarboxylic acid), jalaric acid and shelloic acid (polycyclic terpenoide acids) [1,2]. Shellac is a hard and brittle resinous solid, coloured from light yellow to dark red. It is a thermoplastic, polar resin and highly soluble in organic polar solvents, especially alcohols. Aqueous solutions may be obtained in alkaline medium (e.g., NaOH 10%, as recently reported [4]).

Alcoholic solutions prepared from shellac flakes (the commercial form of SL), known as “polishes”, are employed for wood finishing. Film formation occurs very quickly as a result of a typical physical process of solvent evaporation, so that shellac finishes have limited resistance to water, and solvents and are reversible against alcohols, though this property decreases with ageing due to possible cross-linking reactions [5,6]. Investigations by FTIR and XPS of thin shellac films irradiated with UV light concluded that SL may be used as protective coating under solar radiation conditions for organic electronics [7].

The shellac coating films have very good adhesion to the wood substrate and excellent aesthetic features, including gloss and characteristic colour. Gloss and colour of the coated surfaces may be affected by ageing under the action of UV light [8–11]. In a study on the protective effect of different coatings, it was demonstrated that SL provides a better protection of wood surfaces against photo-degradation than beeswax in terms of colour changes. However, after long-term exposure, the protective effect of these coatings turned out to be very low, only slightly reducing the chemical changes of wood components [12]. Shellac and beeswax films cannot block UV radiation to reach the underlying wood surface, and consequent chemical modifications were found relevant for both uncoated and coated wood.

As a nontoxic, eco-friendly and biodegradable material, shellac is also often employed as edible coating film for postharvest protection for fruits (e.g., [13]); food products and pharmaceutical applications, including drug delivery systems [14]; and in many other applications and modern technologies, as recently reviewed [1].

Recent research reports on the employment of shellac as a shell (e.g., [15,16]) or core [17,18] of microcapsules or nanoparticles for various applications, including water-borne, self-repairing coatings with improved mechanical properties and increased ageing resistance [18–21]. Shellac coating films reduce water uptake in wood [22], while wood impregnation with shellac solutions results in its dimensional stabilisation [23]. All these data demonstrate the versatility and potential of shellac, which may be further increased by various modifications, such as cross-linking with polyamines or polyaziridines [2], or the employment of additives, such as nanoparticles of SiO<sub>2</sub>, ZnO and ZrO<sub>2</sub>, to improve UV ageing resistance and hardness [9,11]. Moreover, consecutive applications on maple wood surfaces of a nanostructured ZnO layer and shellac resulted in increased resistance to UV radiation and mould growth [10].

Clove (*Eugenia caryophyllata*) and thyme (*Satureja hortensis*) essential oils (C-EO, T-EO), as many other essential oils (EOs), are organic natural products of vegetal origin, with a complex chemical composition (up to around 30 components, with 1 to 3 of them in higher concentration), including a high content of phenolic compounds (e.g., 67–89% eugenol in C-EO; 47–87% carvacrol in T-EO) [24,25], alongside various terpenes (e.g.,  $\beta$ -caryophyllene in C-EO and T-EO;  $\alpha$ -pinene and  $\alpha$ - and  $\gamma$ -terpinene in T-EO) and terpenoids (e.g., caryophyllenyl alcohol in C-EO;  $\alpha$ -linalool in T-EO). This complex chemical composition confers EOs complex biological activities including antifungal, antimicrobial and antioxidant properties [24,26–28]. These properties are valuable features in various application fields including pharmacology and medicine, the food industry [24,29] and wood protection and cultural heritage conservation [30–32].

The antioxidant activity of EOs results from their good radical-scavenging activity, related especially to their content in phenols [28,33,34].

Nanoencapsulation of EOs to increase their efficiency and reduce their volatility is a correlated important research topic [35,36], while shellac is one of the natural resins employed in the shell structure [15,16]. Cinnamon essential oil as alternative fungicide [37]

or carvacrol and thymol [38] were incorporated in shellac coating for an improved citrus fruit bioprotection during storage and marketing. Biodegradable active packaging films of various polymers (e.g., poly-butylene adipate-co-terephthalate PBAT, polylactide PLA, gelatine/agar) modified with clove and thyme essential oils demonstrated good UV protection (UV blocking) and antioxidant activity, while transparency to visible light was maintained [39,40].

Previous research of the authors highlighted the antifungal properties of C-EO and T-EO against wood decay fungi and their potential for preventive and curative antifungal treatments in the process of wood/furniture conservation [41–44] when employed as alcoholic solutions of 5% and 10%.

The research presented in this paper aims to explore the potential of modifying the alcoholic shellac solutions employed for wood coating with essential oils (C-EO, T-EO), in terms of compatibility issues and recurrent effects on the traditional wood finishing technique and properties of the coated surfaces. The paper focuses on the influence of these modifications on the colour and UV light resistance of the finished wood surfaces, analysed by FTIR and colour measurements in the CIELab system

## 2. Materials and Methods

### 2.1. Materials

Standard shellac flakes (Masserini) and colophony resin (Masserini) were purchased from Complex Art: Creative Hobby Timișoara–Romania [45], products codes GMLSCKG5 and 2055036265006. Clove essential oil (*Eugenia caryophyllata*) and Thyme essential oil (*Satureja hortensis*) as pure oils (100%) were purchased from Steaua Divină–Romania [46], products codes SKU: PN100061 and SKU: PN10039. Ethyl alcohol (absolute, proanalysis, C = 99.3%) from Chemical Company Romania (Iași, Romania) [47] was employed as solvent.

Two hardwood species: European maple (*Acer pseudoplatanus*) and European walnut (*Juglans regia*), were employed. These species were chosen as being representative for both historic and modern furniture and because of their different natural colours: white–yellowish (maple) and reddish brown (walnut), rendering a beautiful contrast, often capitalised in the design of furniture.

Experimental test samples with dimensions of (120 × 80 × 5) as (length × width × thickness) in mm, with smoothly planned radial/semiradial faces, were processed from the same batch of wood material (MC 10–12%). The surfaces were further sanded with abrasive paper H120 and H150 and cleaned from dust by air blowing. All samples were conditioned at 20 ± 2 °C and 55 ± 5% RH before and after finishing and prior to any investigation. A number of 48 samples were prepared from each wood species.

### 2.2. Experimental Methods

#### 2.2.1. Preparation of Shellac Polishes

A reference SL solution (polish), coded SL\_Ref, was prepared from the solid shellac flakes (50 g) and an addition of 10% rosin (5 g) by dissolution in ethyl alcohol (500 mL, density 0.79 g/mL) under stirring on a warm water bath (40–50 °C). The solution was filtered through a fine plastic mesh and stored in the lab at 20 °C until utilisation. The calculated solids content of SL\_Ref solution was 13.2%.

With the view of modifying the reference SL solution with EOs, the miscibility and compatibility of the two essential oils (C-EO and T-EO) with the ethyl alcohol was previously tested. Mixtures of EO/ethyl alcohol at the ratio 1:10 (v:v) were prepared for this purpose. Physical compatibility was evaluated by direct observation (homogeneity and clarity of the mixture), while chemical compatibility was associated with the nonreactivity of the EOs components with the ethyl alcohol and was assessed by FTIR (see Section 2.3.2).

Modified SL polishes by 5% and 10% EOs were further prepared and coded, as presented in Table 1. These proportions of modification were chosen based on previous

research on the antifungal properties of the two EOs and their potential for wood conservation, found as appropriate at volumetric concentrations of 5–10% in ethyl alcohol [41–43].

**Table 1.** Reference and modified shellac polishes.

No	Type of SL Polish	Composition (Volumetric Proportions)			Research Code (Coating Variant)
		SL_Ref (13.2% *)	C-EO 100%	T-EO 100%	
1	Reference SL	100	-	-	SL_Ref
2	Modified SL-C-EO	95	5	-	SL_C-EO_5
3		90	10	-	SL_C-EO_10
4	Modified SL-T-EO	95	-	5	SL_T-EO_5
5		90	-	10	SL_T-EO_10

\* Note: 13.2% represents the calculated solids content of the reference shellac solution (SL\_Ref) composed of 50 g shellac flakes, 5 g rosin and 500 mL ethyl alcohol 99.3% (density 0.79 g/mL). The modified SL solutions were prepared by mixing SL\_Ref with C-EO or T-EO at the volumetric ratios presented in the table.

### 2.2.2. Finishing of Wood Samples

The test samples were finished manually following the traditional technique. A base coat was applied by brushing three successive layers of about 110 g/m<sup>2</sup> at intervals of 2–4 h (drying time) without intermediary sanding. An extension of the drying time for the third layer of the basecoat, from 4h to overnight, was necessary in the case of SL modified by 10% C-EO. Afterwards, the samples were sanded with 360 grit size abrasive paper, and finishing was continued by employing a polishing “rubber” to apply the shellac solution in thin coats until a satisfactory degree of pores filling/covering of the wood structure and glossy surfaces were obtained. The final coating film thickness was about 40–50 µm. A series of 8 test samples were prepared for each type of SL solution, resulting in 5 finishing variants and 40 coated samples/wood species.

### 2.2.3. Accelerated UV Ageing Procedure

A Feutron 400 FKS environmental climatic chamber (Feutron Klima Simulation—GmbH- Langenwetzendorf, Germany) equipped with a UVA Spot 400T lamp (Dr. Hoenle UV Technology—Gilching, Germany), fitted with a glass H2 filter, was employed to expose the wood samples to light in the range of 295 to 600 nm, which is a combination of UV-B (292–315 nm), UV-A (315–400 nm) and visible light (400–600 nm), simulating natural light filtered by window glass. More details on this light source were previously published [48]. As emission in the UV range (mainly UV-A) is maximum for this lamp and this type of radiation with higher energy than visible light is mostly responsible for wood and coatings’ photo-degradation [49], UV light was considered as the main ageing factor in this test, and the term “UV ageing” was employed for the procedure. However, it should be acknowledged that visible light with wavelength up to 515 nm may contribute to surface and subsurface wood colour changes, while visible violet radiation up to 430 nm may have a contribution to lignin degradation [50]. The samples were placed vertically on a rack at a distance of 60cm from the UV source. The actual UV irradiation procedure (similar to previously reported research [51]) included an initial conditioning of 0.5 h (20 °C, 55% RH, no light), followed by 3 cycles of 24 h UV exposure separated by a conditioning phase of 24 h (20 °C, 55% RH, no light) inserted to allow for the removal of samples for measurements. Each cycle of 24 h UV exposure consisted in four steps of 6 h UV irradiation at 40 °C alternated with dark periods of 0.5 h. Cycles of 24 h UV exposure are in accordance with ISO 16474-3:2013, exposure method B: daylight behind window glass. This procedure was repeated three times so that data refer to samples exposed for 24, 48 and 72 h to UV, coded 24 UV, 48 UV and 72 UV, respectively. Two replicates from each finishing variant and wood species, alongside corresponding uncoated controls, were tested simultaneously.

### 2.3. Characterisation Methods

#### 2.3.1. Colour Measurements

Colour measurements in the CIELab system were performed with an AvaSpec-USB2 spectrometer (Avantes B.V., Apeldoorn, Netherlands), employing D65 standard illuminant under 2° standard observer and an integrating AVA sphere. Data were processed with AVASOFT—version 7.7/Colour application.

The colour coordinates: lightness  $L^*$  (varying from 0 for black to 100 for white), redness  $a^*$  (varying from negative values for green to positive values for red on the green–red axis) and yellowness  $b^*$  (varying from negative values for blue to positive values for yellow on the blue–yellow axis) of all wood samples were measured before and after coating with SL, prior to and after different periods of ageing. Experiments were carried out in duplicates. For each test sample, colour measurements were performed on 5 points (actually circular areas of about 8mm in diameter), and an average was calculated. A fixing device was employed to repeat measurements of each sample in the same points.

Colour differences were calculated based on the Equation (1):

$$\Delta E = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2}, \quad (1)$$

where  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  are the differences of initial and final values (before and after finishing or ageing for different periods of time) of  $L^*$ ,  $a^*$  and  $b^*$  parameters, respectively.

Lower calculated colour differences correspond to lower differences of visual perception. Different ranges of  $\Delta E$  values were associated with smallest/barely visible difference by human eye ( $0.2 < \Delta E < 2.0$ ), small colour difference ( $2.0 < \Delta E < 3.0$ ), medium colour difference ( $3.0 < \Delta E < 6.0$ ) and high colour differences ( $6.0 < \Delta E < 12.0$ ), while  $\Delta E$  values above 12 units account for visual perception as different colours [52].

#### 2.3.2. FTIR Investigations

FTIR–ATR spectra in the range  $4000\text{--}400\text{ cm}^{-1}$  at a resolution of  $4\text{ cm}^{-1}$ , and 24 scans/spectrum were recorded employing an ALPHA Bruker spectrometer (Bruker Optics GmbH & Co. KG, Ettlingen, Germany). The shellac solutions, the pure EOs and the mixtures EOs/ethyl alcohol were analysed as droplets placed directly on the ATR device. Spectra of wood surfaces were registered directly on three randomly chosen measuring areas for one replicate from each category of wood samples (uncoated, coated and aged). All spectra were further processed for baseline correction and smoothing, and average spectra were computed employing OPUS software (version 7.2) for each type of sample. These were further normalised (min–max normalisation) and analysed in order to highlight specific chemical features of the materials employed and/or chemical changes brought about by ageing. The assignment of characteristic absorption bands was based on references in the literature.

For assessing the chemical compatibility of the C-EO and T-EO with the ethyl alcohol, the experimental recorded spectra of the prepared mixtures of EO/Ethyl alcohol (1:10) were compared with the corresponding theoretical calculated spectra for the nonreactive mixture, employing the spectrum calculator function of the OPUS software (Equation (2)). Similar experimental and calculated spectra mean no reactivity, hence compatibility.

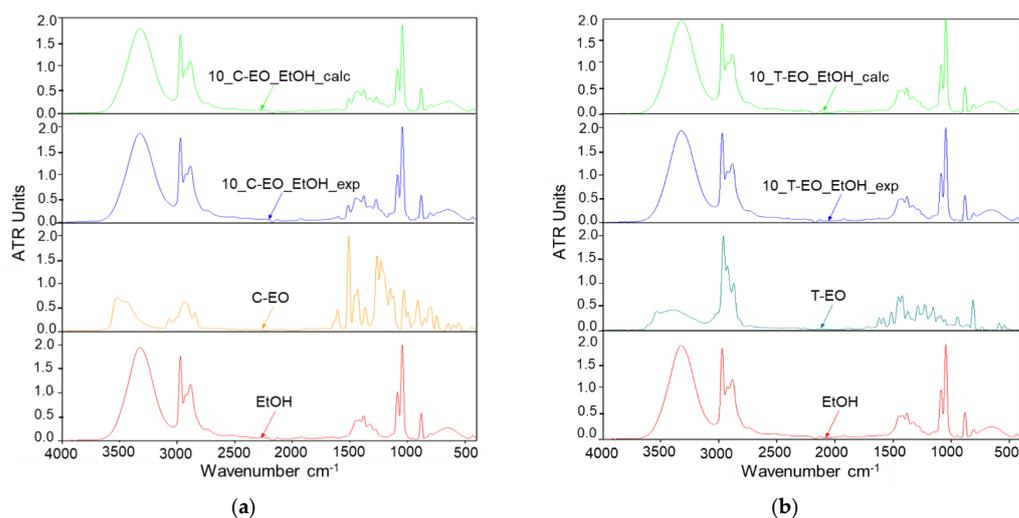
$$\text{Theoretical spectrum of mixture} = 1 \times \text{Spectrum of EO} + 10 \times \text{Spectrum of Ethyl alcohol} \quad (2)$$

## 3. Results

### 3.1. Modification of Shellac Solutions with EOs

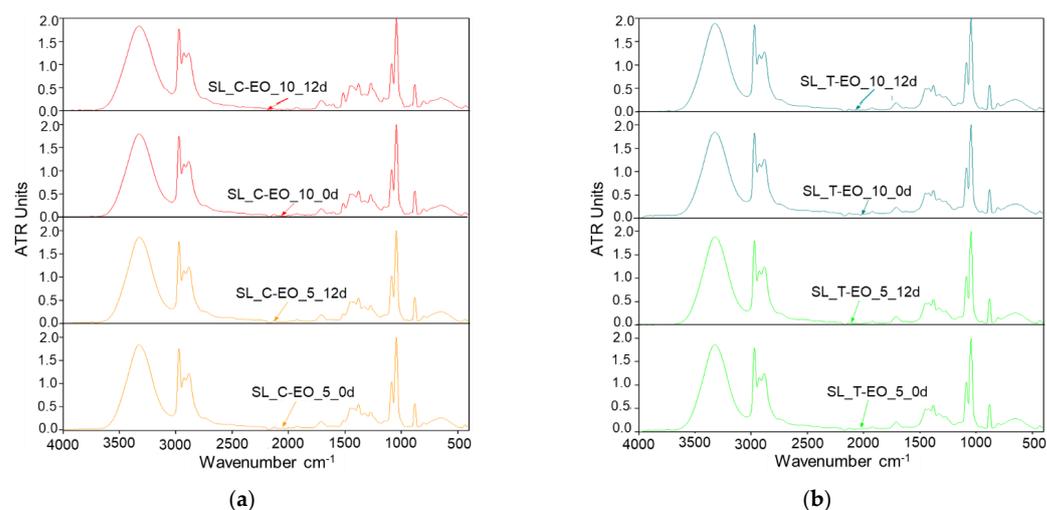
The miscibility of the EOs with ethyl alcohol, the solvent employed for SL dissolution, was initially tested. The two essential oils C-EO and T-EO were miscible with ethyl alcohol at the volumetric ratio of 1:10. A perfectly clear, slightly yellowish solution was obtained in the case of C-EO (10\_C-EO\_EtOH), while the corresponding T-EO mixture (10\_T-EO\_EtOH) was almost colourless but slightly opalescent, though without any trend of separation,

suggesting that one or some of its components were less miscible with ethyl alcohol. The experimental FTIR spectra of the alcohol-diluted EOs (10\_C-EO\_EtOH and 10\_T-EO\_EtOH), which were recorded immediately after the preparation of the mixtures and again after 12 days of storage in normal lab conditions, were similar to the OPUS-calculated theoretical spectra of the respective mixtures, suggesting no chemical interactions between the chemical components of the EOs and the ethyl alcohol (Figure 1). Furthermore, no changes could be observed in the FTIR spectra of the prepared solutions after 12 days of storage.



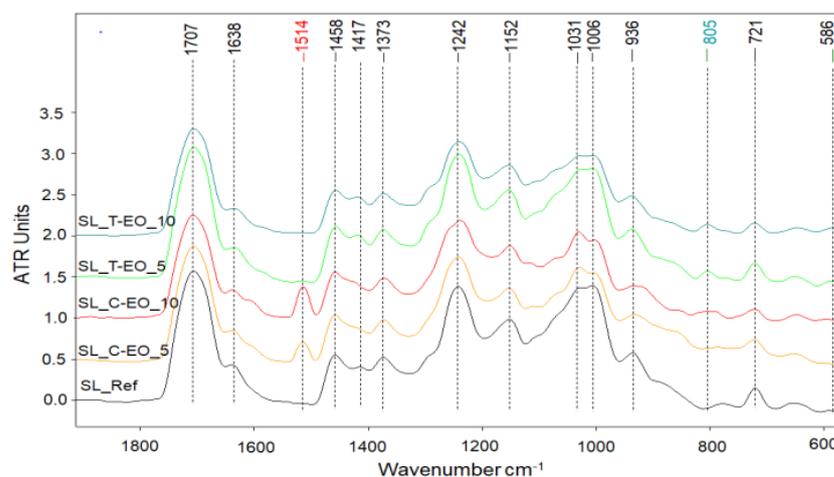
**Figure 1.** FTIR–ATR spectra of C-EO (a) and T-EO (b) as pure products and diluted in ethyl alcohol (1:10): experimental spectra, respectively coded 10\_C-EO\_EtOH\_exp and 10\_T-EO\_EtOH\_exp (blue spectra) compared to the OPUS-calculated theoretical spectra, respectively code 10\_C-EO\_EtOH\_calc and 10\_T-EO\_EtOH\_calc (green spectra).

As a result, homogenous and stable modified shellac solutions by 5% and 10% EOs (composition presented in Table 1) could be prepared. Their FTIR spectra recorded immediately after preparation and after 12 days of storage (Figure 2) were similar, indicating that no detectable chemical interactions occurred between the SL and the EO components.



**Figure 2.** FTIR–ATR spectra of the shellac solutions modified with: (a) clove essential oil C-EO (5\_C-EO\_SL; 10\_C-EO\_SL) and (b) thyme essential oil T-EO (5\_T-EO\_SL; 10\_T-EO\_SL), freshly prepared (coded 0d) and after 12 days of storage (coded 12d).

The FTIR spectra of the shellac cured films casted on microscope lamellas (Figure 3) present only minor changes brought about by the modification of the SL solutions with the two EOs. This is because most of the absorptions characteristic to the vibration modes of different functional groups (e.g., hydroxyl, carbonyl, carboxyl), chemical bonds (e.g., C–H, =C–H, O–H, C–O–C, C–O–, –C=C–) and other structural moieties (e.g., aliphatic methylene) are common for both the shellac and the EOs components, natural products with a very complex and also variable composition (spectra of the two essential oils employed in this research are presented in Figure S1).



**Figure 3.** Comparative FTIR spectra of reference and modified shellac films (casted on glass lamellas) in the fingerprint region (1800–600  $\text{cm}^{-1}$ ).

The main absorption bands in the spectra of SL and their assignment based on literature (centralised references in [53]) are as follows: 3300–3400  $\text{cm}^{-1}$  (–OH stretching), double peak 2926–2858  $\text{cm}^{-1}$  (asymmetric and symmetric C–H stretching in methylene groups), 1707  $\text{cm}^{-1}$  (stretching of unconjugated C=O bonds in carboxylic acids, esters and free aldehydes or ketones), 1636  $\text{cm}^{-1}$  as small shoulder (stretching of conjugated carbonyl, stretching of C=C double bonds), 1457 and 1373  $\text{cm}^{-1}$  (asymmetric bending and deformation of C–H bond in methylene –CH<sub>2</sub>– and methyl –CH<sub>3</sub> groups, symmetric deformations of C–CH<sub>3</sub>), 1242  $\text{cm}^{-1}$  (O–H bending and C–O stretching of carboxyl and hydroxyl groups overlapping with C–O stretch of –COOR), 1152  $\text{cm}^{-1}$  (C–O–C stretching, C–O stretching in esters and alcohols), broadband from 1031 to 1007  $\text{cm}^{-1}$  (C–O stretching of alcohols, ether/acetal linkage), 936  $\text{cm}^{-1}$  (rocking vibration of C–CH, C–H wagging of di-substituted trans olefins) and 722  $\text{cm}^{-1}$  (CH<sub>3</sub> rocking; C–H wagging of *cis*-olefins). However, in the fingerprint region, some differentiations were visible not only as relative intensity of different absorption peaks but also as specific absorptions due to the EOs components. The SL films modified with C-EO present a new peak (medium intensity) at 1514  $\text{cm}^{-1}$ , which could be assigned to the skeletal vibration of the aromatic ring [54] and also to the methyl substitution group [55] in eugenol and ethyl eugenol, the main chemical components of C-EO. The SL films modified with T-EO present a new peak (small intensity) at 805  $\text{cm}^{-1}$ , assignable to the out-of-plane wagging vibration of the C–H band in the aromatic ring (805–811  $\text{cm}^{-1}$ , depending on the relative position of substitution), and could be due to the presence of thymol in the composition of T-EO [55,56]. A trend of small absorption in this region, though not a clearly differentiated peak, can also be observed for the films modified with 10% C-EO, considering the substituted aromatic ring in the structure of eugenol, with a corresponding vibration at 816  $\text{cm}^{-1}$  [54].

### 3.2. Colour of Wood Surfaces

Colour analysis further presented in this paper is based on the colour measurements in the CIELab system. However, in order to enable a correlation of those data with visual

perception, scanned images of the uncoated and coated wood samples, before and after ageing, are comparatively presented in Figure 4 for maple and Figure 5 for walnut.



**Figure 4.** Images illustrating the aspect of maple (*Acer pseudoplatanus*) wood samples before and after coating with the five different types of shellac solutions: control samples before ageing and aged samples after 72 h UV exposure.



**Figure 5.** Images illustrating the aspect of walnut (*Juglans regia*) wood samples before and after coating with the five different types of shellac solutions: control samples before ageing and aged samples after 72 h UV exposure.

The results of the colour measurements in the CIELab system for the two wood species before and after finishing with the five types of shellac solutions are summarised in Table 2 as average values and standard deviations of the lightness  $L^*$  and chromatic coordinates  $a^*$  (redness) and  $b^*$  (yellowness).

**Table 2.** Colour parameters for uncoated and coated wood samples (controls before ageing)—average values and standard deviations (*italics* in brackets).

Colour Parameter	Type of Surface/Coating					
	Uncoated	SL_Ref	SL_C-EO_5	SL_C-EO_10	SL_T-EO_5	SL_T-EO_10
	Maple ( <i>Acer pseudoplatanus</i> )					
L*	85.14 (1.37)	70.31 (2.51) <sup>a</sup>	73.26 (1.96) <sup>b</sup>	72.39 (2.96) <sup>b</sup>	74.11 (1.52) <sup>b</sup>	71.39 (2.73) <sup>a</sup>
a*	3.65 (0.47)	11.06 (1.38) <sup>a</sup>	8.34 (1.26) <sup>b</sup>	8.69 (1.59) <sup>b</sup>	8.32 (0.97) <sup>b</sup>	9.53 (1.50) <sup>b</sup>
b*	14.89 (0.96)	41.12 (1.14) <sup>a</sup>	38.98 (2.99) <sup>b</sup>	39.29 (2.51) <sup>b</sup>	38.43 (1.64) <sup>b</sup>	40.97 (2.32) <sup>a</sup>
ΔE	-	31.03	4.54	3.65	5.41	1.88
	Walnut ( <i>Juglans regia</i> )					
L*	56.81 (2.68)	45.35 (2.55) <sup>a</sup>	45.25 (2.40) <sup>a</sup>	43.59 (2.08) <sup>b</sup>	44.15 (2.15) <sup>a</sup>	43.59 (3.21) <sup>b</sup>
a*	6.33 (0.97)	10.81 (1.72) <sup>a</sup>	9.55 (1.57) <sup>b</sup>	9.84 (1.06) <sup>a</sup>	9.35 (0.97) <sup>b</sup>	9.03 (1.29) <sup>b</sup>
b*	13.29 (1.69)	17.50 (3.47) <sup>a</sup>	16.97 (3.01) <sup>a</sup>	16.60 (2.98) <sup>a</sup>	15.84 (3.08) <sup>a</sup>	15.18 (4.04) <sup>a</sup>
ΔE	-	13.00	1.36	2.20	2.52	3.41

Notes: (1) L\*, a\*, b\* values are averages of 20 samples (100 measuring points) for the uncoated control samples and 4 samples (20 measuring points)/variant for the coated samples, respectively. Standard deviations are given in brackets. (2) Different letters (a,b) as exponents of the L\*, a\*, b\* values of the coated samples with the different types of modified SL solutions highlight values found as statistically significantly different from the corresponding values for the reference SL solution (SL\_Ref), when analysed as pairs by ANOVA single factor test, at a level of confidence of 95% ( $\alpha = 0.05$ ). (3) ΔE given values refer to surfaces coated with reference shellac solution (SL\_Ref) vs. uncoated wood and, respectively, to wood coated with modified SL solutions vs. wood coated with SL\_Ref.

Maple (Figure 4) is a diffuse-porous, light-coloured hardwood species with distinct annual rings but no marked difference between early and late wood. Numerous rays, grouped in shiny “mirrors”, are visible with the naked eye on the radial surfaces. The average values of the measured colour parameters were 85.14 for lightness (L\*), 3.65 for redness (a\*) and 14.89 for yellowness (b\*). The quite uniform colour and little variability among the samples resulted in relatively small standard deviations (0.47–1.37) for 20 samples (100 measuring points).

Walnut (Figure 5) is also a diffuse porous but dark-coloured wood species. On the radial section, the colour is brown with dark-brown or black stripes. Accordingly, the values of the measured colour parameters were different, namely: lower for lightness (L\* = 56.81) and increased for redness (a\* = 6.33), while only little changed for yellowness (b\* = 13.29) compared to maple. The characteristic nonuniform colour of each sample and variability among the 20 replicates resulted in higher standard deviations (0.97–2.68), especially for lightness.

A significant colour change occurred following finishing with the reference shellac solution for both wood species, but this was higher in the case of maple (ΔE = 31.03) in comparison with walnut (ΔE = 13.00). This is expectable considering the reddish-brown colour of shellac and the different initial colours of the two wood species. A decrease in lightness (−14.83 units for maple and −11.45 units for walnut) and increases of redness (+7.40 and +4.47 units, respectively) and yellowness (+26.23 and +4.21 units, respectively) were registered. The modifications of all the colour parameters (L\*, a\*, b\*) by coating with shellac (SL\_Ref) were found statistically significant ( $p < 0.05$ ).

Modification of the shellac solution (reddish-brown) by 5% and 10% C-EO (yellow to yellowish-brown) and T-EO (pale-yellow) resulted in small alterations of the colour of solutions and wood finished surfaces when compared to those coated with SL\_Ref (Table 2). These were slightly lighter in colour (by +1 up to +3 units), while the chromatic coordinates a\* and b\* were reduced by 0.5 up to 3 units, depending on the type and amount of EO. Statistical analysis of data showed significantly different colour parameters for the maple surfaces finished with modified SL solutions as compared to the reference polish, except for the finish with SL\_T-EO\_10. In the case of walnut, small statistically significant changes were found only in the redness (except for SL\_C-EO\_10) and lightness of wood samples coated with the SL solutions modified by 10% C-EO or T-EO.

The calculated colour differences between the modified finishes and the reference varied from 1.88 to 5.41 units for maple and 1.36–3.41 for walnut, which accounts for barely visible to small or medium differences in visual perception [52]. Moreover, it has to be pointed out that the colour of wood surfaces finished with shellac might also be influenced to some extent by the thickness of the coloured coating film, especially for the light-coloured wood species. In the manual traditional polishing technique, a strict control of the applied amount and thickness of the film is not really possible, the continuous process being controlled based mostly on qualitative aesthetical features.

### 3.3. Colour Changes Induced by UV Ageing

Exposure of the uncoated and coated wood samples to UV light resulted in colour changes regardless of the type of surface/finish or wood species. These changes evolved as the duration of UV exposure increased from 24 h (first evaluation) to 72 h (end of test and final evaluation). The experimental results, as average values of the  $L^*$ ,  $a^*$ ,  $b^*$  colour parameters and their standard deviations for all types of samples, before ageing (0 UV) and after UV exposure (24 UV, 48 UV, 72 UV), alongside the calculated colour differences  $\Delta E$  for each period of ageing relative to the initial state (0 UV), are summarised in Table 3.

As highlighted by the data in Table 3, the uncoated control samples of both wood species underwent the highest colour changes when compared to the coated ones. Under the action of UV light, uncoated wood became darker (decrease in lightness  $L^*$  by almost 5 units for maple and about 4 units for walnut), while chromatic changes consisted mostly of yellowing (increase in  $b^*$  coordinate of up to 8 units for maple and almost 5 units for walnut) and only small changes of redness (increase in  $a^*$  coordinate of about 1.7 units for both wood species).

These colour modifications are a direct indication of surface chemistry changes associated with wood photo-degradation [49,57,58]. Yellowing has been primarily related to the degradation of lignin leading to the formation of quinones, quinone methides and stilbenes [57,59], while redness of wood and its change as a result of photo-degradation has been associated primarily with the content of extractives [60]. Wood photo-degradation is initiated by the absorption of UV light by lignin, followed by the formation of free phenoxyl radicals and further chemical processes leading to lignin degradation and formation of new chromophores [49,57,58], which explains the highest modification of  $b^*$  chromatic coordinate. Wood extractives can act as UV absorbers, scavenge free radicals and undergo photo-oxidation reactions, retarding the photo-degradation of lignin/wood [61–63]. A higher content of extractives in walnut wood compared to maple wood may explain both the darker colour of walnut and the reduced colour changes compared to maple following light UV exposure, at least for the duration of the test carried out in this research.

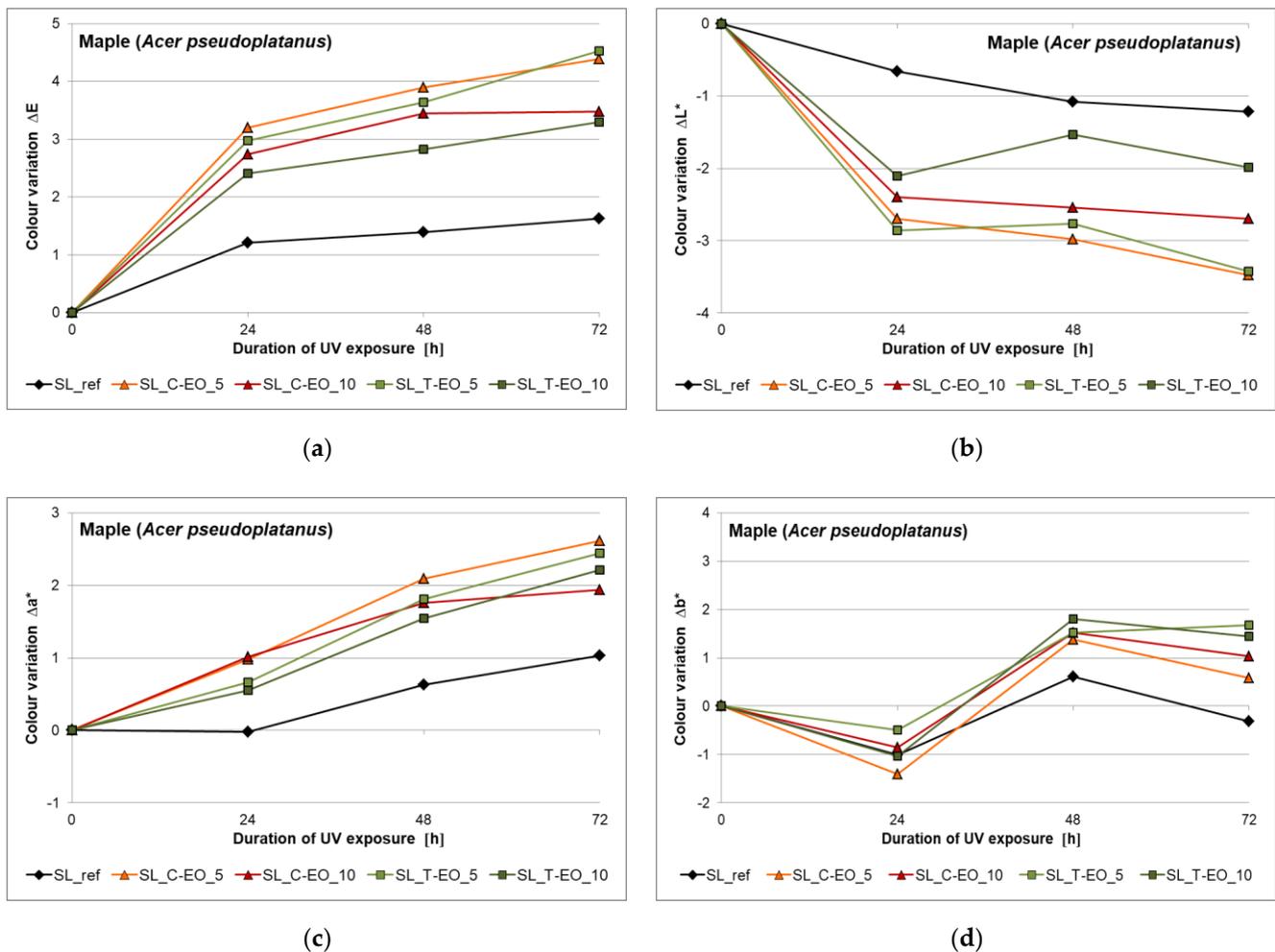
The lower values of colour difference ( $\Delta E$  values in Table 3) registered for the maple and walnut samples finished with shellac as compared to the uncoated controls indicated some protective effect of the shellac film, as previously reported in the literature (e.g., [12]). In the case of maple, coating with unmodified shellac reduced the global colour change after 24 h and 72 h of UV exposure by 63.4% and 83.2%, respectively, while the corresponding values for walnut were 58.8% and 59.0%. A closer look at the data in Table 3 highlights that mostly the chromatic coordinate  $b^*$  (yellowness) was stabilised by coating with shellac and that this protective effect was more effective in the case of maple than walnut.

Light-induced colour changes are complex and dynamic, so they can be better analysed by the variation (change) of all the colour parameters ( $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$ ) alongside the resultant global colour difference ( $\Delta E$ ) during the whole process of UV exposure, as plotted in Figures 6 and 7, comparatively, for the maple and walnut samples coated with all the five variants of shellac solutions. Generally, specific patterns could be observed for the variation of the colour parameters, though the actual values were influenced by both wood species and the type of shellac solution. Darkening of samples, expressed by decrease in lightness (negative  $\Delta L^*$  values), continued during the entire period of testing. This was more advanced and clearly occurring more rapidly in the first 24 h of exposure for the

samples coated with the shellac solutions modified with EOs. A continuous increase in redness (positive  $\Delta a^*$  values) was registered, and this was more advanced for the maple samples coated with modified shellac solutions. Changes of yellowness followed a wavy evolution with a trend of decrease after the first 24 h of exposure, then a sharp increase in the next 24 (more advanced for the walnut samples), followed by a new trend of decrease, so that a maximum increase in yellowness was registered after 48h UV exposure for both wood species and all the five shellac solutions.

**Table 3.** Summary of the experimental colour data for all the wood samples before and after UV ageing for 24, 48 and 72 h—average values and standard deviation (*italics*, in brackets).

Type of Surface/Finish	Colour Parameter	Maple ( <i>Acer pseudoplatanus</i> )				Walnut ( <i>Juglans regia</i> )			
		0 UV	24 UV	48 UV	72 UV	0 UV	24 UV	48 UV	72 UV
Uncoated (Control C)	L*	85.86 (1.44)	84.70 (0.85)	82.92 (0.93)	81.14 (0.81)	58.95 (0.90)	56.92 (1.02)	55.90 (0.92)	55.02 (2.00)
	a*	3.36 (0.53)	3.45 (0.41)	4.52 (0.37)	5.07 (0.90)	6.81 (0.26)	7.98 (0.56)	8.30 (0.84)	8.45 (0.89)
	b*	14.44 (0.11)	17.53 (0.54)	20.79 (0.54)	22.50 (0.52)	12.22 (0.64)	13.35 (0.94)	16.66 (0.74)	16.94 (0.95)
	$\Delta E$	-	3.30	7.09	9.49	-	2.60	5.59	6.36
SL_Ref	L*	68.18 (1.01)	67.52 (0.96)	67.10 (0.91)	66.96 (0.91)	44.09 (1.80)	43.11 (1.24)	42.68 (0.96)	42.75 (1.45)
	a*	12.20 (0.52)	12.17 (0.58)	12.83 (0.54)	13.23 (0.56)	10.09 (1.47)	10.14 (1.34)	10.41 (1.43)	11.14 (1.46)
	b*	41.37 (1.08)	40.36 (0.57)	41.98 (1.04)	41.06 (1.61)	14.71 (1.84)	14.10 (2.09)	17.80 (1.97)	16.69 (1.85)
	$\Delta E$	-	1.21	1.39	1.63	-	1.15	3.41	2.61
SL_C-EO_5	L*	72.57 (1.48)	69.87 (2.26)	69.58 (1.21)	69.09 (1.27)	45.48 (1.99)	43.87 (1.56)	43.22 (1.61)	42.68 (2.07)
	a*	9.15 (0.81)	10.13 (0.70)	11.24 (0.63)	11.77 (0.47)	9.70 (1.24)	10.03 (1.34)	10.22 (1.20)	11.04 (1.43)
	b*	39.76 (1.85)	38.34 (1.64)	41.14 (1.58)	40.34 (1.27)	15.32 (2.32)	14.26 (2.16)	18.84 (1.93)	17.04 (1.88)
	$\Delta E$	-	3.20	3.90	4.39	-	1.95	4.22	3.55
SL_C-EO_10	L*	71.08 (3.66)	68.68 (4.09)	68.54 (3.76)	68.38 (3.88)	44.33 (1.97)	43.33 (1.63)	42.13 (1.41)	42.08 (1.84)
	a*	9.52 (1.91)	10.53 (1.81)	11.27 (1.70)	11.45 (1.96)	10.16 (0.96)	10.56 (1.08)	10.93 (1.11)	11.68 (1.55)
	b*	37.66 (2.05)	36.81 (1.96)	39.18 (1.60)	38.70 (1.93)	15.81 (3.15)	16.00 (2.29)	18.54 (1.99)	18.15 (2.65)
	$\Delta E$	-	2.74	3.45	3.48	-	1.10	3.59	3.58
SL_T-EO_5	L*	73.63 (1.46)	70.77 (2.19)	70.86 (1.33)	70.21 (1.16)	43.30 (1.71)	41.24 (2.31)	41.21 (1.83)	41.25 (1.76)
	a*	8.61 (1.08)	9.27 (0.98)	10.42 (0.94)	11.05 (0.89)	9.02 (1.01)	9.08 (1.00)	9.81 (1.06)	10.25 (1.17)
	b*	38.64 (0.89)	38.14 (1.14)	40.16 (0.86)	40.31 (1.39)	14.02 (1.98)	12.70 (2.34)	16.88 (2.63)	15.79 (1.91)
	$\Delta E$	-	2.98	3.64	4.53	-	2.44	3.63	2.97
SL_T-EO_10	L*	72.16 (1.64)	70.05 (2.14)	70.63 (1.11)	70.17 (1.36)	42.13 (2.86)	41.15 (2.01)	40.65 (2.22)	40.35 (2.58)
	a*	8.83 (0.61)	9.38 (0.84)	10.37 (0.63)	11.04 (0.83)	8.67 (1.08)	8.81 (0.99)	9.22 (1.34)	9.60 (1.39)
	b*	39.19 (1.41)	38.15 (2.35)	41.00 (1.24)	40.63 (1.57)	12.88 (3.79)	12.71 (2.08)	15.13 (3.20)	14.18 (2.77)
	$\Delta E$	-	2.41	2.83	3.30	-	1.00	2.75	2.39

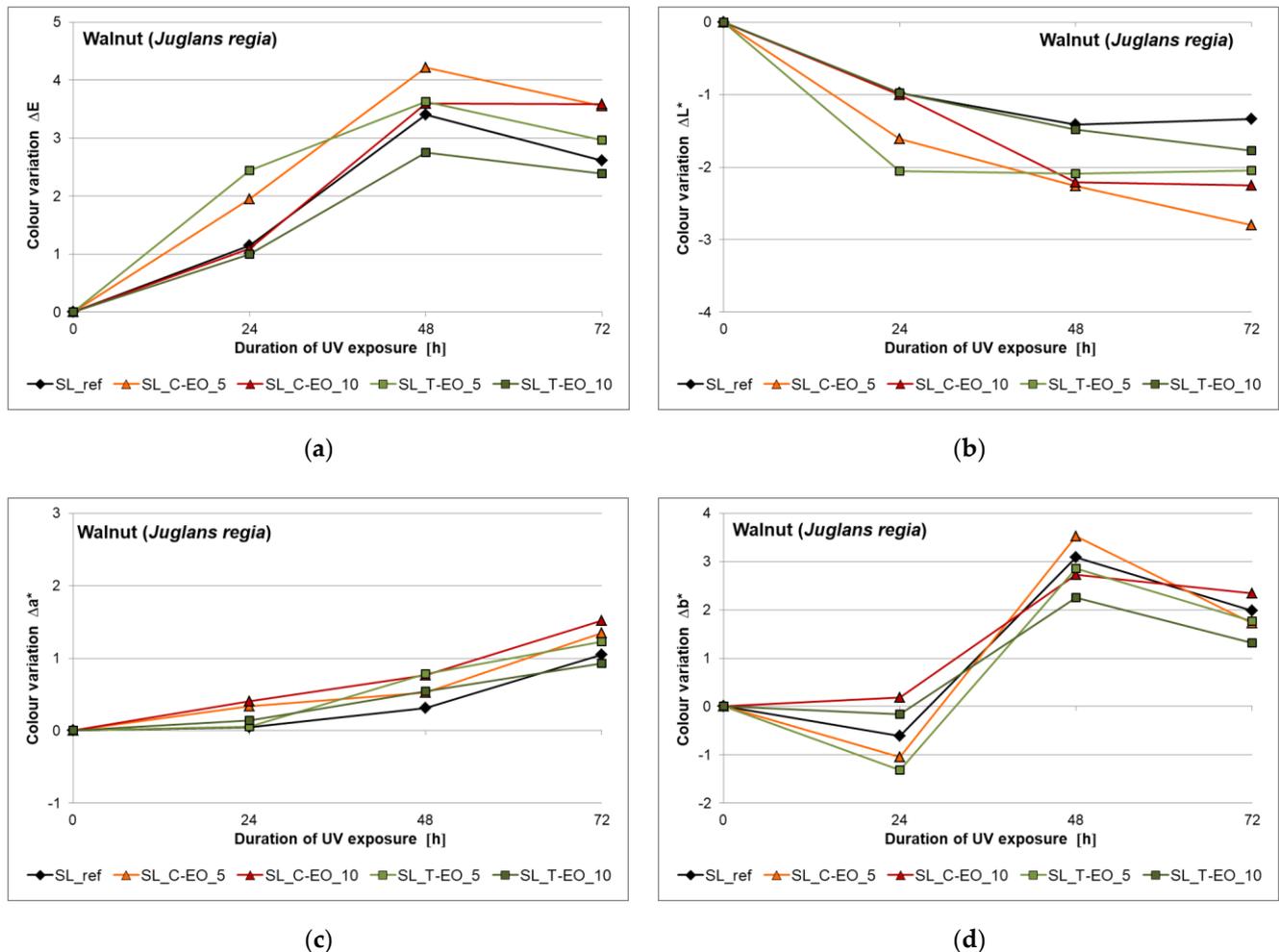


**Figure 6.** Evolution of colour changes of maple wood (*Acer pseudoplatanus*) surfaces finished with reference (SL\_Ref) and EO-modified shellac solutions (SL\_C-EO\_5, SL\_C-EO\_10, SL\_T-EO\_5, SL\_T-EO\_10): (a)  $\Delta E$ ; (b)  $\Delta L^*$ ; (c)  $\Delta a^*$ ; (d)  $\Delta b^*$ .

A change in the dynamics of global colour changes, which are more rapid at the beginning of the process and slow down later, results from the pattern of  $\Delta E$  curves, in accordance with the literature (e.g., [12]). This evolution change was registered after 24 h UV exposure for maple (Figure 6) and 48 h UV exposure for walnut (Figure 7). This difference between the two wood species under study might be related to a combined protective effect of extractives of walnut and shellac coating in delaying/slowing down UV degradation effects for the examined period. However, this protective effect might be diminished in time as extractives are also sensitive to photo-degradation under the action of light (UV-VIS) [58,61,62]. For both maple and walnut samples coated with reference shellac, a significant lightening associated with extractives degradation was determined after 7 years of indoor exposure to the natural light filtered by window glass (unpublished research data of the authors).

Modification of shellac solutions with EOs generally increased the changes of the individual colour parameters  $L^*$ ,  $a^*$ ,  $b^*$  and global colour difference  $\Delta E$  following UV exposure, this unexpected negative effect being more obvious for maple than for walnut while also influenced by the type of EO (C-EO>T-EO) and its concentration. Colour changes ( $\Delta E$ ) after 72 h exposure for maple wood surfaces coated with modified shellac were 103–180% higher as compared to surfaces coated with the reference shellac. In the case of walnut, a slight increase in surface colour changes, by 5–24%, was determined only when shellac was modified with C-EO. Contrarily, modification of shellac by 10%

T-EO resulted in a slight improvement of the light fastness of the finished surfaces, the colour changes after 72 h UV exposure being by approximately 19% lower than that of the reference. However, it is important to highlight that, despite these variations, all the colour difference values after 72 h UV exposure were situated in the ranges 1.63–4.53 for maple and 2.61–3.58 for walnut, which correspond to only small to medium differences in visual perception.



**Figure 7.** Evolution of colour changes of walnut wood (*Juglans regia*) surfaces finished with reference (SL\_Ref) and EO-modified shellac solutions (SL\_C-EO\_5, SL\_C-EO\_10, SL\_T-EO\_5, SL\_T-EO\_10): (a)  $\Delta E$ ; (b)  $\Delta L^*$ ; (c)  $\Delta a^*$ ; (d)  $\Delta b^*$ .

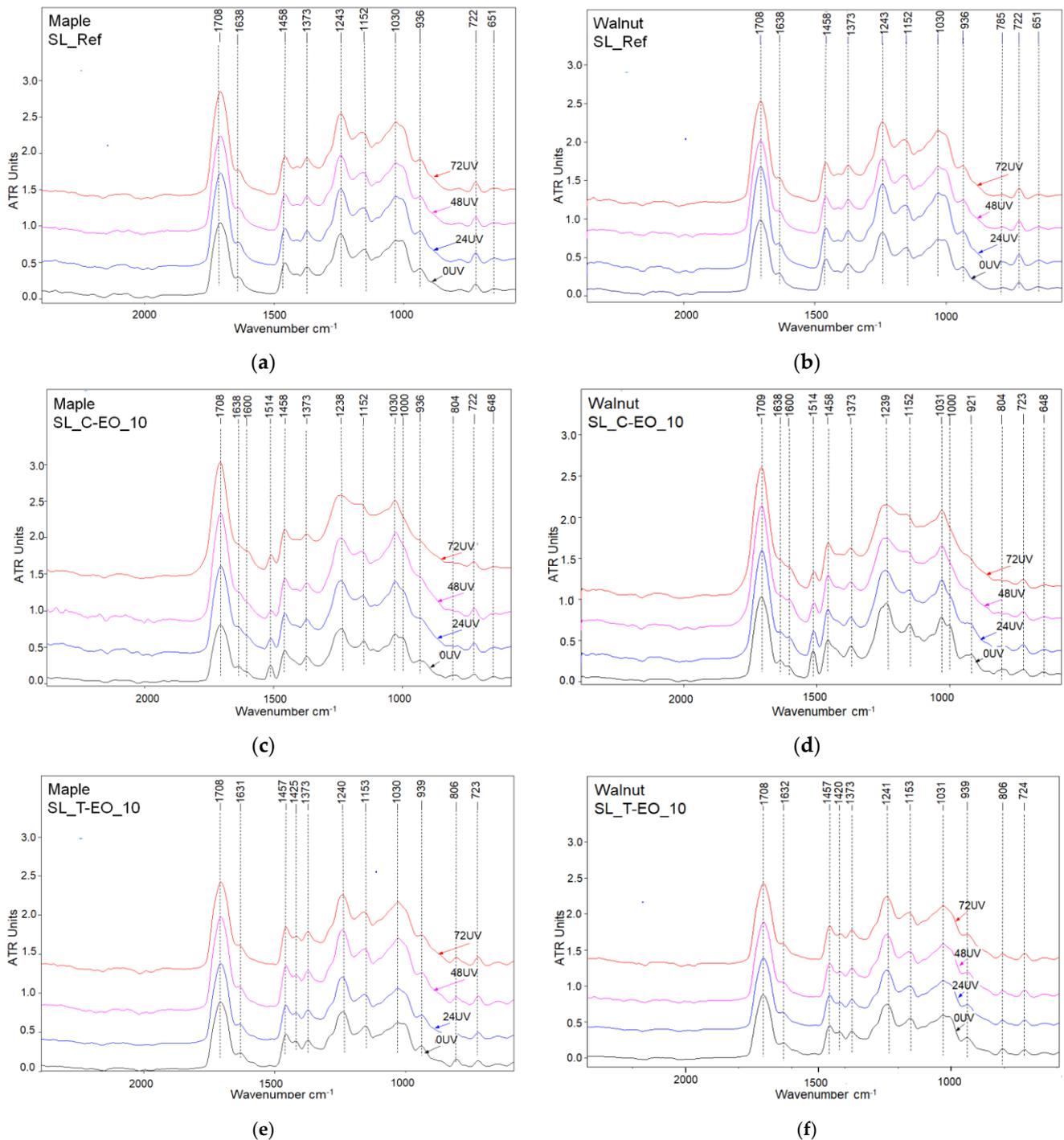
### 3.4. FTIR Investigation of UV Ageing Effects

The results of the FTIR investigation of the coated samples prior to and after different periods of UV ageing are cumulated in Figure 8 for the two species under investigation and three types of shellac solutions: the unmodified reference (SL\_Ref) and the solutions modified by 10% EOs (SL\_E-EO\_10, SL\_T-EO\_10).

Considering the ATR technique employed, these spectra reflect only chemical changes of the coating film, not those occurring on the wood surface. Accordingly, the spectra for the finished maple and walnut samples and their changes as result of ageing were quite similar, though some differences were observed in terms of colour changes, as presented in the previous sections.

No obvious changes could be directly observed in the FTIR spectra of surfaces finished with the reference shellac solutions following UV ageing up to 72 h. The small shoulder at around  $1637\text{ cm}^{-1}$  (conjugated carbonyl) might have been little affected, but this cannot

be confirmed without further processing the spectra by integration. This indicates a good chemical stability of the unmodified shellac film when exposed up to 72 h to UV-VIS radiation simulating window-filtered daylight, which supports previous research in this field [53]. However, chemical changes such as some cross-linking by esterification could be detected by FTIR of thin shellac films irradiated with higher energy UV-C light (254 nm, 1.1 mW/cm<sup>2</sup>) already after 240 min [7].



**Figure 8.** Comparative FTIR spectra of maple (a,c,e) and walnut (b,d,f) wood surfaces coated with reference (a,b) and modified shellac solutions SL\_C-EO\_10 (c,d) and SL\_T-EO\_10 (e,f) before (0UV) and after 24, 48 and 72 h UV-induced artificial ageing.

In contrast to SL\_Ref, some small but evident changes occurred during UV exposure in the spectra of the samples coated with shellac modified with C-EO. The small shoulder at  $1637\text{ cm}^{-1}$  decreased and finally disappeared, while a trend of an increased absorption at around  $1600\text{ cm}^{-1}$  (aromatic ring) was observed. Furthermore, the absorption at  $1151\text{ cm}^{-1}$  (C–O and C–O–C stretching) decreased during UV ageing. It is important to note that all these changes, which were not observed for unmodified SL, occurred in parallel with a decrease in the peak at  $1514\text{ cm}^{-1}$  (aromatic skeletal vibration), found as distinctive for the presence of C-EO in the modified coating film and assigned to eugenol and ethyl eugenol, the main components of C-EO. Accordingly, it seems reasonable to believe that UV radiation affected more the C-EO components present in the film, not the SL resin itself.

In the case of coatings modified with T-EO, some very minor changes were barely visible in the range  $1640\text{--}1600\text{ cm}^{-1}$ , while no evident change/decrease could be observed for the distinctive peak of T-EO in the film ( $806\text{ cm}^{-1}$  assigned to thymol).

#### 4. Discussions

To the best of our knowledge, this might be the first reported research exploring the opportunities of modifying shellac solutions employed for wood finishing with clove (*Eugenia carryophyllata*) and thyme (*Satureja hortensis*) essential oils, though their demonstrated antimicrobial, antifungal and antioxidant properties might impart some improved protective properties to the resulting coating films. In contrast, the idea of combining in a synergistic way the film-forming properties of shellac or other biopolymers with the antifungal, antioxidant or UV-blocking properties of these EOs has been widely explored for other application fields, such as protective coatings for fruits, active packaging for food and drug delivery systems [37–40], as detailed in Section 1.

The research reported in this paper focussed on the stability of modified shellac solutions and the influence of this modification on the wood finishing technology, the colour of the resulting coated surfaces and their UV ageing resistance, evaluated by colour changes and FTIR. Colour changes have been recognised as the most sensitive parameter indicating photo-degradation for both uncoated and coated wood. Photo-degradation of both wood and coatings is initiated by absorption of UV light and occurs by a chained radical mechanism. C-EO and T-EO were reported as free radical scavengers and UV absorbers reducing transmission of UV light through transparent films, so an expectable improved UV resistance/colour stability of the wood surfaces coated with modified shellac films was assumed, especially in the case of C-EO, considering that it was reported as the most effective antioxidant essential oil (from among the commonly employed ones) due to its high content in eugenol [33,34].

However, the experimental results contrarily indicated slightly increased colour changes for the wood surfaces coated with modified SL solutions, though all colour changes are visually perceived as small to medium.

There are several aspects which should be considered in an attempt to understand and possibly explain these results. First of all, the measured colour changes for coated wood result from both colour changes of the wooden substrate and colour changes of the coating film, their individual contribution being difficult to assess [49] unless a special experimental design is employed (e.g., [12]). Secondly, the amount of incident light reaching the underlying wood surface and its wavelength distribution would depend on the capability of the coating film to absorb and transmit light, influenced mainly by the chemical nature/structure of the film-forming resin and the presence of different additives/modifiers with a specific interaction with the incident light. For instance, different organic UV absorbers, hindered amine light stabilisers (HALS) or nanometal oxides are often employed as pretreatments or additives to increase the weathering/light resistance of clear coatings on wood [64,65]. Thirdly, absorption of UV light by some modifiers might result in their own photo-induced oxidation and recurrent colour change. Consequently, in the colour changes of wood surfaces finished with modified SL coatings, a possible contribution of all partners and their interaction should be considered.

Sharma et al. [39] found that transmittance of UV radiation (280–380 nm) through organic active biofilms modified by 10% C-EO was reduced by 80% as a consequence of a high absorption of UV radiation by C-EO, in relation to its high content in eugenol. In comparison, the composite films modified by 10% T-EO (*Thymus vulgaris*) were substantially less effective UV barriers, reducing by only 20% the transmittance of 280 nm UV radiation, while transmittance increased continuously with increasing wavelength of radiation in the range 280–380 nm. C-EO is not only a very good UV absorber but is also a product highly sensitive to oxidation. Different mechanisms of eugenol oxidation, including photo-induced and electro-chemical oxidation, were proposed, while the possible resulting products include para- and ortho-quinoid structures [66–68], known as chromophores [69]. Pretreatment of spruce wood with C-EO resulted in an increased colour change under the action of UV light in a natural and an artificial weathering test [70]. Accordingly, a hypothesis explaining, at least partially, the increased UV-induced colour changes determined in this research for the wood samples coated with shellac modified with C-EO as compared to the reference could be that its own photo-induced oxidation is a result of UV absorption, not a more advanced photo-degradation of the wood substrate. The FTIR investigation of the SL films modified with C-EO indicated a reduction of the distinctive aromatic ring absorption of eugenol, which supports chemical changes of this main compound. This might result in a better protection of the wood substrate for longer exposure times, but more research and longer UV exposure times are needed.

## 5. Conclusions

This research explored the modification of shellac solutions for wood finishing with clove (*Eugenia carryophyllata*) and thyme (*Satureja hortensis*) essential oils (C-EO, T-EO). The two essential oils were found compatible with the alcoholic shellac solutions, and stable modified polishes with a content of 5% and 10% C-EO and T-EO were prepared and successfully employed for coating maple (*Acer pseudoplatanus*) and walnut (*Juglans regia*) wood samples by the traditional manual polishing technique to obtain aesthetic glossy surfaces. Colour measurements in the CIELab system revealed a slight influence of shellac modification on the colour of finished surfaces when compared to unmodified shellac, respectively,  $\Delta E$  values of 1.88 to 5.41 units for maple and 1.36–3.41 for walnut, which account for barely visible to small or medium differences in visual perception.

Coating with shellac significantly improved UV light resistance of wood surfaces, as shown by the decrease in the global colour changes ( $\Delta E$ ) after 72 h UV exposure by 83.2% for maple and 59% for walnut. The corresponding UV-induced colour changes of wood surfaces coated with modified shellac solutions were generally slightly higher when compared to unmodified shellac (by 1.7–2.9 units for maple; 0–1 unit for walnut). A possible UV-induced photo-oxidation process of eugenol resulting in the formation of new chromophores might explain higher colour changes of wood surfaces coated with shellac modified with C-EO after 72 h exposure to artificial light, though longer exposure times and complementary investigation methods would be necessary to verify this hypothesis and reveal possible long-term protective effects. The differences in the behaviour of the two wood species could be related to differences in their extractives content, which can delay photo-degradation of the main wood components, as previously reported in the literature.

Future research will look at the influence of shellac modification with C-EO and T-EO on the long-term effects of indoor exposure of coated wood surfaces to natural light filtered by glass and their fungal colonisation in high atmospheric humidity conditions. All data are intended to assist preventive and active conservation of historic furniture, while also rebranding ancient natural coating materials and techniques for novel applications.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12101591/s1>, Figure S1: Comparative FTIR–ATR spectra of clove (*Eugenia carryophyllata*) and thyme (*Satureja hortensis*) essential oils (C-EO, T-EO) employed in the experimental research.

**Author Contributions:** Conceptualization, M.C.T. and E.C.B.; methodology, M.C.T. and E.C.B.; formal analysis, M.C.T.; validation, M.C.T.; materials and wood samples preparation, M.C.T. and E.C.B.; colour measurements and data processing M.C.T. and E.C.B.; FTIR investigation and data processing, M.C.T.; resources, M.C.T.; writing—original draft preparation, M.C.T.; writing—review and editing, M.C.T. and E.C.B.; visualization, E.C.B.; project administration, M.C.T. and E.C.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** We hereby acknowledge the structural funds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, No. 11/2009) for providing the infrastructure used in this work within the ICDT research institute of the Transilvania University of Braşov–Romania. The authors acknowledge the technical support of Melania Cristea and thank the students Oana Maria Chivu, Dragoş Ştefan-Tiţu, Radu Mihai Dumitreache, Florina Petcu and Antonius Androne for their work on the preparation of the materials and wood samples, running the accelerated UV ageing test, colour measurements and primary data processing.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Thombare, N.; Kumar, S.; Kumari, U.; Sakare, P.; Yogi, R.K.; Prasad, N.; Sharma, K.K. Shellac as a multifunctional biopolymer: A review on properties, applications and future potential. *Int. J. Biol. Macromol.* **2022**, *215*, 203–223. [CrossRef] [PubMed]
2. Licchelli, M.; Malagodi, M.; Somaini, M.; Weththimuni, M.; Zanchi, C. Surface treatments of wood by chemically modified shellac. *Surf. Eng.* **2013**, *29*, 121–127. [CrossRef]
3. Šimůnková, K.; Pánek, M.; Zeidler, A. Comparison of selected properties of shellac varnish for restoration and polyurethane varnish for reconstruction of historical artefacts. *Coatings* **2018**, *8*, 119. [CrossRef]
4. Sözen, E. Determination of changes in the mechanical and color properties of some wood species treated with shellac. *BioResources* **2022**, *17*, 1703–1716. [CrossRef]
5. Derry, J. Documenting the Process, Defining the Product. A Study on the Processing Methods of Shellac and the Analysis of Selected Physical and Chemical characteristics. Master's Thesis, Institute of Archeology, Conservation and History, University of Oslo, 2012. Available online: <https://www.duo.uio.no/handle/10852/34480> (accessed on 18 October 2022).
6. Timar, M.C.; Varodi, A.M.; Liu, X.Y. The influence of artificial ageing on selected properties of wood surfaces finished with traditional materials—An assessment for conservation purposes. *Ser. II For. Wood Ind. Agric. Food Eng.* **2020**, *13*, 81–94. [CrossRef]
7. Bercea, A.; Mitu, B.; Matei, A.; Marascu, V.; Brajnicov, S. Esterification process induced by UV irradiation of shellac thin films deposited by matrix assisted pulsed laser evaporation. *Rev. De Chim.* **2019**, *70*, 2982–2984. [CrossRef]
8. Ghosh, M.; Gupta, S.; Kumar, V.K. Studies on the loss of gloss of shellac and polyurethane finishes exposed to UV. *Maderas Cienc. Y Tecnol.* **2015**, *17*, 39–44. [CrossRef]
9. Weththimuni, M.L.; Capsoni, D.; Malagodi, M.; Milanese, C.; Licchelli, M. Shellac/nanoparticles dispersions as protective materials for wood. *Appl. Phys. A* **2016**, *122*, 1058. [CrossRef]
10. Weththimuni, M.L.; Capsoni, D.; Malagodi, M.; Licchelli, M. Improving wood resistance to decay by nanostructured ZnO-based treatments. *J. Nanomater.* **2019**, *2019*, 6715756. [CrossRef]
11. Weththimuni, M.L.; Milanese, C.; Licchelli, M.; Malagodi, M. Improving the protective properties of shellac-based varnishes by functionalized nanoparticles. *Coatings* **2021**, *11*, 419. [CrossRef]
12. Capobianco, G.; Calienno, L.; Pelosi, C.; Scacchi, M.; Bonifazi, G.; Agresti, G.; Picchio, R.; Santamaria, U.; Serranti, S.; Monaco, A.L. Protective behaviour monitoring on wood photo-degradation by spectroscopic techniques coupled with chemometrics. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2017**, *172*, 34–42. [CrossRef]
13. Miranda, M.; Sun, X.; Ference, C.; Plotto, A.; Bai, J.; Wood, D.; Assis, O.B.G.; Ferreira, M.D.; Baldwin, E. Nano- and micro-carnauba wax emulsions versus shellac protective coatings on postharvest citrus quality. *J. Am. Soc. Hortic. Sci.* **2021**, *146*, 40–49. [CrossRef]
14. Yuan, Y.; He, N.; Dong, L.; Guo, Q.; Zhang, X.; Li, B.; Li, L. Multiscale shellac-based delivery systems: From macro- to nanoscale. *ACS Nano* **2021**, *15*, 18794–18821. [CrossRef]
15. Liao, W.; Badri, W.; Dumas, E.; Ghnimi, S.; Elaissari, A.; Saurel, R.; Gharsallaoui, A. Nanoencapsulation of essential oils as natural food antimicrobial agents: An overview. *Appl. Sci.* **2021**, *11*, 5778. [CrossRef]
16. Bonda, A.F.; Candiani, A.; Pertile, M.; Giovannelli, L.; Segale, L. Shellac gum/carrageenan alginate-based core-shell systems containing peppermint essential oil formulated by mixture design approach. *Gels* **2021**, *7*, 162. [CrossRef]

17. Yan, X.X.; Wang, L. Preparation of shellac resin microcapsules coated with urea formaldehyde resin and properties of waterborne paint films for *Tilia amurensis* Rupr. *Membranes* **2020**, *10*, 278. [CrossRef]
18. Tao, Y.; Yan, X.X.; Chang, Y.J. Effect of coating process on mechanical, optical, and self-healing properties of waterborne coating on basswood surface with MF-coated shellac core microcapsule. *Polymers* **2021**, *13*, 4228. [CrossRef]
19. Chang, Y.J.; Yan, X.X. Preparation and self-repairing properties of MF-coated shellac water-based microcapsules. *Coatings* **2020**, *10*, 778. [CrossRef]
20. Yan, X.X.; Tao, Y.; Chang, Y.J. Effect of shellac waterborne coating microcapsules on the optical, mechanical and self-healing properties of waterborne primer on *Tilia europaea* L. wood. *Coatings* **2021**, *11*, 785. [CrossRef]
21. Yan, X.X.; Li, W.B.; Han, Y.; Yin, T.Y. Preparation of melamine/rice husk powder coated shellac microcapsules and effect of different rice husk powder content in wall material on properties of wood waterborne primer. *Polymers* **2021**, *14*, 72. [CrossRef]
22. Gupta, S.; John, A.; Kumar, V.S.K. Studies on effect of coat thickness on the moisture uptake by a hardwood substrate. *Maderas Cienc. Y Tecnol.* **2016**, *18*, 443–456. [CrossRef]
23. Liu, M.; Xu, G.L.; Wang, J.A.; Tu, X.W.; Liu, X.Y.; Wu, Z.H.; Lv, J.F.; Xu, W. Effects of shellac treatment on wood hygroscopicity, dimensional stability and thermostability. *Coatings* **2020**, *10*, 881. [CrossRef]
24. Haro-González, J.N.; Castillo-Herrera, G.A.; Martínez-Velázquez, M.; Espinosa-Andrews, H. Clove essential oil (*Syzygium aromaticum* L. myrtaceae): Extraction, chemical composition, food applications, and essential bioactivity for human health. *Molecules* **2021**, *26*, 6387. [CrossRef]
25. Bimbiraitė-Survilienė, K.; Stankevičius, M.; Šuštauskaitė, S.; Gegotek, A.; Maruška, A.; Skrzydlewska, E.; Barsteigienė, Z.; Akuneca, I.; Ragažinskienė, O.; Lukošius, A. Evaluation of chemical composition, radical scavenging and antitumor activities of *Satureja hortensis* L. herb extracts. *Antioxidants* **2021**, *10*, 53. [CrossRef]
26. Dhifi, W.; Bellili, S.; Jazi, S.; Bahloul, N.; Mnif, W. Essential oils' chemical characterization and investigation of some biological activities: A critical review. *Medicines* **2016**, *3*, 25. [CrossRef]
27. Xie, Y.; Wang, Z.; Huang, Q.; Zhang, D. Antifungal activity of several essential oils and major components against wood-rot fungi. *Ind. Crops Prod.* **2017**, *108*, 278–285. [CrossRef]
28. Mutlu-Ingok, A.; Devecioglu, D.; Dikmetas, D.N.; Karbancioglu-Guler, F.; Capanoglu, E. Antibacterial, antifungal, antimycotoxic, and antioxidant activities of essential oils: An updated review. *Molecules* **2020**, *25*, 4711. [CrossRef]
29. Perumal, A.B.; Huang, L.; Nambiar, R.B.; He, Y.; Li, X.; Sellamuthu, P.S. Application of essential oils in packaging films for the preservation of fruits and vegetables: A review. *Food Chem.* **2022**, *375*, 131810. [CrossRef]
30. Pánek, M.; Reinprecht, L.; Hulla, M. Ten essential oils for beech wood protection—Efficacy against wood-destroying fungi and moulds, and effect on wood discoloration. *BioResources* **2014**, *9*, 5588–5603. [CrossRef]
31. Stupar, M.; Grbić, M.L.; Džamić, A.; Unković, N.; Ristić, M.; Jelikić, A.; Vukojević, J. Antifungal activity of selected essential oils and biocide benzalkonium chloride against the fungi isolated from cultural heritage objects. *S. Afr. J. Bot.* **2014**, *93*, 118–124. [CrossRef]
32. Kakakhel, M.A.; Wu, F.; Gu, J.-D.; Feng, H.; Shah, K.; Wang, W. Controlling biodeterioration of cultural heritage objects with biocides: A review. *Int. Biodeterior. Biodegradation* **2019**, *143*, 104721. [CrossRef]
33. Morsy, N.F.S. Chemical structure, quality indices and bioactivity of essential oil constituents. In *Active Ingredients from Aromatic and Medicinal Plants*; El-Shemy, A.H., Ed.; Cairo University: Cairo, Egypt, 2017; Available online: <https://www.intechopen.com/chapters/53045> (accessed on 26 August 2022).
34. Fadel, H.H.M.; El-Ghorab, A.H.; Hussein, A.M.; El-Massry, K.F.; Lotfy, S.N.; Ahmed, M.Y.S.; Soliman, T.N. Correlation between chemical composition and radical scavenging activity of 10 commercial essential oils: Impact of microencapsulation on functional properties of essential oils. *Arab. J. Chem.* **2020**, *13*, 6815–6827. [CrossRef]
35. Bakry, A.M.; Abbas, S.; Ali, B.; Majeed, H.; Abouelwafa, M.Y.; Mousa, A.; Liang, L. Microencapsulation of oils: A comprehensive review of benefits, techniques, and applications. *Compr. Rev. Food Sci. Food Saf.* **2015**, *15*, 143–182. [CrossRef] [PubMed]
36. Dupuis, V.; Cerbu, C.; Witkowski, L.; Potarniche, A.-V.; Timar, M.C.; Żychska, M.; Sabliov, C.M. Nanodelivery of essential oils as efficient tools against antimicrobial resistance: A review of the type and physical-chemical properties of the delivery systems and applications. *Drug Deliv.* **2022**, *29*, 1007–1024. [CrossRef] [PubMed]
37. Khorram, F.; Ramezani, A. Cinnamon essential oil incorporated in shellac, a novel bio-product to maintain quality of 'Thomson navel' orange fruit. *J. Food Sci. Technol.* **2020**, *58*, 2963–2972. [CrossRef]
38. Yan, J.; Zhang, J.; Hu, C.; Deng, L.; Ritenour, M.A. Use of carvacrol and thymol in shellac coating to control stem-end rot on 'ruby red' grapefruit and maintain fruit quality during simulated storage and marketing. *Sci. Hortic.* **2020**, *272*, 109606. [CrossRef]
39. Sharma, S.; Barkauskaite, S.; Duffy, B.; Jaiswal, A.K.; Jaiswal, S. Characterization and antimicrobial activity of biodegradable active packaging enriched with clove and thyme essential oil for food packaging application. *Foods* **2020**, *9*, 1117. [CrossRef]
40. Roy, S.; Rhim, J.-W. Gelatin/agar-based functional film integrated with pickering emulsion of clove essential oil stabilized with nanocellulose for active packaging applications. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *627*, 127220. [CrossRef]
41. Pop, D.M.; Varodi, A.M.; Timar, M.C. Essential oils as potential ecological wood preservatives—A preliminary test on thyme essential oil. *Innov. Woodwork. Ind. Eng. Des.* **2019**, *15*, 28–36. Available online: <https://www.scjournal-inno.com/bg/author-278-dana-mihaela-pop.htm> (accessed on 18 October 2022).
42. Reiprecht, L.; Pop, D.M.; Vidholdova, Z.; Timar, M.C. Anti-decay potential of five essential oils against the wood-decaying fungi *Serpula lacrymans* and *Trametes versicolor*. *Acta Fac. Xylogologiae Zvolen* **2019**, *61*, 63–72. [CrossRef]

43. Pop, D.M.; Timar, M.C.; Beldean, E.C.; Varodi, A.M. Combined testing approach to evaluate the antifungal efficiency of clove (*Eugenia caryophyllata*) essential oil for potential application in wood conservation. *BioResources* **2020**, *15*, 9474–9489. [CrossRef]
44. Pop, D.-M.; Timar, M.C.; Varodi, A.M.; Beldean, E.C. An evaluation of clove (*Eugenia caryophyllata*) essential oil as a potential alternative antifungal wood protection system for cultural heritage conservation. *Maderas Cienc. Y Tecnol.* **2022**, *11*, 1–16. [CrossRef]
45. Complex Art: Creative Hobby Timisoara. Available online: <https://complexart.ro/> (accessed on 27 August 2022).
46. Steaua divina—produse naturale. Available online: <https://www.steauadivina.ro/en/> (accessed on 27 August 2022).
47. Chemical Company SA—Romania. Available online: [https://www.chemical.ro/en/products-index/ethyl-alcohol/ethyl-alcohol-abs-99-3\\_p247/](https://www.chemical.ro/en/products-index/ethyl-alcohol/ethyl-alcohol-abs-99-3_p247/) (accessed on 27 August 2022).
48. Timar, M.C.; Varodi, A.M.; Gurău, L. Comparative study of photodegradation of six wood species after short-time UV exposure. *Wood Sci. Technol.* **2015**, *50*, 135–163. [CrossRef]
49. Evans, P.; Chowdhury, M.J.; Mathews, B.; Schmalzl, K.; Ayer, S.; Kiguchi, M.; Kataoka, Y. Weathering and UV protection of wood surfaces (chapter 14). In *Handbook of Environmental Degradation of Materials*, 1st ed.; Myer, K., Ed.; Elsevier Inc.: Amsterdam, The Netherlands, 2005; pp. 277–297. ISBN 9780815517498.
50. Kataoka, Y.; Kiguchi, M.; Williams, R.; Evans, D. Violet light causes photodegradation of wood beyond the zone affected by ultraviolet radiation. *Holzforschung* **2007**, *61*, 23–27. [CrossRef]
51. Liu, X.Y.; Timar, M.C.; Varodi, A.M. A comparative study on the artificial UV and natural ageing of beeswax and Chinese wax and influence of wax finishing on the ageing of Chinese Ash (*Fraxinus mandshurica*) wood surfaces. *J. Photochem. Photobiol. B Biol.* **2019**, *201*, 111607. [CrossRef]
52. Allegretti, O.; Cividini, R.; Travan, L. Drying process for white beech. *Pro Ligno* **2008**, *4*, 11–19.
53. Liu, X.Y. Contributions to the Study of Ageing Phenomena of Wooden Substrate and Traditional Materials for Transparent Finishes—A Comparative Approach for Europe and China with Applicability in Furniture Conservation/Restoration. Ph.D. Thesis, Transilvania University of Brasov, Brasov, Romania, 2017.
54. Tarhan, I.; Bakır, M.R.; Kalkan, O.; Yöntem, M.; Kara, H. Rapid determination of adulteration of clove essential oil with benzyl alcohol and ethyl acetate: Towards quality control analysis by FTIR with chemometrics. *Vib. Spectrosc.* **2022**, *118*, 103339. [CrossRef]
55. Valderrama, A.C.S.; Rojas De, G.C. Traceability of active compounds of essential oils in antimicrobial food packaging using a chemometric method by ATR-FTIR. *Am. J. Anal. Chem.* **2017**, *8*, 726–741. [CrossRef]
56. Schulz, H.; Ozkan, G.; Baranska, M.; Krüger, H.; Özcan, M. Characterisation of essential oil plants from Turkey by IR and Raman spectroscopy. *Vib. Spectrosc.* **2005**, *39*, 249–256. [CrossRef]
57. Fengel, D.; Wegener, G. *Wood—Chemistry, Ultrastructure, Reactions*; Walter de Gruyter: Berlin, Germany; New York, NY, USA, 1984.
58. William, R.S. Weathering of wood. In *Handbook of Wood Chemistry and Wood Composites*, 1st ed.; Roger, M.R., Ed.; CRD Press: London, UK; New York, NY, USA, 2005; pp. 9–32. ISBN 0-8493-1588-3.
59. Müller, U.; Rätzsch, M.; Schwanninger, M.; Steiner, M.; Zöbl, H. Yellowing and IR-changes of spruce wood as result of UV-irradiation. *J. Photochem. Photobiol. B Biol.* **2003**, *69*, 97–105. [CrossRef]
60. Persze, L.; Tolvaj, L. Photodegradation of wood at elevated temperature: Colour change. *J. Photochem. Photobiol. B Biol.* **2012**, *108*, 44–47. [CrossRef] [PubMed]
61. Chang, T.-C.; Chang, H.-T.; Wu, C.-L.; Chang, S.-T. Influences of extractives on the photodegradation of wood. *Polym. Degrad. Stab.* **2010**, *95*, 516–521. [CrossRef]
62. Chang, T.-C.; Chang, H.-T.; Wu, C.-L.; Lin, H.-Y.; Chang, S.-T. Stabilizing effect of extractives on the photo-oxidation of *Acacia confusa* wood. *Polym. Degrad. Stab.* **2010**, *95*, 1518–1522. [CrossRef]
63. Chang, T.-C.; Lin, H.-Y.; Wang, S.-Y.; Chang, S.-T. Study on inhibition mechanisms of light-induced wood radicals by *Acacia confusa* heartwood extracts. *Polym. Degrad. Stab.* **2014**, *105*, 42–47. [CrossRef]
64. Evans, P.D.; Haase, J.G.; Seman, B.M.; Kiguchi, M. The search for durable exterior clear coatings for wood. *Coatings* **2015**, *5*, 830–864. [CrossRef]
65. Pánek, M.; Oberhofnerová, E.; Hýšek, Š.; Sedivka, P.; Zeidler, A. Colour stabilization of oak, spruce, larch and douglas fir heartwood treated with mixtures of nanoparticle dispersions and UV-stabilizers after exposure to UV and VIS-radiation. *Materials* **2018**, *11*, 1653. [CrossRef]
66. Elgendy, E.M.; Khayyat, S. Oxidation reactions of some natural volatile aromatic compounds: Anethole and eugenol. *Russ. J. Org. Chem.* **2008**, *44*, 823–829. [CrossRef]
67. Gülçin, I. Antioxidant activity of eugenol: A structure—Activity relationship study. *J. Med. Food* **2011**, *14*, 975–985. [CrossRef]
68. Yildiz, G.; Aydogmus, Z.; Cinar, M.E.; Senkal, F.; Ozturk, T. Electrochemical oxidation mechanism of eugenol on graphene modified carbon paste electrode and its analytical application to pharmaceutical analysis. *Talanta* **2017**, *173*, 1–8. [CrossRef]
69. Alfieri, M.L.; Panzella, L.; Crescenzi, O.; Napolitano, A.; D’Ischia, M. Nature-inspired functional chromophores from biomimetic o-quinone chemistry. *Eur. J. Org. Chem.* **2021**, *2021*, 2982–2989. [CrossRef]
70. Oberhofnerová, E.; Pánek, M.; Böhm, M. Effect of surface pretreatment with natural essential oils on the weathering performance of spruce wood. *BioResources* **2018**, *13*, 7053–7070. [CrossRef]