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Protective behaviour monitoring on wood photo-degradation by spectroscopic techniques coupled with chemometrics

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ABSTRACT

This paper reports the investigation on the effect of protective materials on poplar (*Populus* sp.) wood modifications as consequence of artificial photo-degradation in controlled environment. The novelty of this work is to try to understand what happens to wood surface under the protective layer. Shellac, beeswax and Linfoil® were tested to compare traditional and novel products generally used for wood. The samples, uncovered and covered by these protective layers, were artificially aged. Colour and chemical modifications due to ageing were investigated at different time intervals by reflectance spectrophotometry, Fourier transform infrared spectroscopy and hyperspectral imaging. The obtained data were elaborated by statistical and chemometric tools in order to verify their significance and to assess the relationship between groups of measurements.

The results highlighted that shellac, beeswax and Linfoil® materials have a very low protective effect on wood photo-degradation for long times of exposure, by little reducing the changes of wood components.

1. Introduction

Wood protection is an important topic due to the wide use of this material both as structural building component and as a material for panels, statues, furniture, doors [1–4]. Unprotected wood, exposed to outdoor and indoor conditions undergoes a variety of degradation reactions induced by diverse factors such as light, moisture, heat, oxygen, and pollutants, causing chemical and colour changes of wood surface [5–10]. For this reason wood surfaces need to be protected by using different kinds of traditional and innovative products [11–15]. The effectiveness of these products in wood protection has been evaluated by measuring colour and chemical changes by different spectroscopic techniques applied on protected and unprotected wood samples photo-irradiated in controlled environment [16–19]. The measurements performed on treated wood are affected by the contribution of both wood and protective product. In order to understand the real protective effect, it would be necessary to measure the irradiated wood surfaces by removing the protective layer. In some cases this can be reached due to the possibility of obtaining a free film that can be easily removed from the surface [20]. But usually the protective materials cannot be prepared as free film, so a support to apply the products should be necessarily used. In the present paper three different protective were tested: shellac and beeswax as traditional treatment systems [1,21–24], and Linfoil® as new commercial product specifically addressed for wood [16–17]. These products were applied on poplar wood (*Populus* sp.), a species chosen for its widespread use in Italy to create different kinds of artefacts and objects such as statues, ceilings, furniture, doors, painted panels, etc. [17].

Shellac and beeswax were chosen for their wide use in the past but also nowadays for wood protection [25–26]. Linfoil® is a new product, based on natural sources, guaranteed by the manufacturer as an innovative protective for wood. So, a comparison between traditional and new materials was investigated.

The chosen products were applied on a thin glass support, layered on the wood samples and aged in a climatic box simulating sunlight exposure. The changes occurring during times were evaluated by measuring colour, infrared spectra in the mid-region and performing hyperspectral imaging based determinations [27–30]. All data were elaborated by statistical and chemometric tools in order to verify the significance of the measurements and to compare samples at chosen ageing times and with the different protective layers.

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2. Materials and methods

2.1. Sample preparation and ageing

Wood samples were obtained by a board of poplar. After cutting, the samples were stored in darkness in a conditioned room at 65% relative humidity and a temperature of 22 °C to reach the 12% of moisture content. To perform the FT-IR analysis directly on wood surface, slices with a size of 10 mm (diameter) × 2 mm (thickness) were obtained from the specimens of poplar. The dimensions of the slices were suitable for the FT-IR diffuse reflectance accessory. The same slices were used also to perform the *hyperspectral imaging* (HSI) based measurements.

Seventy-five slices were prepared in order to have statistically significant sample sets. Each set was made of fifteen slices and was aged without protective, with only glass, glass and shellac, glass and beeswax, glass and Linfoil® respectively.

Shellac and beeswax were supplied by Zecchi (Florence, Italy) whereas Linfoil® was supplied by GEAL (Agliana, Pistoia, Italy). Simple microscope floatglass (chemically a soda-lime glass, according to ISO 8037/I) slides were used as support for protective application, with the following dimensions: 76 × 26 × 1 mm.

The amounts of protective products on the glasses were: 35.6 mg for beeswax, 37.3 mg for shellac and 24.6 for Linfoil®.

The artificial ageing was performed in a Model 1500E Solar Box (Erichsen Instruments). The system is equipped with a 2.5 kW xenon-arc lamp and an UV filter that cuts off the spectrum at 280 nm. The samples were exposed in the Solar Box chamber from 1 to 1008 h at 550 Wm^{-2}, 55 °C and the UV filter at 280 nm. The experimental conditions were chosen following the specifications supplied by Erichsen, in order to simulate the sunlight exposition. Inside the Solar Box chamber relative humidity was constant (50%) and determined by the irradiation conditions. Relative humidity was monitored by a data logger positioned inside the Solar Box.

2.2. Colour monitoring

After exposure for a given length of time the samples were removed from the Solar Box chamber and the colour was measured using an X-Rite CA22 reflectance spectrophotometer according to the CIELAB colour system, where L^* describes the lightness while a^* and b^* describe the chromatic coordinates on the green-red and blue-yellow axes, respectively. The characteristics of the colour measuring instrument are the following: colour scale CIEL*a*b*; illuminant D65; standard observer 10°; geometry of measurement 45°/0°; spectral range 400–700 nm; spectral resolution 10 nm; measurement diameter 4 mm; white reference supplied with the instrument. The differences in lightness (ΔL^*), chromatic coordinates (Δa^* and Δb^*), and total colour (ΔE^*) were then calculated using these parameters according to EN 15886 [31]. The total colour difference, ΔE^*, between two measurements ($L^*_1 a^*_1 b^*_1$ and $L^*_2 a^*_2 b^*_2$) is the geometrical distance between their positions in CIELAB colour space. It is calculated using the following equation: $\Delta E^*_{2,1} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{½}$.

Three measures for each point were performed, so that forty five measurements were taken for each set of slices at the following hour intervals: 0, 12, 24, 96, 168, 312, 504 and 1008 h.

2.3. Fourier transform infrared (FT-IR) spectroscopy

Infrared spectra were obtained using a Nicolet Avatar 360 Fourier transform spectrometer. For each sample 128 scans were recorded in the 4000 to 400 cm^{-1} spectral range (2500–25,000 nm) in diffuse reflection modality (DRIFT) with a resolution of 4 cm^{-1}. As background the spectrum of the KBr powder was used. Spectral data were collected with OMNIC 8.0 (Thermo Fisher Scientific Inc.) software. FT-IR spectra were recorded at the following time intervals: 0, 12, 24, 96, 168, 312, 504 and 1008 h.

Peak heights were measured using OMNIC software according to the method described in the literature [32].

2.4. Hyperspectral imaging (HSI)

Hyperspectral analyses were carried out on each sample set at 0 and 1008 h of irradiation in the wavelength interval 1000–2500 nm (SWIR). The acquisitions were performed with SISUChema XL™ (Specim, Finland), equipped with a 31 mm lens allowing the acquisition of wood samples with a resolution of 300 μm/pixel. The spectral resolution was 6.3 nm. Images were acquired through scanning each investigated sample line by line.

The calibration and image corrections were obtained as previously described [27–29].

2.5. Statistical and spectral analysis

Data obtained by colour measurements and FT-IR spectroscopy were analyzed with the Statistica 2010 advanced statistics software [33]. As a first step, data distribution was plotted and visually checked for normality. Differences between treatments were checked with the standard paired *t*-test, with ANOVA and MANOVA analysis. Post-hoc test was conducted with Tukey HSD test method. Regression analysis was used to develop prediction models.

FT-IR and HSI derived spectral data were analyzed by adopting standard chemometric methods [34–35], with the PLS_Toolbox (Version 7.8 Eigenvector Research, Inc.) running inside Matlab (Version 7.11.1, The Mathworks, Inc.). More in details, the spectra preprocessing was performed as follows: raw spectra were preliminary cut, at the beginning and at the end of the investigated wavelength range, in order to eliminate unwanted effects due to lighting/background noise.

The following preprocessing algorithms were then applied: *Standard normal variation* (SNV), *smoothing, 1st Derivative* and *mean center* (MC).

The basic equation for SNV correction is:

$$x_{corr} = \frac{X_{org-a_0}}{a_{1.}}$$

The value of a_0 will always equal zero, for normalization, while a_1 value depends on the type of applied normalization. SNV transforms each measured spectrum into a signal with zero mean and unitary variance. This algorithm has been originally applied to reduce the scattering effects in the spectra, but also to transform the data in such a way that they generally have a more linear relationship between signal and concentration, as shown in Fig. 1 [36].

The most common technique of differentiation for smoothing is the Savitzky–Golay routine [37]. This routine can be used for smoothing/noise reduction, in order to avoid amplification of high-frequency noise during the derivation process as it happens in the case of finite difference derivation [36].

For derivative the algorithm of polynomial fitting, called Savitzky-Golay, was applied due to its acceptance and simplicity [38]. Derivatives have the capability to remove both additive and multiplicative effects in the spectra and have been used in analytical spectroscopy for decades [39]. Using derivatives, spectral differences can be emphasized and baseline/background are removed as shown in Fig. 2.

Centering and scaling are the two most common types of preprocessing, normally applied before principal component analysis [40]. A lot of other preprocessing methods exist and their appropriate choose typically depends on the nature of the investigated data [41]. The centering method adopted in this work and suitable for continuous data, such as FT-IR spectra, was mean centering. This method has the effect of including an adjustable intercept in multivariate models. For example, mean centering both X and Y blocks in a regression model effectively allows for a non-zero intercept of the regression line [42].

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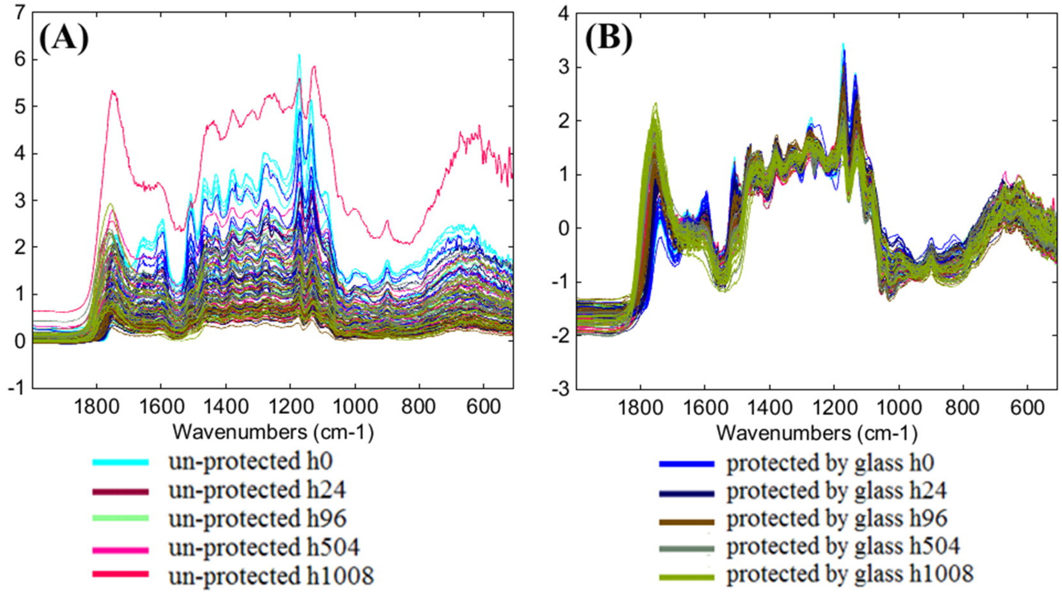

Fig. 1. Raw spectra of un-protected and protected samples before (A) and after (B) standard normal variation (SNV) preprocessing.

A reduction from 256 to 240 was preliminary applied to wavelength of HSI data, resulting in an investigated spectral range of 1005–2500 nm. SNV was used to reduce the variability of light scattering, *smoothing* was applied to reduce the spike effect and, finally, MC for data centering.

Principal component analysis (PCA) was applied as a powerful and versatile method capable of providing an overview of complex multivariate data. PCA can be used for revealing relations between variables and relations between samples (e.g. clustering), detecting outliers, finding and quantifying patterns, generating new hypotheses as well as many other things [41]. In this work, PCA was used to decompose the "processed" spectral data into several principal components (PCs) embedding the spectral variations of each collected spectral data set. The first few PCs, resulting from PCA, are generally utilized to analyze the common features among samples and their grouping: in fact, samples characterized by similar spectral signatures tend to aggregate in the score plot of the first two or three components.

3. Results and discussion

3.1. Colour data

The chromatic coordinates were studied both as raw data, by calculating average values and standard deviation and further elaborated by regression analysis and Tukey test. The results of regression analysis are shown in Table 1 and expressed in terms of irradiation times as function of chromatic coordinates L*, a* and b*.

As first observation, it can be derived that in all cases the data are statistically significant as demonstrated by the values of p-level (Table 1).

In some cases the R^2_{adj} values are quite low due to the possible dispersion between the observed values and those obtained from the calculated prevision model.

The trend of the chromatic coordinates gives a clear decrease of L* and an increase of a* and b*. The decrease in lightness associated to irradiation has been widely observed and discussed and can be associated

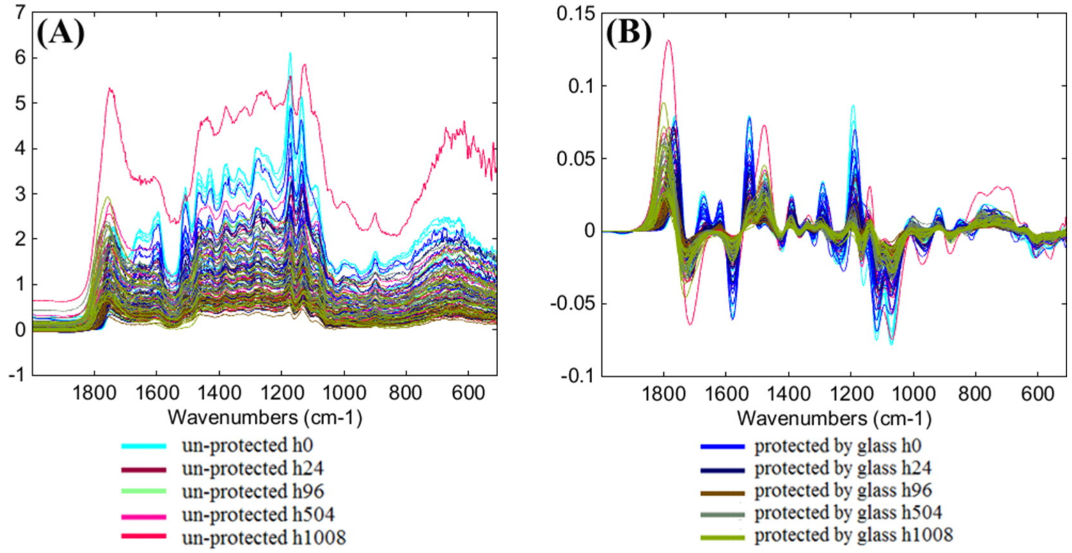

Fig. 2. Raw spectra of un-protected and protected samples before (A) and after (B) smoothing and first derivative preprocessing.

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Table 1
Results of the regression analysis applied to the irradiation time as function of the chromatic coordinates.

Sample set	Chromatic coordinate	Regression	$R^2_{adj.}$	p-level
Unprotected wood	L^*	$t = 4823.962–60.505\,L^*$	0.582	<0.001
Unprotected wood	a^*	$t = -441.965 + 107.369a^*$	0.554	<0.001
Unprotected wood	b^*	$t = -649.964 + 33.050b^*$	0.245	<0.001
Wood protected by glass	L^*	$t = 5069.585–62.710\,L^*$	0.395	<0.001
Wood protected by glass	a^*	$t = -436.401 + 116.805a^*$	0.473	<0.001
Wood protected by glass	b^*	$t = -411.568 + 26.368b^*$	0.121	<0.001
Wood protected by glass + shellac	L^*	$t = 5898.174–73.212\,L^*$	0.561	<0.001
Wood protected by glass + shellac	a^*	$t = -449.344 + 125.219a^*$	0.585	<0.001
Wood protected by glass + shellac	b^*	$t = -438.694 + 27.848b^*$	0.155	<0.001
Wood protected by glass + beeswax	L^*	$t = 6106.615–76.515\,L^*$	0.437	<0.001
Wood protected by glass + beeswax	a^*	$t = -455.615 + 119.496a^*$	0.466	<0.001
Wood protected by glass + beeswax	b^*	$t = -295 + 22.309b^*$	0.085	<0.001
Wood protected by glass + Linfoil®	L^*	$t = 5354.132–66.118\,L^*$	0.375	<0.001
Wood protected by glass + Linfoil®	a^*	$t = -503.386 + 130.064a^*$	0.107	<0.001
Wood protected by glass + Linfoil®	b^*	$t = -365.086 + 24.993b^*$	0.375	<0.001

to lignin photo-degradation which produces chromophoric groups absorbing especially in the UV range of the sunlight spectrum [5–6,8,18]. The decrease of the coordinate L^* is higher in unprotected wood samples $[\Delta L^*(L^*_{1008h} - L^*_{0h}) = -10.261]$ in respect to those protected by glass $[\Delta L^*(L^*_{1008h} - L^*_{0h}) = -7.589]$, by shellac $[\Delta L^*(L^*_{1008h} - L^*_{0h}) = -6.504]$, by beeswax $[\Delta L^*(L^*_{1008h} - L^*_{0h}) = -6.778]$ and Linfoil® $[\Delta L^*(L^*_{1008h} - L^*_{0h}) = -6.893]$. This result suggests that both glass and protective products have a clear influence in wood photo-degradation by reducing the darkening.

The same trend can be observed for the chromatic coordinates a^* and b^*. In fact, for unprotected wood samples the increase of a^* $[\Delta a^*(a^*_{1008h} - a^*_{0h}) = 5.413]$ and b^* $[\Delta b^*(b^*_{1008h} - b^*_{0h}) = 13.522]$ is higher in respect to those protected by glass $[\Delta a^*(a^*_{1008h} - a^*_{0h}) = 4.285;\ \Delta b^*(b^*_{1008h} - b^*_{0h}) = 10.920]$, by shellac $[\Delta a^*(a^*_{1008h} - a^*_{0h}) = 4.424;\ \Delta b^*(b^*_{1008h} - b^*_{0h}) = 10.426]$, by beeswax $[\Delta a^*(a^*_{1008h} - a^*_{0h}) = 4.004;\ \Delta b^*(b^*_{1008h} - b^*_{0h}) = 10.245]$ and Linfoil® $[\Delta a^*(a^*_{1008h} - a^*_{0h}) = 3.899;\ \Delta b^*(b^*_{1008h} - b^*_{0h}) = 10.405]$.

The obtained results further indicate that glass has an important protective effect on wood and that the tested products allowed for little increasing this effect.

The results of Tukey test (see Supplemental informative material) also allow for studying the statistical grouping of the sample sets during the irradiation times. In general no change can be observed after 504 h of irradiation suggesting that wood surface modifications don't occur after this time. Concerning unprotected wood samples group change occurs after 24 h of irradiation, such behaviour confirms previous results, demonstrating that the main colour changes undergo within the first 24 h of artificial ageing [8,18,29,43–46]. On the other hand, wood samples protected by glass, glass + beeswax and glass + Linfoil® exhibit statistical grouping change at 96 h of irradiation. At last, shellac treated samples undergo changes at 168 h. This result suggests that shellac is able to protect wood surface against photo-degradation for a longer time in respect to the other tested protective products.

3.2. FT-IR data

FT-IR spectra were studied in order to investigate the chemical modifications of wood components due to photo-irradiation. By observing the spectra shown in Fig. 3, it can be derived that wood photo-degradation is accompanied by a decrease of the aromatic skeletal vibration in lignin at

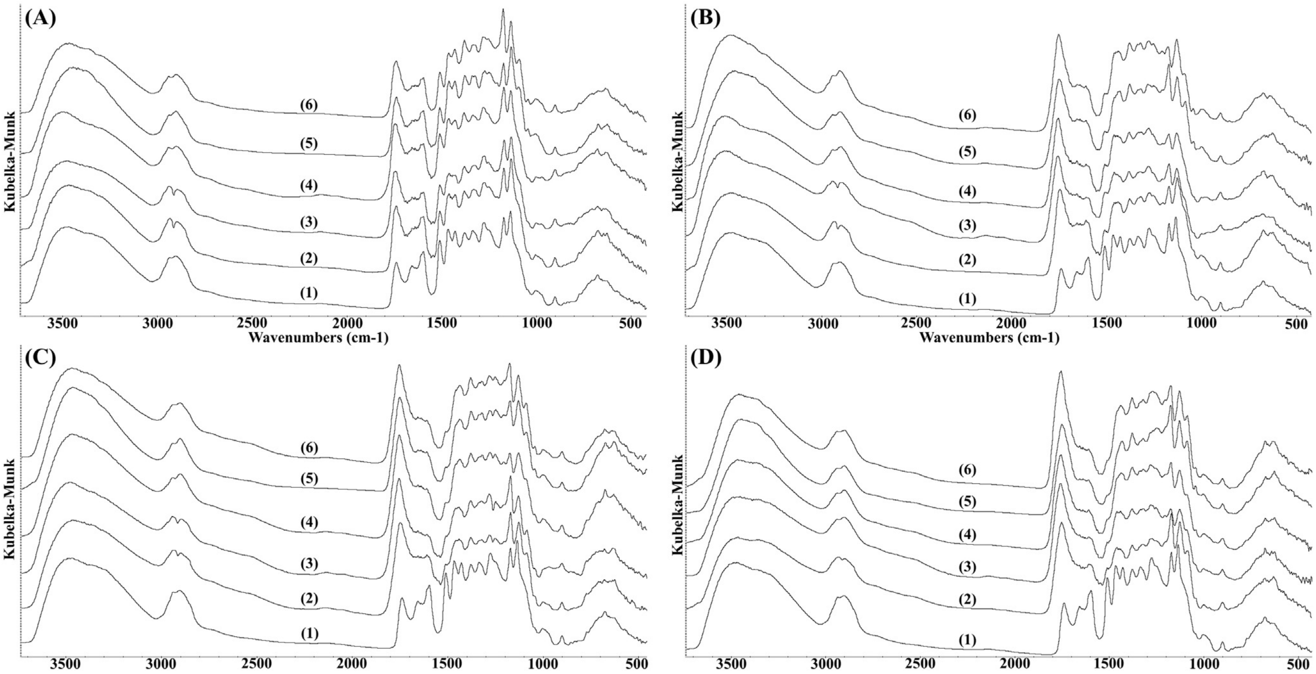

Fig. 3. Time dependant FT-IR spectra of poplar samples at different irradiation times (hours): (A) 24; (B) 312; (C) 504 and (D) 1008 h, in comparison to non-irradiated sample (1). (2) unprotected, (3) protected by glass; (4) protected by glass + shellac; (5) protected by glass + wax; (6) protected by glass + Linfoil®.

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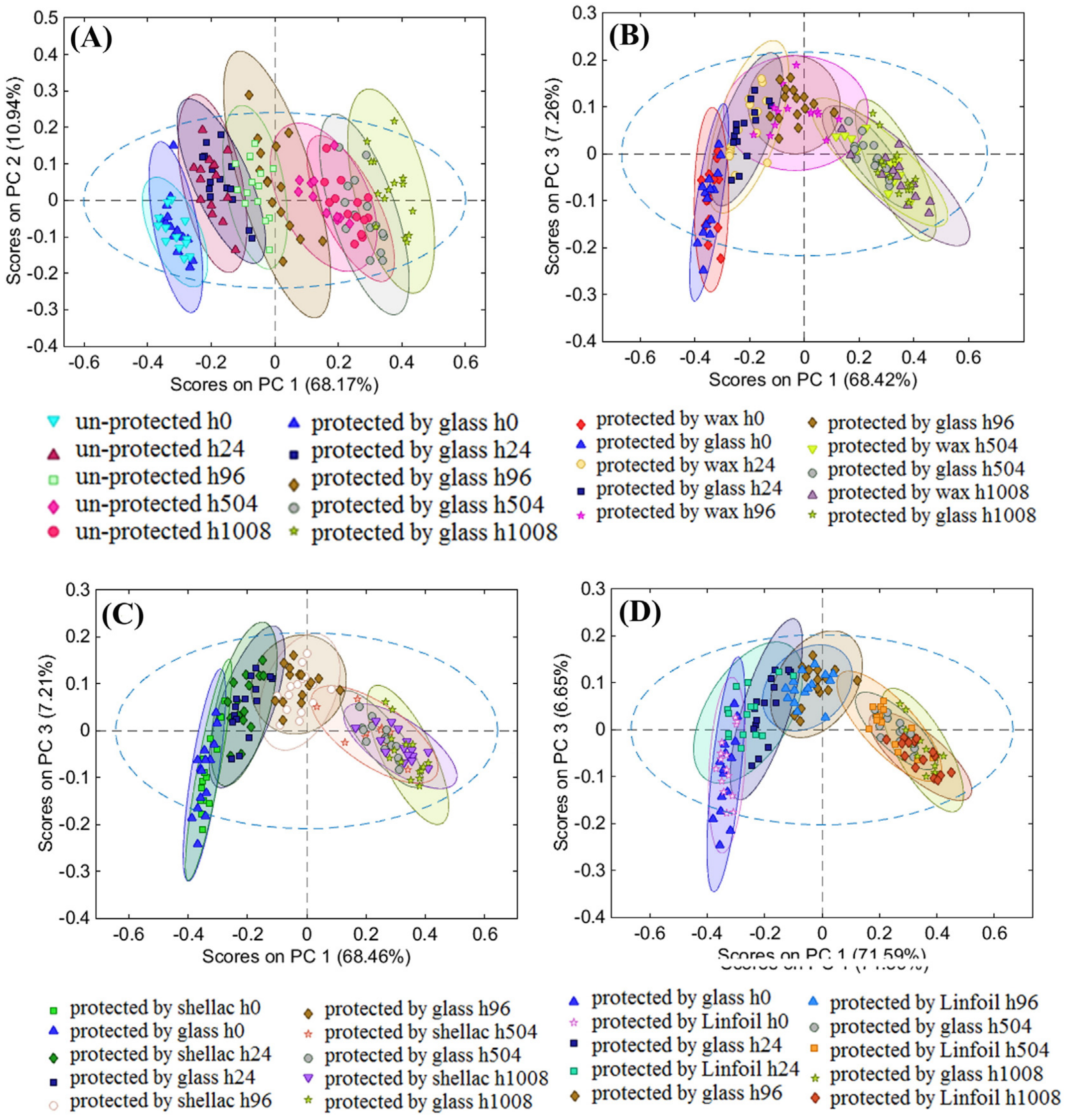

Fig. 4. PCA score plots of FT-IR spectra for samples at different selected ageing times: un-protected against protected by glass (A); protected by wax against protected by glass (B); protected by shellac against protected by glass (C) and protected by Linfoil® against protected by glass (D). The spectrum variations related to lignin photo-degradation are expressed by the first component in all investigated PCA. In each case, the comparison with samples protected by glass allows finding a similar trend for all applied treatments, confirming the low protective effect of the products used against photo-degradation of lignin.

1507 cm^{-1} and an increase of the band at 1737 cm^{-1} due to stretching of the carbonyl group, as previously observed [8,12,18,20,27,29,47–50]. The C—H in-plane deformation for polysaccharides at 1376 cm^{-1} seems to be not affected by irradiation so this band has been used as internal reference to evaluate the lignin decay (Fig. 3). This trend can be observed both in unprotected and protected samples.

In fact, by observing the two bands (1507 cm^{-1} and 1737 cm^{-1}), chosen for evaluating the modifications of wood components, it can be affirmed that no significant differences between samples protected by glass slides only and glass + protective may be observed, concerning the decrease of lignin peak and the increase of the carbonyl band. After 312 h of irradiation (Fig. 3B), the lignin band at 1507 cm^{-1} is almost

Table 2
Results of the regression analysis applied to the FT-IR data calculated as peak height ratio referred to lignin, carbohydrates and carbonyl.

Sample set	Peak ratio	Regression	$R^2_{adj.}$	p-level
Unprotected wood	Lignin/carbohydrate	$I_{1507}/I_{1376} = 1.901360–0.001847t$	0.646	<0.001
Unprotected wood	Carbonyl/carbohydrate	$I_{1737}/I_{1376} = 4.041962 + 0.003387t$	0.499	<0.001
Wood protected by glass	Lignin/carbohydrate	$I_{1507}/I_{1376} = 1.861027–0.001933t$	0.645	<0.001
Wood protected by glass	Carbonyl/carbohydrate	$I_{1737}/I_{1376} = 4.213618 + 0.0056451t$	0.668	<0.001
Wood protected by glass + shellac	Lignin/carbohydrate	$I_{1507}/I_{1376} = 1.996322–0.002034t$	0.619	<0.001
Wood protected by glass + shellac	Carbonyl/carbohydrate	$I_{1737}/I_{1376} = 4.235206 + 0.004456t$	0.595	<0.001
Wood protected by glass + beeswax	Lignin/carbohydrate	$I_{1507}/I_{1376} = 1.891454–0.002057t$	0.632	<0.001
Wood protected by glass + beeswax	Carbonyl/carbohydrate	$I_{1737}/I_{1376} = 4.070576 + 0.004786t$	0.629	<0.001
Wood protected by glass + Linfoil®	Lignin/carbohydrate	$I_{1507}/I_{1376} = 1.902460–0.002001t$	0.609	<0.001
Wood protected by glass + Linfoil®	Carbonyl/carbohydrate	$I_{1737}/I_{1376} = 4.304963 + 0.004260t$	0.493	<0.001

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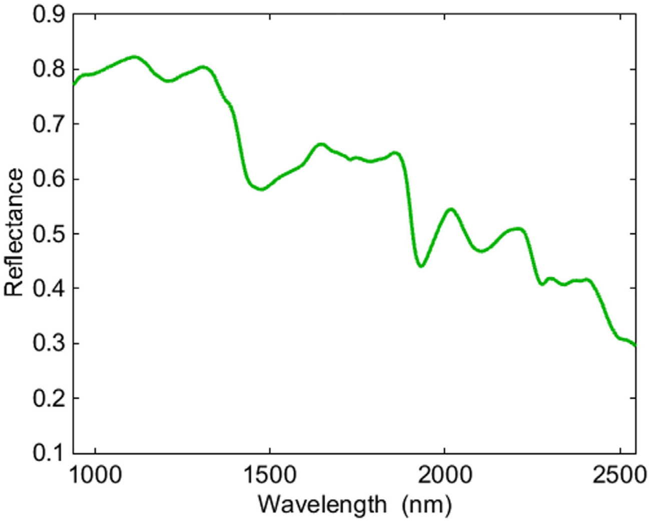

Fig. 5. Average spectra of samples analyzed by *hyperspectral imaging* (HSI) in the SWIR range.

completely disappeared, demonstrating that, after this time, glass and glass + protective have no more effect on wood photo-degradation: their effect can be considered acting on a short-time range.

In order to better evaluate the influence of glass cover on wood changes and the IR band variability, PCA was applied to the pre-processed spectra (Fig. 4). The scores plot of PCA for unprotected and glass covered wood samples highlights changes along ageing time between the two groups, particularly evident at time 1008 h (Fig. 4A). This result can be associated to a protective effect of glass on wood samples. The point clouds suggest that spectral changes continuously occur along the irradiation time. Moreover, the loading plot associated to PCA shows that the spectrum variability is evident around 1700–1800 cm^{-1}, due to carbonyl absorption changes, and around 1500 cm^{-1} due to lignin skeletal vibration.

In accordance to these results, the samples covered by glass and protective product were put in comparison with those protected by glass only (Fig. 4B–D). The scores plots of PCA showed little differences between samples protected by glass and by glass plus products. Spectral variations are visible in all samples at the different times with a decrease of variability after 504 h of irradiation.

FT-IR data were further elaborated and investigated by applying ANOVA and Tukey tests applied to the band intensity ratio. In order to

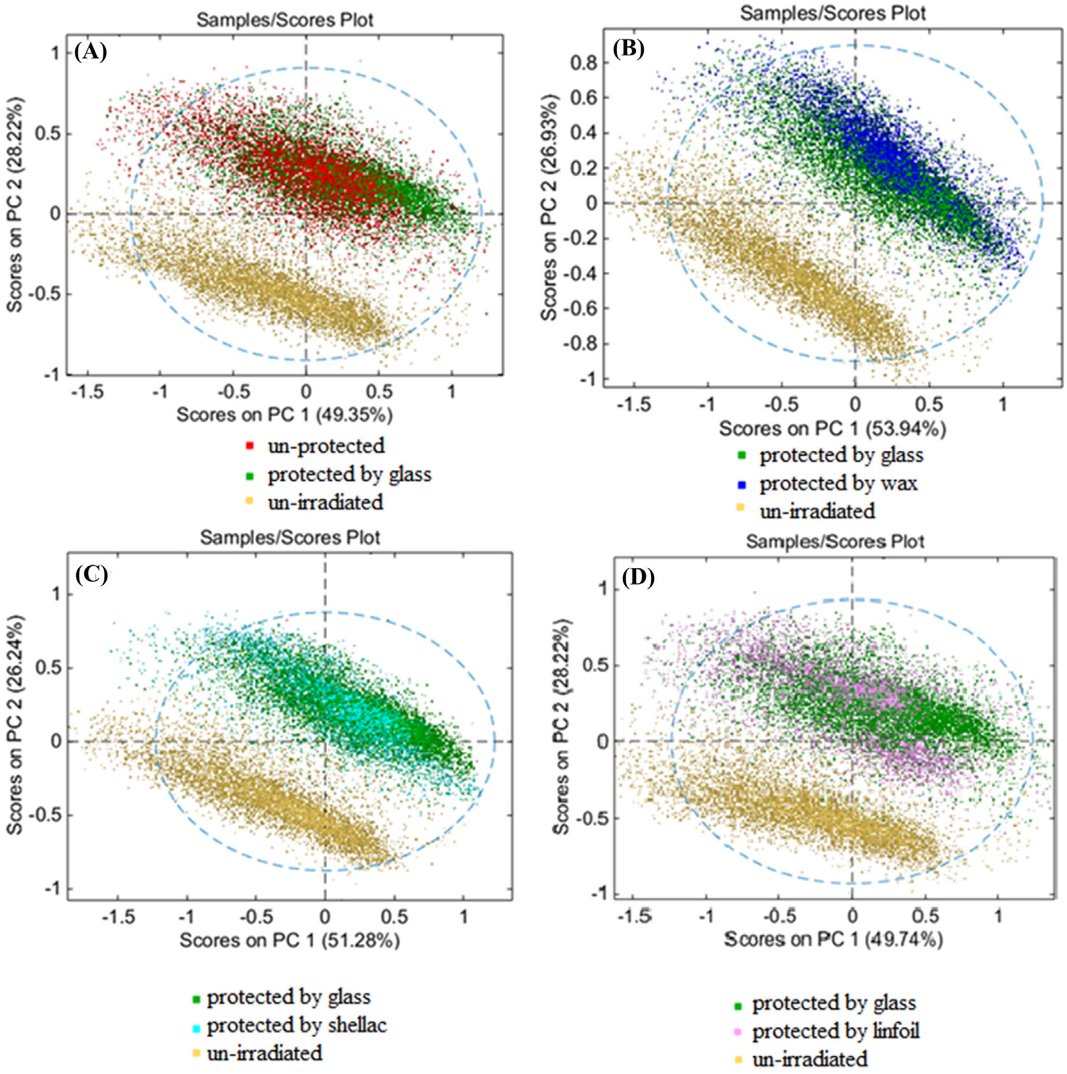

Fig. 6. Score plots as resulting from *principal component analysis* (PCA) showing the comparison between data gathered from glass-protected samples and samples protected by glass + protective products.

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determine the rate of lignin decay and carbonyl formation, the intensities of the lignin band at 1507 cm^{-1}, the carbonyl band at 1737 cm^{-1} and the carbohydrate reference band at 1376 cm^{-1} were calculated [32]. Then the relative changes in ratio of lignin/carbohydrate and carbonyl/carbohydrate bands at different exposure times were derived. In Table 2 the results of the regression analysis are shown, expressed in terms of peak ratio as function of the irradiation time. As first observation, it can be derived that in all cases the data are statistically significant as demonstrated by the values of p-level (Table 2).

The linear regression and the average data (see Supplemental informative material) highlight that the I_{1507}/I_{1376} ratio decreases during irradiation due to the lignin photo-degradation and consequently to the reduction of the band at 1507 cm^{-1}. On the other hand, the I_{1737}/I_{1376} ratio increases as result of the rise of the carbonyl band at 1737 cm^{-1} due to the formation of new carbonyl groups from lignin degradation. This trend can be observed for both unprotected and protected wood sample set. In general, as pointed out for colour data, also in this case no change can be observed after 504 h of irradiation suggesting that wood surface chemical modifications don't occur after this time. In all sample sets the grouping change occurs within 24 h of exposure suggesting that the chemical modifications of wood are statistically significant right from the first hours of irradiation.

3.3. HSI data

To further evaluate and verify the data, the samples aged for 1008 h were acquired by HSI in the SWIR range. The PCA results from unprotected wood, glass and glass + products protected wood were compared with the un-irradiated wood samples (time 0 h).

Cellulose and lignin, in the SWIR range, have strong absorptions at around 1460 nm and 1930 nm which can be attributed to the combination modalities of OH in water molecules (Fig. 5). The water chemical bond vibration around 1460 nm may overlap with those of other OH groups in cellulose molecules or of CH_2 groups in lignin making difficult the accurate band assignment in this region [51]. The weak spectral feature around 1730 nm may be attributed to the presence of OH bond of water molecule in cellulose/lignin and the weak absorption at 1790 nm to O—H stretching in water molecules. The mean absorptions in the 2000–2500 nm wavelength interval can be attributed to the different configurations of the C—H, C═O, C═C, and –COOH functional groups in cellulose and lignin as reported in the literature [51–57] (Fig. 5).

The scores plots of PCA applied to HSI data highlight a clear difference between the samples at time 0 h and time 1008 h due to the chemical changes caused by irradiation. In Fig. 6 the scores plots of the first two PC are shown. The model gave a captured variance, with five PCs, of: 93.85 (A); 95.25 (B); 93.46 (C) and 93.45 (D).

The point clouds associated to the 1008 h irradiated samples, unprotected and covered by glass, are partially overlapped suggesting that glass has low influence on wood protection (Fig. 6A). A similar behaviour can be observed for score plots of samples covered by glass and by glass + protective products, apart from samples covered by glass + wax (Fig. 6B–D). In this last case, the points clouds are overlapped to a less extend.

In Fig. 7 the loadings plots of PC1 and PC2 for HSI spectra are shown. The PC1 in all loadings plots highlights the variability, for negative values, of 1st overtone C—H stretching and O—H stretching in cellulose/lignin from 1400 nm to 1800 nm. The loadings was also influenced,

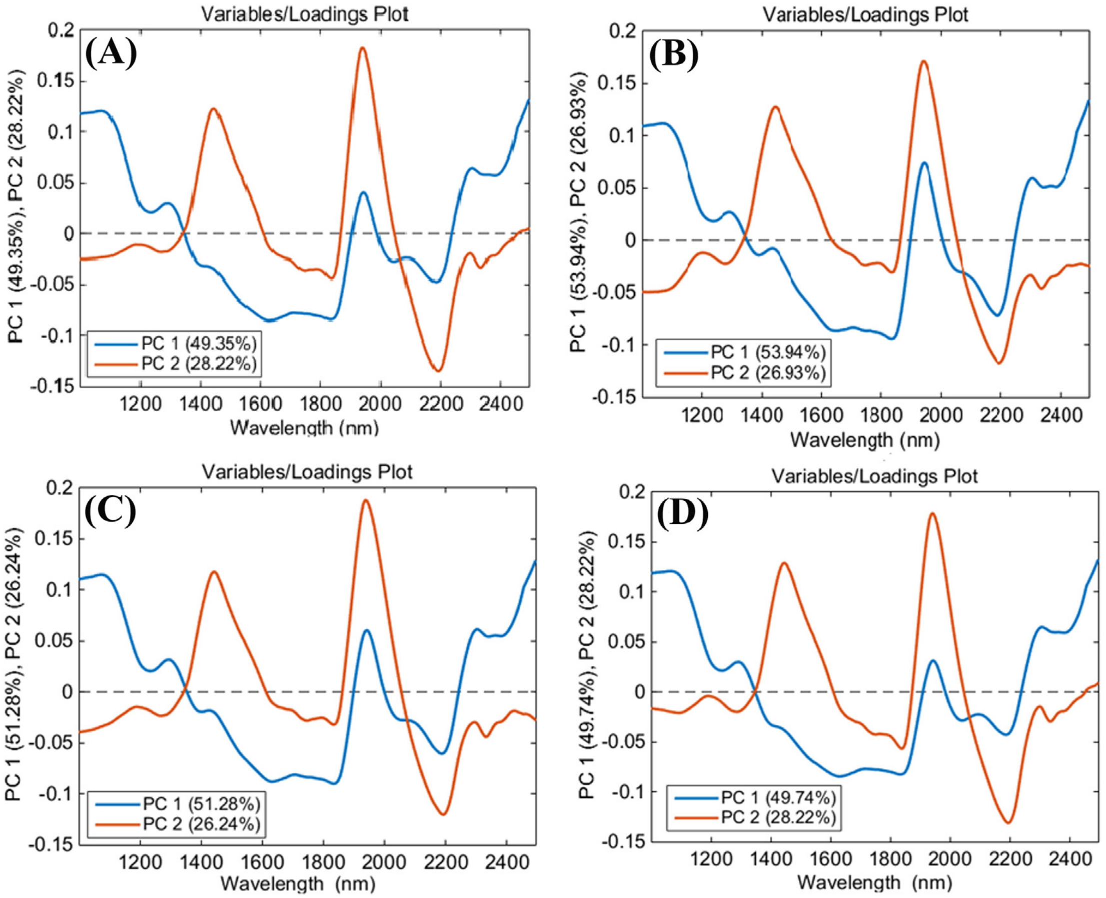

Fig. 7. Loadings plots of PC1 and PC2 for HSI spectra, obtained at time 0 h and time 1008 h of irradiation, showing the variability of bands in the SWIR spectral range. A: un-irradiated, unprotected and glass-protected samples, B: un-irradiated, glass- and glass + wax protected, C: un-irradiated, glass and glass + shellac protected and D: un-irradiated, glass- and glass + Linfoil® protected.

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for positive values, by absorption around 1100 nm, due to C—H 2nd overtone stretching of lignin, at ~1200 nm, related to O—H 1st overtone bending of water, cellulose and lignin, and ~2300 related to different configuration of C—H rotation, C—H stretching, C═O stretching, –CH_2 rotation of cellulose.

PC2 loadings show the variability at ~1400 nm and ~1900 nm related to hydroxyl group in water, cellulose and lignin for positive value (Fig. 7). The variability of the spectra of PC2, for negative values, visible at ~2190 nm is associated to different configurations of the C—H, C═O, C═C, and –COOH functional groups in cellulose and lignin.

4. Conclusions

A combined use of different spectroscopic techniques was tested in order to understand colour and chemical modifications in poplar wood samples, unprotected and protected by glass and different products, as consequence of simulated sunlight exposure.

The experimental data were statistically elaborated to establish their significance and to explain the trend during the ageing time.

The results of colour measurements highlighted that wood surfaces underwent a clear darkening (L^* decrease) and yellowing (b^* increase) due to irradiation. The greatest changes were observed for unprotected wood. Moreover, the greatest modifications occurred within the first 24 h of irradiation for unprotected wood, 96 h for glass, glass + beeswax, glass + Linfoil®, and 168 h for glass + shellac. This result suggests that protective reduced colour modifications and their effect, against surface colour changes, occurred especially in the first steps of ageing.

Shellac demonstrated to be the most suitable protective product by acting for longer times in respects to the other tested product.

FT-IR spectroscopic investigation showed that chemical modifications on wood samples are relevant both in unprotected and protected wood and they are due to lignin photo-degradation. FT-IR data evaluation further supported the results obtained by colour measurements. In fact, also in this case, the study of the infrared spectra demonstrated that the protective products have not significant effect on wood component modifications and that over long times of exposure lignin degrades completely. So, it can be affirmed that the protective effect acts only on short time range.

The results of this work highlighted that the protective materials have only a partial time effect on wood photo-degradation by little reducing the colour changes. No relevant protective effect against chemical modification has been detected over long time of exposure.

This finding is particularly relevant because it can contribute to perform a correct detection of protective materials for wood, to search for new products and to define and set up the best maintenance procedures for wood objects and artefacts.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.saa.2016.05.050.

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