Effects of Ageing on the Color and Surface Chemistry of Paulownia Wood (*P. elongata*) from Fast Growing Crops

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The behavior of paulownia wood (*Paulownia elongata*) was investigated using three different ageing tests: simulated natural ageing under the influence of light under indoor conditions, temperature-induced ageing in the dark, and UV-induced ageing. Ageing effects were evaluated by color measurements in the CIE Lab system. Simulated natural ageing of wood in indoor conditions (6 months) and UV-accelerated ageing (72 h) are complex and dynamic processes, which resulted mostly in yellowing of the samples due to photo-degradation. Temperature-induced ageing (288 h at 100 °C) resulted mostly in a rapid and visible darkening of the paulownia wood. Comparative in-time evolution of color changes during accelerated UV ageing testing and simulated natural ageing testing under indoor conditions allowed the estimation of an acceleration index of about 50X. Fourier transform infrared spectroscopy (FTIR) was used to examine specific chemistry changes occurring during these ageing tests. UV light from natural or artificial sources caused primarily lignin degradation followed by oxidative processes leading to carbonyl-containing chromophores. Temperature-induced partial degradation of hemicelluloses and oxidative processes resulted in the formation of chromophores containing mostly conjugated carbonyl groups. This research highlighted that paulownia wood (*P. elongata*) is quite sensitive to ageing under the action of light and temperature, which cause notable color and surface chemistry changes.

Keywords: Paulownia; Artificial ageing; Natural ageing; Color change; FTIR

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INTRODUCTION

Paulownia (*Paulownia* spp.) is an indigenous genus from China that is represented by nine species (*P. elongata*, *P. tomentosa*, *P. catalpifolia*, *P. fortunei*, *P. taiwaniana*, *P. albiphloea*, *P. australis*, *P. kawakamii*, and *P. fargesii*) of fast growing timber trees (Hulya *et al.* 2005; Barton *et al.* 2007; Manuel *et al.* 2011; Liu *et al.* 2013b). Due to its adaptability, allowing a wide distribution, and extremely fast growth, Paulownia has become one of the most important supply species for the wood industry in China, especially after 1998, when the policy of natural forestry protection was put in force (Zhu *et al.* 1986; Hu 1999; Chen 2003; Zhou and Li 2004; Li *et al.* 2009). Nowadays, more than one billion Paulownia trees exist in China, with the estimated available timber resource from standing trees being more than 80 million m^3 (Zhang *et al.* 2015).

The worldwide research interest focusing on this sustainable wood resource is therefore obvious and well justified, completing the available reference basic information

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on this wood species (Chinese Academy of Forestry 1986) or general technical data (http://www.worldpaulownia.com/html/tech.html). A better knowledge of its chemical composition (Rencoret *et al.* 2009), anatomical structure (Popović and Radošević 2010; Liu *et al.* 2013a; Meier 2015), and physical, mechanical, and technological properties (Chen and James 1999; Ates *et al.* 2008; Kaygin *et al.* 2009; Akyildiz and Kolsahin 2010; Kaymakci *et al.* 2011; Kaymakci *et al.* 2013; Majid 2013; Akyildiz 2014; Kaygin *et al.* 2015) are key points for its rational and diverse utilization (Hulya *et al.* 2005; Mitsui and Tolvaj 2005; Ayrilmis and Kaymakci 2013; Kaymakci and Ayrilmis 2014; Kaygin *et al.* 2015; Tari *et al.* 2015) and appropriate mechanical or chemical processing (Sun *et al.* 2011; Ayrilmis and Kaymakci 2013; Yorgun and Yıldız 2015a,b). Improving Paulownia's natural durability and impregnability is also an interesting recent research topic (Candan and Korkut 2013; Boeva *et al.* 2015; Hamid *et al.* 2015). Additionally, as a fast growing wood species, Paulownia is a candidate for bioenergy production (Lopez *et al.* 2012; Yadav *et al.* 2013; Yavorov *et al.* 2015).

Alongside texture resulting from anatomical features, color represents an important property defining the aesthetics of wood, highly valued for furniture, and other artifacts. The surface of Paulownia wood is light in color and presents an interesting and diverse texture (depending on the cutting direction) resulting from its anatomical structure (*i.e.*, clearly visible annual rings, and semi-ring porous hardwood with large visible pores) (Liu *et al.* 2013a; Meier 2015). However, the color of wood is a property that is influenced by ageing under the action of diverse environmental factors. These factors include natural and artificial light and especially ultraviolet (UV) radiation, ambient temperature, relative humidity, and oxygen (Sonderegger *et al.* 2015; Kránitz *et al.* 2016). Ageing occurs over time, altering the appearance and the properties of all materials, including wood. Ageing results from a slow, gradual, and irreversible alteration of the chemical or physical structure of a material with the passage of time (David 2009). The changes in physical and mechanical properties of wood due to ageing originate from microstructure changes and chemical changes in the wood components (Kránitz *et al.* 2016).

Different chemical mechanisms are involved in wood ageing as a function of the main ageing factor. Light-induced ageing is a complex and dynamic process of photodegradation, primarily related to lignin decomposition by UV light through a stepwise mechanism involving formation of phenoxyl free radicals and their further reaction with oxygen to produce carbonyl-containing chromophore groups (Fengel and Wegener 1984; Williams 2005; Teacă *et al.* 2013). Visible light up to 515 nm, which penetrates deeper into wood, also contributes to surface and especially sub-surface color changes (Živković *et al.* 2014), though it does not affect lignin (Kataoka *et al.* 2007). Temperature-induced ageing (in the absence of light) is the combined effect of hydrolytic and thermo-oxidative processes of wood components, mainly of hemicelluloses (the most labile) leading to formation of chromophore containing products. Cleavage of lignin units followed by condensation and depolymerisation of cellulose may also occur, with the whole process being highly influenced by the environmental conditions (presence of air and humidity) (Tdjeersma and Militz 2005; Esteves *et al.* 2013; Froidevaux and Navi 2013; Chen *et al.* 2014; Kránitz *et al.* 2016). For wood used over a long period under ambient temperature conditions, ageing may be due to the combined effect of thermal oxidation by air-oxygen and acid hydrolysis by bound water and acids contained in the wood, whilst in dry heat conditions thermal oxidation is the main factor for color change during ageing (Matsuo *et al.* 2011).

Evaluating and understanding the ageing phenomena is important for cultural heritage conservation (Feller 1994), including wood cultural heritage (Kránitz *et al.* 2016; Timar *et al.* 2016), as well as for modern technologies, when the preservation of the initial color of wood is desired (Matsuo *et al.* 2009). Accelerated artificial ageing tests under the action of UV radiation (Roşu *et al.* 2010; Persze and Tolvaj 2012; Timar *et al.* 2016) and /or temperature (Matsuo *et al.* 2011; Boeva *et al.* 2015) are often employed to obtain data useful for understanding and potentially predicting natural ageing effects. As color is highly sensitive to ageing, color measurements in the CIE Lab system have been often employed for monitoring wood ageing (Matsuo *et al.* 2009, 2011; Roşu *et al.* 2010; Persze and Tolvaj 2012; Tolvaj *et al.* 2013; Timar *et al.* 2016).

Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) is often employed to reveal chemistry changes associated with ageing. Infrared spectra are sensitive indicators of chemical changes, especially light-induced natural and accelerated ageing (Colom *et al.* 2003; Pandey 2005; Pandey and Vuorinen 2008; Chang *et al.* 2010a,b; Roşu *et al.* 2010; Tolvaj *et al.* 2013). Moreover, chemical changes in thermally treated wood revealed by FTIR (Tdjeersma and Militz 2005; Esteves *et al.* 2013; Chen *et al.* 2014; Tolvaj *et al.* 2014b; Fabiyi and Ogunleye 2015) may be helpful in understanding temperature-induced ageing (Matsuo *et al.* 2011).

Currently, there is no available experimental data on the ageing behavior of Paulownia wood. This work focused on monitoring the ageing of *Paulownia elongata* wood by color measurements in the CIE Lab system. Artificial accelerated ageing tests employing temperature, *i.e.*, UV radiation, as ageing factors were performed. A simulated natural ageing test under the influence of light in indoor conditions was started to compare color changes and possibly estimate an acceleration index. Finally, FTIR was employed to reveal surface chemistry changes related to the ageing factors.

EXPERIMENTAL

Wood Material

All wood samples originated from a single Paulownia (*P. elongata*) tree grown in the Beijing area. The log was cut to timber pieces and air-dried to a moisture content of 10 to 12%. Wood pieces with radial surfaces and thicknesses of 10 mm were processed. Test samples with dimensions of $120 \times 100 \times 8$ mm^3 were sanded successively three times with grit sizes of 120, 180, and 240, thoroughly cleaned of dust, and conditioned in a Feutron climatic chamber (Langenwetzendorf, Germany) at 20 °C and 55% relative humidity (RH) until they reached a constant weight (7 days). Five replicates were exposed to each type of ageing test, and five replicates were kept as controls, totally, 20 replicate specimens were prepared.

Ageing Procedures

A natural ageing test and two accelerated artificial ageing tests (temperature and UV radiation) were conducted. Both artificial ageing tests were carried out in a PC-controlled environmental climatic chamber (FEUTRON FKS 400, Feutron Klimasimulation GmbH, Langenwetzendorf, Germany), endowed with a UVA Spot 400 A UV source.

Simulated natural ageing

A natural ageing test in indoor conditions was set up at the CDI Institute of *Transilvania* University of Brasov (45°39'54''N, 25°33'27''E, Elevation 550 m). The specimens were exposed indoors to natural sunlight filtered through window glass, which is generally recognized as a filter of UVB and transmits UVA and visible light, though the degree of UVA transmission depends on the type of glass (*e.g.* Tuchinda *et al.* 2006; Almutawa *et al.* 2013). The samples were exposed on a special test rack facing South (9 degrees deviation from South to East) in a vertical position with the longitudinal axis (fiber direction) at a 90° angle to the supporting horizontal strips, at a height of 650 to 1350 mm from the ground level.

After each month (30 days) of sunlight exposure, the specimens were measured to quantify color changes due to direct exposure to sunlight filtered by glass window. The experimental data in this work refers to control unaged samples (coded 0) and naturally aged samples for 1 to 6 months (from 1st May to 31st October 2015), coded 1N, 2N, 3N, 4N, 5N, and 6N, respectively. This test is currently in progress. The ambient temperature was around 20 to 25 °C during this experiment.

Temperature-induced artificial ageing

Temperature-induced ageing was conducted at a constant temperature of 100 ± 2 °C and constant relative humidity (RH = 55 ± 5 %), under a normal atmosphere (air) and absence of light. The test was run for a total duration of 288 h (12 days), which corresponds to approximately 100 years under normal temperature conditions (Feller 1994). The ageing effects were evaluated by color measurements after intervals of 72 h (3 days), so that four measurements were recorded during the treatment. Accordingly, the experimental data refers to temperature-aged samples for 72, 144, 216, and 288 h, coded 72T, 144T, 216T, and 288T, respectively. Prior to all color measurements, the samples were conditioned for 24 h at 20 °C and 55% RH in the absence of light.

UV-induced artificial ageing

UV radiation is a main ageing factor for wood, causing surface and sub-surface color and chemical changes; short-waved visible light (violet-blue domain), with a slightly deeper penetration into wood than UV light, also contributes to color changes (Kataoka *et al.* 2007). Within these experiments the wood samples were exposed to light in the UVB, UVA, and VIS range from 295 to 600 nm. The radiation was emitted by a UVA Spot 400A lamp, fitted with a glass H_2 filter that cut off UV radiation below 295 nm (similar to that described by Timar *et al.* (2016)). However, emission in the UV range (mainly UVA) was the maximum for this lamp, so it seemed appropriate to consider UV as the main ageing factor in this test. The samples were placed vertically on a rack at a distance of 60 cm from the UV source inserted into one of the side walls of the climatic chamber. The actual UV irradiation procedure included an initial conditioning of 0.5 h (20 °C, 55 % RH, no light), followed by four steps of 6 h UV irradiation at 40 °C, alternated with dark periods of 0.5 h. After these four steps of a cumulative 24 h of UV exposure, a conditioning phase of 24 h (20 °C, 55 % RH, no light) was added prior to removing the samples for color measurements. This procedure was repeated three times so that the samples exposed for 24, 48, and 72 h were coded 24 UV, 48 UV, and 72 UV, respectively.

Visual Assessment and Color Measurements

Before and after different periods of ageing, the samples were visually assessed and scanned at a resolution of 300 dpi with a HP LaserJet ProCM1415 Color Multifunction Printer to document the aspect changes.

Color measurements in the CIE Lab system were performed with an AvaSpec-USB2 spectrometer (10° standard observer, under standard D65 illuminant, Avantes, Apeldoorn, Netherlands), equipped with an integrating AVA sphere with a diameter of 80 mm, interconnected by optical fibers. This was linked to a PC for data acquisition and processing, employing the dedicated color application software AVASOFT (version 7.7, provided by Avantes, Apeldoorn, Netherlands).

The color coordinates were as follows: 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). For all wood samples, these values were measured both initially and after different periods of ageing. For each test sample, color measurements were performed at 4 points (actually circular areas of about 8 mm diameter), and an average value was calculated.

To repeat the measurements in the same areas, a sample fixing plate was designed and prepared. This ensured that color measurements were made on identical areas. If this had not been done, a much higher dispersion of the experimental values would have been expected, as wooden surfaces do not have a uniform color (*i.e.*, differences between latewood and early wood).

Color differences between the aged and not-aged control samples were calculated based on Eq. 1,

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

where ΔL^*, Δa^*, and Δb^* are the differences of the initial and final values (before and after ageing for different periods of time) of the L^*, a^*, and b^* parameters, respectively. A low ΔE value corresponds to a low color difference.

FTIR Investigation

FTIR spectra were recorded on an ALPHA Bruker spectrometer equipped with ATR (attenuated total reflection) module in the range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and 24 scans/spectrum (Bruker Optik GMBH, Ettlingen, Germany). Two replicates from each batch of samples (control and aged) were investigated by FTIR. Spectra from three randomly chosen measuring areas were registered for each sample, resulting in six spectra for each tested variant. Spectra were further processed for baseline correction and smoothing, and an average spectrum of the six individually recorded ones were computed.

Average spectra were further normalised (Max-Min normalisation) and compared to highlight the chemical changes due to ageing. The assignment of characteristic absorption bands was based on literature references. A semi-quantitative evaluation of chemical changes resulting from ageing was made based on the calculated ratios of the integrated areas of some relevant absorption bands. The OPUS software (version 7.2, provided by Bruker Optik GMBH, Ettlingen, Germany) was employed for all spectra processing and calculations.

RESULTS AND DISCUSSION

Visual Assessment of Color Changes

All samples suffered a slight or more obvious color change as a result of ageing, generally perceived as lightness and shade modifications over time (Fig. 1). However, among the different types of ageing tests, these color changes were different. The most obvious color changes (darkening and shade modifications) were perceived after the temperature-induced ageing (maximum of 288 h). Natural ageing and UV artificial ageing induced less pronounced color changes, perceived as yellowing and slight darkening. Color changes after 5 months of natural ageing seemed comparable with those induced by UV radiation after 72 h of exposure in the artificial accelerated test.
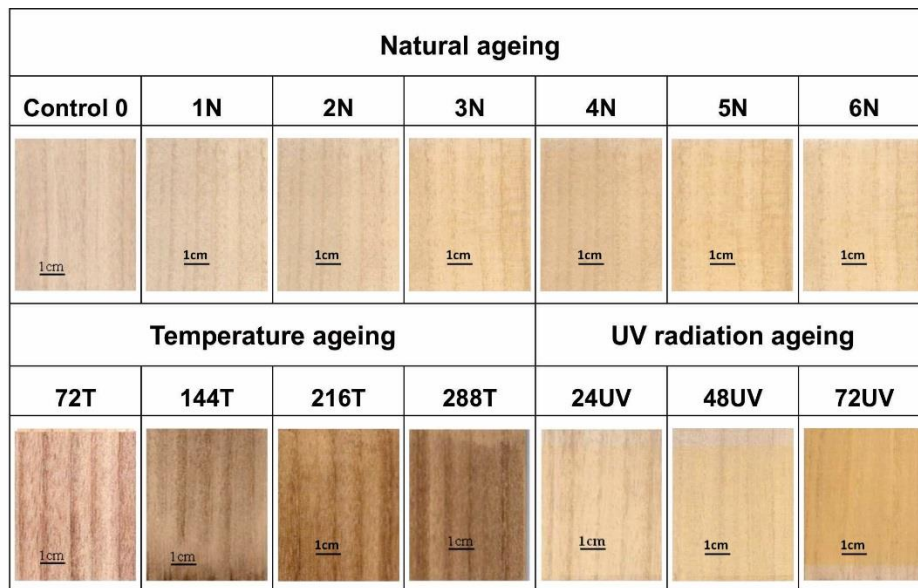

Fig. 1. Color changes in Paulownia wood due to different types of ageing.

It has to be noted that visual assessment of wood color and color change is important for consumers, but it is also prone to subjectivity, as eye sensitivity varies from person to person, being also influenced by experience (Yamauchi *et al.* 2001; Stockman and Brainard 2013; Brainard and Hurlbert 2015). Moreover, early wood and latewood are always perceived distinctively due to their color difference, and their visual impact persists in assessing color changes. Therefore, color measurements on several samples from several areas are preferred to visual perception when discussing color changes due to ageing or other treatments.

Monitoring Ageing by Color Measurements

The measured color data (*L**, *a**, and *b**) for the control and aged samples, including average values on five replicates and standard deviations, are summarized in Table 1 alongside the calculated color differences Δ*E*. Ageing under different conditions caused color changes reflected by all three coordinates, and these color changes evolved over time.

However, the actual ageing conditions determined the color changes. These are compared in the graphs in Fig. 2a-c, which depict the in-time variation of each of the three color coordinates as differences between the initial control values (ΔL^*, Δa^*, and Δb^*), as well as the total calculated color difference ΔE, for the three ageing tests.

Table 1. Colour Measurements for Control and Aged Samples (type of samples results from their specific codes)

CIE Lab Coordinate	Control	Natural Ageing (codes include duration of natural ageing in months)					
	0	**1N**	**2N**	**3N**	**4N**	**5N**	**6N**
L^*	74.83 (1.52)	75.83 (1.39)	75.51 (0.81)	74.51 (1.55)	72.51 (1.84)	73.87 (1.21)	73.58 (0.98)
a^*	5.13 (0.47)	3.61 (0.32)	4.11 (0.50)	4.41 (0.25)	4.75 (0.42)	4.46 (0.26)	4.35 (0.03)
b^*	15.64 (1.56)	16.93 (1.57)	19.88 (0.31)	21.97 (0.76)	23.92 (2.35)	25.58 (0.88)	24.97 (0.35)
ΔE	-	2.23	4.41	6.38	8.61	10.01	9.45
CIE Lab Coordinate	Temperature Ageing (codes include duration of temperature ageing in hours)				UV Radiation Ageing (codes include duration of UV ageing in hours)		
	72T	**144T**	**216T**	**288T**	**24UV**	**48UV**	**72UV**
L^*	60.73 (3.49)	59.51 (4.01)	58.99 (3.78)	57.69 (3.77)	73.69 (1.01)	73.78 (1.32)	72.60 (1.07)
a^*	6.58 (0.57)	7.06 (0.48)	6.90 (0.72)	6.56 (0.62)	4.60 (0.37)	5.17 (0.45)	4.68 (0.36)
b^*	16.96 (1.43)	15.09 (1.05)	17.94 (1.54)	20.99 (1.84)	20.90 (1.62)	22.31 (1.33)	26.09 (1.44)
ΔE	14.24	15.45	16.10	18.01	5.41	6.75	10.69

Note: L^*, a^*, and b^* coordinates are presented by average values and (stand deviations). ΔE, calculated color difference

The plots in Fig. 2a show that color changes under natural ageing occurred mostly in yellowing, with the Δb^* values being positive and clearly greater than the lightness (ΔL^*) or redness (Δa^*) variations. Moreover, the Δb^* curve is almost superimposed on the color difference (ΔE) curve, which cumulates the global color modification following ageing. Maximum Δb^* (9.94) and ΔL^* (10.01) values were obtained after 5 months of ageing, and a slight decrease being registered continuing simulated natural ageing up to 6 months. This natural ageing test is ongoing to investigate further color change evolutions. This natural ageing test is currently still being continued to investigate further evolution. The curve ΔL^*, depicting lightness variation during natural ageing, shows that within the first 3 months a slight trend of lightening occurred, but this trend was reversed continuing ageing up to 6 months, when only a slight darkening was registered ($\Delta L^* = -1.25$). Redness (Δa^*) slightly decreased during natural ageing. The described evolution of color correlates with the role of light as the main actor in natural ageing, pointing towards degradation of lignin as a main photo-chemically induced process.
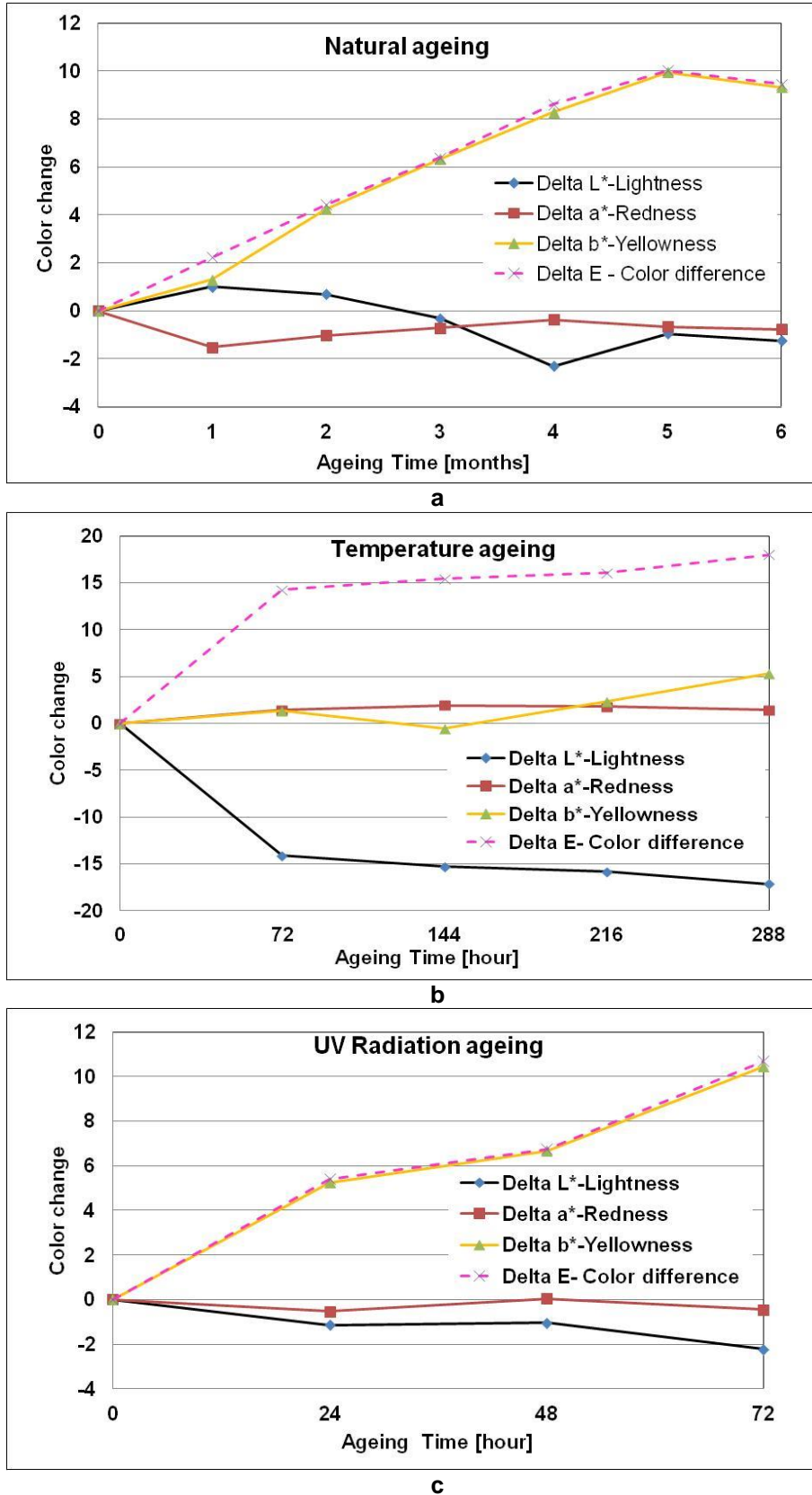
a

b

c

Fig. 2. Color modifications (ΔL^*, Δa^*, Δb^*, and ΔE) of Paulownia wood as a result of (a) natural ageing, (b) temperature ageing, and (c) UV radiation ageing.

In fact, in the simulated natural ageing test in indoor dry conditions (RH of 50 to 55%, at 20 to 25 °C), the natural light filtered by glass was the main ageing factor. This caused photo-degradation of the surface as was perceived as a color change, resulting actually from chemical changes in the main chemical components of the wood and the extractives. Lignin is the wood component most sensitive to UV radiation, which produces degradation of lignin followed by photo-oxidative effects. Modification of lignin results mostly in yellowing due to the formation of quinones, quinone methides, and stilbenes (Fengel and Wegener 1984; Müller *et al.* 2003). However, extractives contribute to both the initial color and light/UV-induced color changes. The initial slight lightening and decrease of redness (up to 2.5 months) might be related to bleaching of extractives, which can also delay lignin degradation (Chang *et al.* 2010a,b).

Some similarities can be observed when comparing the curves in Fig. 2a (natural ageing) with those in Fig. 2c, depicting the measured color variations during artificial accelerated ageing induced by UV radiation (with some contribution of visible light) from an artificial powerful source (see details on the emission range on the methodology section). The most important color change resided in yellowing, as results from the almost superimposed Δb^* and ΔE curves, which after 72 h of UV exposure reached values of 10.45 and 10.69, respectively. These values are only slightly higher than the maximum corresponding values obtained after 5 months of simulated natural ageing, but a clear trend of further increasing is suggested in the case of UV ageing. Only a slight progressive decrease in lightness (up to ΔL^*= -2.23 units after 72 h) was registered, while redness variation could be considered negligible.

In contrast to simulated natural ageing and UV-induced ageing, accelerated artificial ageing under the effect of temperature in the presence of air, without light, resulted mostly in a rapid and important darkening of paulownia wood, reflected in Fig. 2b by the negative ΔL^* values. A decrease in lightness (L^*) of 14.10 units was measured after the first measuring time of 72 h of accelerated ageing at 100 °C. Lightness continued to decrease slowly afterwards, so that after 288 h of temperature ageing at 100 °C, corresponding to approximatively 100 years of natural ageing (Feller 1994), a ΔL^* value of -17.14 units was measured. During temperature ageing, redness slightly increased (Δa^* between 1.43 and 1.93 units), while yellowness had a wavy variation with a final increase of 5.35 units after 288 h of temperature ageing. The total color difference (ΔE) at the end of this test was 18.01, the highest among all the three tests run. This is in good accordance with the visual perception of the color changes.

The chemical changes leading to thermally induced color changes in wood are complex and not yet completely understood, but they are related to degradation products of hemicelluloses, lignin, and certain extractives (Fengel and Wegener 1984; Sandquist 2004; Chen *et al.* 2012, 2014).

Comparative Aspects of Color Changes of Paulownia Wood in Different Ageing Tests

As previously presented, both visual examination and color data indicated that color changes due to natural ageing in the presence of light, under indoor conditions at normal ambient temperature (around 20 to 25 °C), relate to those resulting from an accelerated test under the action of a UV-rich artificial light filtered by a H_2 daylight filter. This relationship between accelerated and natural ageing is better highlighted in the combined graph in Fig. 3, where the in-time evolution of color changes (ΔL^*, Δa^*, Δb^*,

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and ΔE) were mirrored against the vertical axis crossing two opposite horizontal time axes (with different scale units) at the 0 common point. The *x*-axis on the left refers to UV-accelerated ageing, with each unit representing 24 h of UV exposure. The *x*-axis on the right refers to natural ageing under the effect of natural light filtered by glass, with each unit representing 30 days of exposure, cumulating a total of 720 h (day and night). The horizontal lines at different values of color changes allow interpolating the corresponding ageing times for approximately similar color changes. For instance, a color difference of 6 units, resulting after almost 3 months of natural exposure will result in about 36 h of UV exposure. However, in this color difference only the contribution of increased yellowness is similar, but some shade differences and lightness differences are possible. Similarly, a color difference and yellowness increase of 10 units, resulting after 5 months (3600 h) of simulated natural ageing, will result from approximately 68 h of UV-accelerated ageing. This would result in an acceleration index of about 50X for UV exposure compared to exposure to natural sunlight.
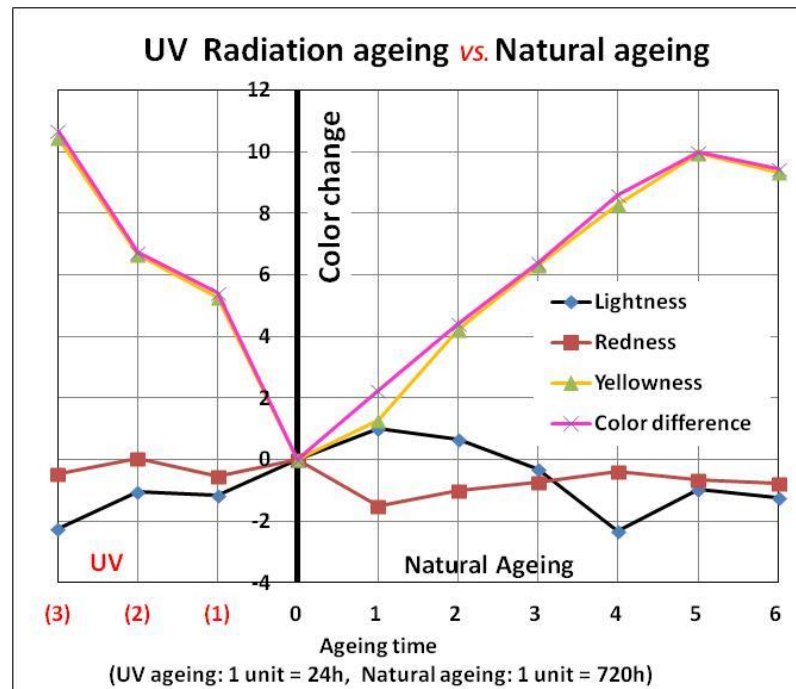

Fig. 3. Comparative in-time evolution of colour changes of Paulownia wood during accelerated UV ageing test and simulated natural ageing test under indoor conditions

A comparison of the in-time progressive global color changes (expressed by the color difference ΔE) occurring during the three tests conducted in this research is presented in Fig. 4. To allow for a better representation of data (spread on a large time scale among those tests), a logarithmic time scale (log ^{t}) was employed.

The accelerated ageing effects of temperature and UV radiation clearly result from this plot. Moreover, the highest color changes brought about by the high temperature of 100 °C are visible. For the temperature-induced ageing, the color difference data fit well ($R^2 = 0.9938$) on a linear trend-line against the logarithm of the ageing time. A linear trend with a lower slope can be associated with the UV ageing data, but at a lower correlation of confidence ($R^2 = 0.8945$). The limited amount of data and

different mechanisms involved in the UV and temperature-induced ageing explain this difference. A clear grouping of data for simulated natural ageing can be observed, as well as their trend of similar evolution (with accelerated UV data) after a longer induction time. More data from the still ongoing natural ageing test are necessary to identify an evolution trend with higher confidence.
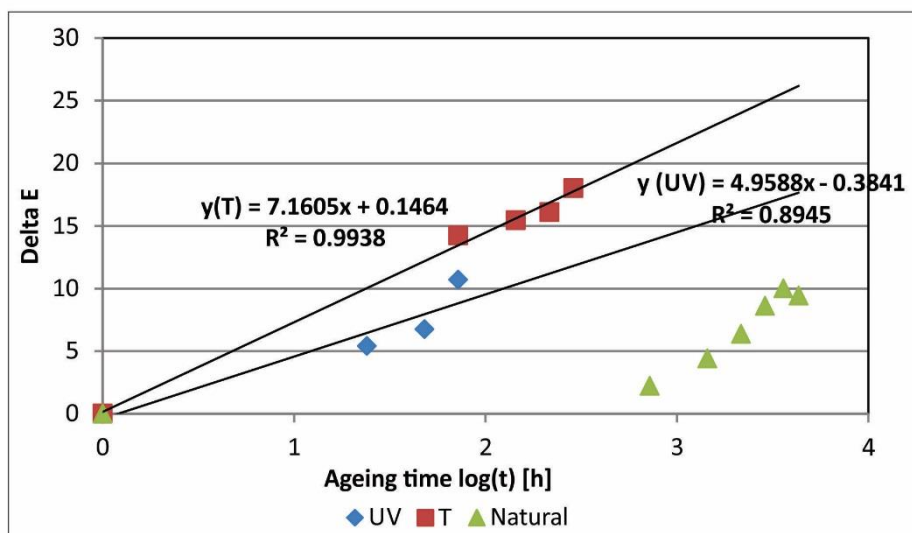

Fig. 4. In-time evolution of global colour change expressed as Δ*E* during the three types of ageing tests (simulated natural indoors, UV ageing, and temperature ageing)

FTIR Investigation of Surface Chemical Changes

Color modifications following the different ageing tests are the result of various and specific chemical processes undergone by both the main chemical components of the wood and the extractives. Therefore, it was considered important to highlight the specific changes in the chemistry of the wood associated with different ageing factors. The limitations of the method with regard of capability of reflecting chemical changes of extractives, due to their general low content (up to 5 to 10% for most common wood species) (Fengel and Wegener 1984; Wagenführ 2000), has to be, however, considered (Tolvaj *et al.* 2013) when interpreting FTIR data in relation to color changes. The measured color changes (Δa^*, Δb^*, ΔL^*, and ΔE) cumulate the specific contribution of all the wood components including extractives, while very likely only the chemical changes of main wood components are reflected by FTIR.

The different ageing procedures within this research induced specific chemical changes reflected by the comparative spectra of the control and aged samples of Paulownia wood (Fig. 5). The comparative data is shown in Table 2.

In the range of 4000 to 2500 cm^{-1}, all spectra showed strong bands of H-bonding and O-H stretching absorption at around 3300 to 3400 cm^{-1} and C-H asymmetric and symmetric stretching of methylene groups at around 2920 to 2850 cm^{-1}, usually appearing as two sharp absorption peaks. However, a slight decrease in the O-H absorption band was observed for all the aged samples, alongside a trend of shifting to lower wavenumbers for those aged under the influence of natural or UV artificial light. It has to be also remarked that for the control and temperature-aged samples the methylene stretching in this region was cumulated to a single absorption band (2875 cm^{-1}), while

after natural ageing the two peaks are well differentiated. A similar trend was observed for the UV-aged samples.

However, the most interesting and specific chemical changes associated with the different types of ageing were visible in the fingerprint region. At first sight, it was obvious that, as expected and also as indicated by the color measurements, the changes following the simulated natural and UV-accelerated ageing were quite similar and differentiate from those caused by temperature ageing.
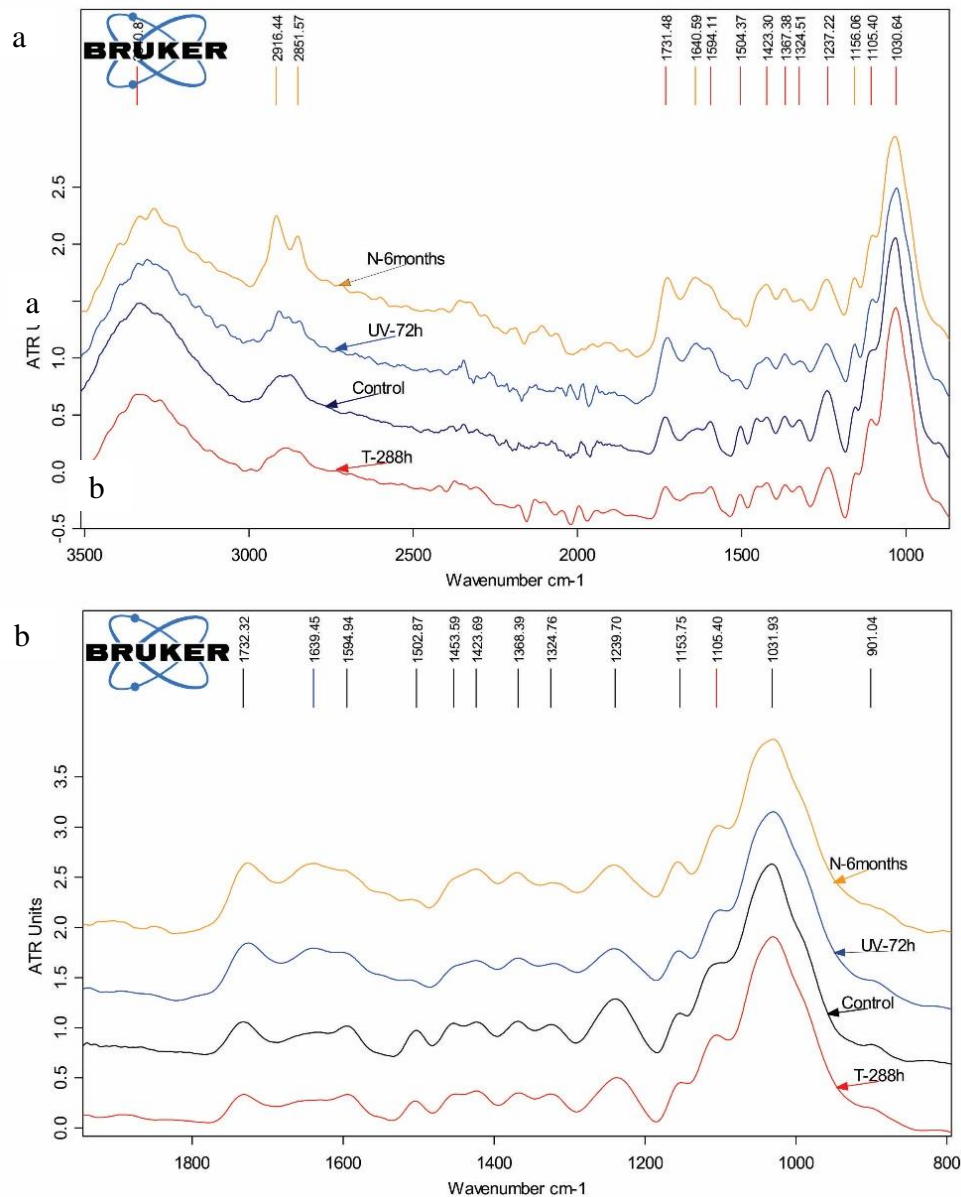

Fig. 5. Comparative spectra of the control and aged samples (6N, 288T, and 72UV) on the range of 3500 to 1000 cm^{-1} (a) and the fingerprint region of 1800 to 800cm^{-1} (b)

Table 2. Variation of Selected FTIR Ratios Following Ageing of Paulownia Wood

FTIR Ratios	Control Samples	Aged Samples		
		6N	72UV	288T
A1506/A1370	1.00	0.18	0.13	1.04
A1730/A1370	1.00	1.55	1.51	0.88
A1506/A3400	1.00	0.22	0.15	1.09
A1730/A3400	1.00	1.59	1.27	1.18
A1640/A1730	1.00	2.28	1.32	1.41

Note: relative values reported to control

Of all the components of wood, lignin is the main UV absorber and the most sensitive to photodegradation. The most important lignin-related absorption bands are: ~ 1596 cm^{-1} (aromatic skeletal vibration of lignin plus C=O stretching)，~1506 cm^{-1} (aromatic skeletal vibration of lignin), 1455 cm^{-1} (aromatic CH deformation and asymmetric bending of CH$_3$ in lignin), and ~1324 cm^{-1} (syringyl ring breathing with CO stretching and C1–O vibration in syringyl derivatives of lignin and C–H vibration in cellulose). Lignin contributes also to other peaks identifiable in the spectra, as follows: ~1422 cm^{-1} (C–H deformation in lignin and carbohydrates; CH$_2$ bending in cellulose), and ~1240 cm^{-1} (C–O stretch in lignin and xylan, syringyl ring). Following natural light-induced and UV ageing all these bands decreased, though the most obvious decrease (almost disappearing) was clearly visible for the skeletal vibration at 1506 cm^{-1}, which is mostly specific and frequently employed in following lignin degradation (Pandey and Vuorinen 2008; Tolvaj *et al.* 2013; Timar *et al.* 2016). The band at 1596 cm^{-1} also decreased becoming less evident, so that there was a trend of being cumulated with the slightly increasing absorption band at 1643 cm^{-1} (conjugated C=O and C=C, and aromatic ketones). Increase of absorption bands for conjugated (1643 cm^{-1}) and un-conjugated (1730 cm^{-1}) carbonyl groups is related to the formation of different carbonyl-containing chromophores by oxidative processes. A slight increase and better differentiation of the absorption band at ~1155 cm^{-1}, assigned to C–O–C asymmetric bridge stretching vibration in cellulose and hemicelluloses, was observed in the FTIR spectra of UV and naturally aged samples and is possibly explained by surface delignification. The absorption band at about 1370 cm^{-1}, assigned to C-H deformation in cellulose and hemicelluloses, is mostly representative of these compounds and remains practically unchanged following light-induced ageing, and is thus often employed as an internal standard (Pandey 2005). Therefore, variation of the ratios A1506/A1370 (lignin/hollocellulose) and A1730/A1370 (carbonyl/hollocellulose) are most often employed to evaluate chemical changes associated with photodegradation (Pandey and Vuorinen 2008; Chang *et al.* 2010a).

Compared to UV, temperature-induced ageing had only slight chemical changes detectable by FTIR in the structure of the wood components. A slight decrease in the absorption bands at 1730 cm^{-1} (unconjugated carbonyl found mostly as acetyl groups in hemicelluloses) and 1370 cm^{-1} (C-H in cellulose and hemicelluloses) is visible after 288 h of temperature ageing. These changes can be associated with the thermal degradation of hemicelluloses, which are more sensitive to temperature. In fact, temperature-induced color changes are mostly related to chromophores resulting from hydrolytic and oxidative processes of hemicelluloses, though lignin and extractives may contribute to some extent (Chen *et al.* 2012, 2014).

Table 2 shows the ratios of the integrated areas of some relevant absorption bands, as relative values are reported to the corresponding values of the control samples. These values better highlight and allow comparison of chemical changes following ageing under different conditions. They show at a glance strong similarities of chemical changes occurring under the effect of natural light and UV-rich artificial light, both filtered by glass, as well as their clear differentiation from those induced by temperature. These observations are explained by the different mechanisms involved in these ageing processes, as briefly presented in this work.

UV light from natural or artificial sources caused primarily lignin degradation, reflected by the decrease in relative ratios of lignin/carbohydrates (A1506/A1370) and lignin/hydroxyl (A1506/A3400) from the control value of 1 to ratios of 0.18 to 0.13 and 0.22 to 0.15, respectively. These decreases in ratios could roughly suggest a degradation of lignin in proportion of around 80% on the surface of the light-exposed samples. These relative ratios were slightly lower for UV-accelerated artificial ageing (72UV) than those of the samples exposed to natural light for 6 months (6N), which clearly highlights the accelerated lignin degradation in the test employing a powerful UV lamp. This is in good agreement with the color change measured after these intervals: $\Delta E_{72UV} = 10.69$ slightly higher than $\Delta E_{6N} = 9.45$.

Oxidative processes following lignin degradation results in the formation of carbonyl-containing chromophores, which is reflected by the increase in the relative ratios A1730/A1370 and A1730/A3400 from the control value of 1.00 to ratios of 1.55 and 1.59, respectively, for simulated light-induced natural ageing (6N) and to 1.51 and 1.27, respectively, for accelerated UV ageing. This suggests that oxidative processes leading to the formation of carbonyl chromophores are slightly more advanced under natural lighting conditions. Also, the increase in the relative ratio A1643/A1730 suggests that more conjugated/aromatic carbonyl groups were formed during light-induced ageing, meaning an increased contribution of quinone-type chromophores. Again, this process seemed more intensive under natural light exposure.

Temperature-induced ageing showed different chemical changes, and generally the values of the different relative ratios (closer to 1.00) suggest that the chemical changes were less intense, or practically slower than those induced by light, taking into account the 288 h of temperature ageing compared to 72 h of UV ageing. Moreover, this testing time should indicate changes happening during a much longer period of time of about 100 years under a normal temperature, without the contribution of light (changes that are not only on the surface but also in the bulk material). Degradation of hemicelluloses and the occurrence of thermo-oxidative processes are reflected by an apparent slight increase in lignin content (relative A1506/A1370 and A1506/A3400 increasing from 1.00 to 1.04 and 1.09, respectively) and the formation of a chromophore structure containing predominantly conjugated carbonyl groups (A1643/A1730 increasing from 1.00 to 1.41). The fact that there was a slight decrease in the relative ratio A1730/A1370 (from 1.00 to 0.88), though hemicelluloses were degraded (A1370 decreased), might suggest that less unconjugated carbonyl groups were formed by oxidation following the initial presumable deacetylation of hemicelluloses. Thermo-oxidative processes mostly conduct to quinone-type chromophores. The formation of extensive conjugated structures, such as unsaturated ketones and quinones, due to the cleavage of lignin units has been previously reported and proven by FTIR analysis (Chen *et al.* 2012).

CONCLUSIONS

1. Three ageing tests, employing the two main wood ageing factors (temperature and light/UV radiation), were designed and conducted on Paulownia wood. As a result of ageing, all samples suffered at least a slight color change.

2. Natural ageing caused minor color changes as compared with temperature-induced ageing. During simulated natural ageing, yellowness increased significantly, while lightness (L^*) and redness (Δa^*) of the samples slightly decreased. Maximum ΔL^* (10.01) and Δb^* (9.94) values were obtained after 5 months of ageing. Continuing the test, a trend of lightening and decrease of yellowing was observed.

3. Temperature-induced ageing resulted mostly in a rapid and important darkening of the Paulownia wood. After 288 h of temperature ageing at 100 °C, corresponding to approximatively 100 years of natural ageing, a ΔL^* value of -17.14 units was measured. During temperature ageing, redness and yellowness slightly increased.

4. During UV-induced accelerated ageing, the most important color change resided in yellowing, similarly to natural ageing. After 72 h of UV radiation ageing, yellowness (Δb^*) increased by 10.45 units and this trend of increasing is still being maintained. Data from longer UV-accelerated tests would be useful and will be considered in future research.

5. Comparative in-time evolution of color changes of Paulownia wood during accelerated UV ageing testing and simulated natural ageing testing under indoor conditions suggests an acceleration index of about 50X.

6. FTIR spectra highlighted the specific surface chemistry changes occurring during the ageing tests. UV light from natural or artificial sources caused primarily lignin degradation, which was reflected by a decrease in the relative ratios of lignin/carbohydrates, followed by oxidative processes leading to the formation of carbonyl containing chromophores. Accelerated tests under UV radiation resided in a slightly more advanced lignin degradation, while oxidative processes, especially those leading to unconjugated carbonyls, were more advanced for simulated ageing under the action of natural light. This conclusion is valid for the exposure times reported in this research, but this should be confirmed by continuing the experiments for longer periods of time.

7. Temperature-induced ageing showed different and slower chemical changes. Thermo-oxidative processes following hemicellulose degradation conducted mostly to chromophore structures containing conjugated carbonyl groups. Though the relative FTIR ratios may indicate less advanced chemical changes, the color differences measured were the most profound. The contribution of extractives should be considered.

Overall, this research highlighted that paulownia wood (*P. elongata*) is quite sensitive to ageing under the action of light and temperature, which cause notable color and surface chemistry changes. Most certainly other surface properties are affected as result of these changes, which finally may have an influence on the in-time behavior of paulownia wood products. Knowledge on ageing behavior of paulownia wood will become increasingly important considering that this wood resource, with a long history in

China, has become a universal, sustainable resource of wood material from fast growing crops. We do hope that the novel data on the ageing behavior of paulownia wood resulted from this research will be useful for conservators, scientists, and technologists interested in this material.

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