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ORIGINAL

The impact of natural and artificial weathering on the visual, colour and structural changes of seven tropical woods

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Abstract This study investigates the effects of wood weathering on changes in its macroscopic and colour characteristics in connection with changes in its molecular and anatomical structure. Seven hardwoods suitable for outdoor architecture—bangkirai, cumaru, cumaru rosa, ipé, jatobá, kusia, and massaranduba—were exposed to the exterior out of ground contact for 1–36 months according to EN 927-3, and for 1–12 weeks in Xenotest with water spraying according to partly modified EN 927-6. With prolonged weathering, the following changes occurred in the top surfaces of all tropical woods: (1) visual—creation of longitudinal macrocracks, (2) spectrophotometry and CIE-$L^*a^*b^*$—darkening in exterior exposure mainly due to pollutants, except for ipé, and vice versa lightening in Xenotest, as well as greening and blueing in both modes of exposure, (3) FTIR—faster decrease of guaiacyl than syringyl lignin, absolute decrease of conjugated and unconjugated carbonyl groups in the newly formed lignin-polysaccharide-extractive substrate in the photo-oxidized and washed-out cell walls, and decrease of cellulose crystallinity, (4) SEM—damaging of cell-walls by micro-cracks, and their degradation by thinning. Connections between changes of the individual characteristics of weathered woods, for example, between the colour (ΔE^*, etc.) and the molecular structure (carbonyls, etc.), were also determined.

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1 Introduction

Resistance of wooden products against weathering is predetermined by (1) their structure, i.e. molecular, anatomical, morphological and geometric, and (2) their exposure conditions, i.e. the dosages of ultraviolet and other types of radiation, extreme temperatures, precipitations, exposure to ground contact or without ground contact, values of air relative humidity, prevailing winds and storms, emissions, presence of microorganisms, fungi, insects, etc. (Feist and Hon 1984; Williams 2005; Reinprecht 2016).

The number of tropical woods—those which have a great resistance to biological agents and mechanical wears, and also good dimensional stability and nice aesthetics—belongs to species commonly used for exterior constructions, decking, claddings, garden furniture or special plywood (Reinprecht et al. 2012). Tropical woods usually well resist decaying fungi, insects and dimensional changes thanks to extractives having (1) biocide effect, for example coumarins, flavonoids and tannins, and (2) hydrophobic effect, for example fats, oils and waxes. However, these extractives have a partly lesser positive impact on retardation of the weathering processes in wood surfaces started by photodegradation of lignin. Photodegradation processes in wood begin by adsorption of photons from sunlight with chromophores of lignin macromolecules—conjugated carbonyls, etc. Then, these processes continue with radical reactions of activated chromophores with hydroxyl, methoxyl or other non-activated surrounding functional groups of lignin and other components of wood (Feist 1990; Pandey and Vuorinen 2008; Liu et al. 2015).

During the photodegradation of wood, the amount and distribution of syringyl and guaiacyl lignin units in its cell walls play a crucial role (Sudiyani 1999; Sudiyani et al. 2003; Evans 2008). In this view, a purely abiotic weathering

of various wood species (i.e. without action of bacteria, fungi, insects or other biotic agents—taking place during artificial weathering in Xenotest, etc., but only theoretically in real exterior) is influenced mainly by the type and amount of lignin. Effects of the type and amount of extractives or hemicelluloses on wood photodegradation are also important, but usually less relevant (Pastore et al. 2004; Yamauchi et al. 2004; Pandey 2005; Barreto and Pastore 2009). In spite of these knowledge related to photodegradation of wood components, the total weathering of wood surfaces in exteriors (determined as erosion, e.g. in µm per year)—due to synergy of UV and VIS light, oxygen, rain, wind, sand particles, emissions and other abiotic effects causing mechanical tearing of cellulose fibrils—depends first of all on the exposure conditions and the wood density (Feist 1990; Pandey and Vuorinen 2008).

The principles of wood weathering in the exterior were described by Feist (1990). Weathering starts with absorption of UV light in approx. 75 µm-thick layer of wood, together with adsorption of visible light in approx. 200 µm-thick layer (Kataoka et al. 2007; Živković et al. 2014). Weathering of wood continues with primary and then secondary photolytic, photo-oxidation, oxidation and hydrolytic reactions taking place in lignin and partly also in hemicelluloses, extractives and amorphous cellulose in depth of 400–700 µm (Teaca et al. 2013). These chemical reactions in the molecular structural level of wood are usually connected with extinction of existing and creation of new carbonyl and carboxyl groups (Sundqvist 2002; Ayadi et al. 2003; Pandey 2005). Thanks to newly created carbonyls the weathered wood obtains yellow shades or other typical colour changes. The final step of the cyclic outdoor wood weathering is a physical–mechanical destruction of its cellulose fibrils due to actions of sand, rain, etc., and also an adsorption of pollutants and greying of its surfaces. According to newer research, outdoor weathering of wood is also connected with changes in the crystallinity index of cellulose (Lionetto et al. 2012), and in colour of cellulose at higher temperatures (Matsuo et al. 2012). Tolvaj et al. (2011) reported that such changes in the weathered macromolecules of cellulose occur probably as a result of simultaneous thermally activated processes in their arrangement.

Various damages in the surfaces of weathered woods, i.e. erosion, creation of micro-cracks and macro-cracks, greying, etc., are usually the most significant under horizontal exposure (Evans 1989). Creation of cracks can also be attributed to the specific molecular and anatomical structural levels of individual wood species, and to the parallel or corrugated orientation of cell elements (fibers, etc.) in wood products. Colour changes in weathered tropical woods were observed by many researchers studying the following effects: -wood species, -technology of surface treatment, -environmental conditions (Williams et al. 2001; Kishino and Nakano 2004; Pastore et al. 2004; Yamauchi et al. 2004; Mattos et al. 2014; Valverde and Moya 2014; Pánek and Reinprecht 2016). Generally, during outdoor weathering of woods changes in their molecular structure (e.g. in the chemical composition and spatial organization of lignin) and anatomical structure (e.g. in the amount of lignin in individual layers of cell walls) arise, both accompanied by changes in the geometric structural level (e.g. in the surface erosion, creation of micro-cracks and macro-cracks, darkening, and/or loss of a nice aesthetics) (Reinprecht 1992; Williams et al. 2001; Williams 2005).

Nowadays, in practice and theory, it is important to determine changes in the surface quality, colour and other characteristics of various tropical woods during weathering in known climatic conditions. Along with that it should be interesting to connect the changes in wood-surface properties with changes in its molecular and anatomical structure. In this context, the simulation of wood outdoor weathering with its accelerated ageing is also important, for example in Xenotests. More researchers, for example Creemers et al. (2002), Schnabel et al. (2009), Rüther and Jelle (2013), Mattos et al. (2014), studied the effects of different climatic conditions on weathering rate of various wood species. However, this problem has not yet been investigated in detail, especially for tropical woods exposed to urban or industrial environment of Central Europe. Therefore, the aim of this study was to determine the basic macroscopic and colour changes of seven tropical woods during outdoor and artificial weathering, together with analysing selected changes in their molecular and anatomical structural levels.

2 Materials and methods

2.1 Tropical woods

Test samples (free of sapwood, biological damages, macro-cracks, knots or other growth inhomogeneity) were prepared from naturally dried boards of seven tropical woods: (1) kusia (*Nauclea diderichii* Merill)—795 kg/m^3, (2) bangkirai (*Shorea obtusa* Wall.; Sh. spp.)—987 kg/m^3, (3) massaranduba (*Manilkara bidentata* A. Chev.; M. spp.)—1012 kg/m^3, (4) jatobá (*Hymenaea courbaril* L.)—907 kg/m^3, (5) ipé *(Tebebuia serratifolia* Nichols.; T. spp.)—1042 kg/m^3, (6) cumaru [*Dipteryx odorata* (Aubl.) Wild.]—996 kg/m^3, and (7) cumaru rosa [*Dipteryx magnifica* (Ducke) Ducke]—1014 kg/m^3.

The dimensions of the wood samples for natural weathering in exterior were $375 \times 78 \times 20$ mm^3 (longitudinal × tangential/radial × tangential/radial), and for artificial weathering in Xenotest $38 \times 38 \times 8$ mm^3 (longitudinal × tangential/radial × tangential/radial). Prior to weathering, samples were conditioned to a constant

moisture content of 12 ± 1%. Their top surfaces were sanded along the grain, firstly with 60-grit and then with 120-grit sandpapers. All transverse sections of the samples were treated with silicone as protection against water during weathering.

2.2 Natural and artificial weathering of wood surfaces

The natural weathering of samples was performed from 1st August 2010 to 31st July 2013 by outside exposure at the Technical University in Zvolen, at a height above sea level of approx. 300 m, under a slope of 45° in south orientation according to the standard EN 927-3 (2006). The exposure place is located in a hollow with high occurrence of foggy days, smog and high temperature differences between summer (to about 35 °C) and winter (to about −25 °C), 3 km from the weather station for measuring the climate conditions (Table 1). The visual and colour analyses of samples were performed before and after 1, 3, 6, 12, 24, and 36 months of natural weathering, while the chemical and anatomical analyses only before and after 36 months of weathering.

Artificial weathering of wood samples was performed during 12 weeks in the Q-SUN Xe-1-S Xenotest (Q-Lab Corporation, USA), equipped with 1800 W xenon lamp emitting UV and VIS light (Daylight—Q filter was used), and spray section of redistilled water. Each 1-week-long (168 h) exposure cycle consisted of the 1st step, i.e. exposure of 24 h in the dark at 45 ± 3 °C, and the 2nd step, i.e. 48 sub-cycles each lasting 3 h—firstly 2.5 h exposure to xenon lamp and then 0.5 h exposure to water spraying at temperature of 20 ± 1 °C. Unlike the standard EN 927-6 (2006), at the 2nd step of weathering a lower UV irradiance 0.55 Wm^{-2} at 340 nm (instead of 0.89 Wm^{-2} at 340 nm), and a lower temperature measured on black panel 50 ± 3 °C (instead of 60 ± 3 °C) were used. The visual and colour analyses of samples were performed before and after each week of artificial weathering lasting from 1 to 12 weeks, while the chemical and anatomical analyses only before and after 12 weeks of exposure in Xenotest.

2.3 Visual analyses

Visual analyses of the weathered top surfaces of tropical woods were aimed at the determination of visible longitudinal macro-cracks, using magnifier with 10× magnification. Rating of cracks was as follows: [0] no cracks, [1] small cracks with width of 0.1–0.3 mm, [2] medium cracks with width of 0.3–0.6 mm, [3] large cracks with width of >0.6 mm.

2.4 Colour spectrophotometric and CIE-L*a*b* analyses

Colour analyses of the top surfaces of native and weathered tropical woods were performed in their conditioned state (12 ± 1% EMC of surfaces, i.e. after 72 h exposure of samples in conditioning room at 20 °C and 65 ± 3% RH of air) using the spectrophotometer Minolta CM 2600d and the Color Reader CR-10.

2.4.1 Spectrophotometric analyses

The spectrophotometer Minolta CM 2600d (Konica Minolta, Japan), with Xenon discharge tube D65 as a source of light and a standard measuring aperture of 8 mm diameter, and with the aid of the SpectraMagic software, is an illuminating system which was set to measuring mode including scattering components (SCI). Measurements of wavelengths, ranging from 360 to 740 nm, were performed with resolution of 10 nm. The reflectance (R) represents an ability of the wood surface to reflect an incident light, i.e. it is a ratio between the amount of reflected light (radiation in percentage) from the surface of wood and the amount of reflected light from the surface of white etalon TiO_2 having 100% radiation (Mamoňová and Reinprecht 2014). In the following, courses of the differential reflectance spectra (DRS, in percentage) were computed by subtracting the reflectance of the weathered tropical wood (R_w) from the reflectance of the non-weathered/reference one (R_r). Within the reflectance, the colour changes of tropical woods caused by weathering were analysed as well as in the whole range of visible spectra.

Table 1 Weather conditions during natural outdoor exposure of tropical woods for 0–36 months (selected from measurements by Leštianska et al. 2014)

Weather conditions	Weathering time (months)					
	0–1	1–3	3–6	6–12	12–24	24–36
Mean temperature (°C)	18.5	8.9	−2.6	14.7	9.4	9.4
Mean RH (%)	86	91	92	77	80	86
Sum of precipitation (mm)	87.6	256.7	92.3	373.2	538.9	860.0
Sum of global radiation (kWh/m^2)	138.2	177.7	86.6	846.4	1176.8	1089.1
Sum of snow cover days (day)	–	–	23	14	68	57

2.4.2 CIE-L*a*b* analyses

The Color Reader CR-10 (Konica Minolta, Japan) with a CIE 10° standard observer, CIE standard illuminate D65, sensor head with a diameter of 8 mm, and a detector with 6 silicon photocells, was set to measuring the L^*, a^*, and b^* colour coordinates of samples, where: L^* is lightness from 0 (black) to 100 (white), a^* is chromaticity coordinate + (red) or − (green), and b^* is chromaticity coordinate + (yellow) or − (blue). From the relative colour changes ΔL^*, Δa^*, and Δb^* (i.e. changes between the weathered and initial state of sample) the total colour differences ΔE^* were calculated by Eq. 1 (CIE 1986):

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

2.5 FTIR analyses

Analyses of the carbonyl and other function groups of the lignin-polysaccharide matrix and the cellulose crystallinity on the top surfaces of tropical woods were carried out with the ATR-FTIR spectrometer i10 (Thermo Nicolet) having the ZnSe crystal. The measured spectra were recorded in the range 3800–800 cm^{-1} at a resolution of 2 cm^{-1}, and standardised using the baseline method. Applying the OMNIC software, the average spectrum from six measurements was obtained for the top surface of each wood species before and after weathering.

2.6 SEM analyses

The anatomical structure of tropical woods was analysed on the top surfaces of specimens $10 \times 10 \times 8$ mm^3 prepared by sawing from samples not subjected to weathering (reference) and samples subjected to all weathering time. Specimens covered with gold were analysed by the scanning electron microscope Tescan VEGA TS 5130.

2.7 Evaluation of measurements

Two replicates ($375 \times 78 \times 20$ mm^3) from natural weathering in exterior and two replicates ($38 \times 38 \times 8$ mm^3) from artificial weathering in Xenotest were tested for each wood species. The results present (a) visual analyses as one total measurement per two replicates (n = 2) before and during individual times of weathering, (b) colour analyses as three measurements per two replicates in the same places (n = 6) before and during individual times of weathering, (c) FTIR analyses as mean value from three measurements per two replicates in the same places (n = 6) before and after weathering, and (d) SEM analyses as more measurements per specimens prepared from replicates (n = from 4 to 8) before and after weathering.

3 Results and discussion

3.1 Visible cracks in surfaces of weathered woods

Due to weathering, the largest macro-cracks occurred in the top surfaces of kusia wood, i.e. the species having the lowest density of all tropical woods tested (see Sect. 2.1). Larger cracks were also observed in surfaces of massaranduba, cumaru and cumaru rosa woods. On the other hand, surfaces of the most dense ipé wood, and also jatobá wood with a medium density, well withstood creation of cracks even after 36 months of outdoor exposure or after 12 weeks of artificial exposure in Xenotest (Table 2). In summary, creation of larger visible cracks in the top surfaces of tested

Table 2 Visible macro-cracks in the top surfaces of tropical woods created during weathering

Weathering	Visible cracks in the top surfaces of tropical woods (0–3)						
	Kusia	Bangkirai	Massaranduba	Jatobá	Ipé	Cumaru	Cumaru rosa
Natural (months)							
1	1.5	0.5	0	0	0	1	1
3	2	1	0	0	0.5	1	1
6	2	1	1	0	0.5	1.5	1.5
12	2.5	1	1.5	0.5	1	2	2
24	3	1.5	2	1	1	2.5	2
36	3	1.5	2.5	1	1	2.5	2.5
Artificial (weeks)							
3	0	0	0	0	0	0	0
6	1	0	1	0	0	0.5	1
9	1.5	1	1.5	0	0	1	1
12	1.5	1	1.5	0	0	1	1

Average values from two replicates

tropical woods was influenced by their density and specific anatomical structure (see Sect. 3.4).

The potential for creation of larger cracks increased with prolongation of weathering (Table 2). Cracks were created in a larger number and with greater dimensions during natural outdoor weathering than during artificial weathering in Xenotest, which could be attributed to major temperature differences during a longer period of natural weathering (see Sect. 2.2, Table 1).

3.2 Colour changes in surfaces of weathered woods

3.2.1 Knowledge obtained from spectrophotometric analyses

The differential reflectance spectra (DRS) of tropical woods during 36 months of natural weathering in exterior completely differed compared to the 12 weeks of artificial weathering in Xenotest (Figs. 1, 2).

The DRS of the naturally weathered tropical woods (Fig. 1) showed that their top surfaces at the relatively longer wavelengths (from 420–650 nm to 740 nm) were always characterized by a light absorbability, where the maximum negative reflectance of −40% was achieved by kusia wood at 740 nm. On the other hand, at the relatively shorter wavelengths (from 360 nm to 420–650 nm), the weathered surfaces of all tropical woods had a positive reflectance, with the maximum positive reflectance of +12% by jatobá and ipé woods, or the minimum positive reflectance of +4% by kusia wood. Zero reflectance (a transition between positive and negative reflectance, i.e. when the reflectance of weathered wood was equal to the reflectance of reference wood) was achieved by the individual tropical species at various wavelengths: bangkirai and cumaru at 430 nm, kusia at 490 nm, cumaru rosa at 480 nm, jatobá at 590 nm, masaranduba at 620 nm, and ipé at 650 nm (Fig. 1).

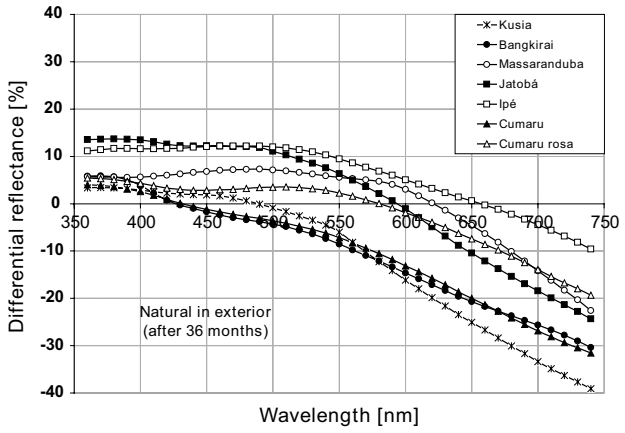

Fig. 1 Differential reflectance of tropical woods after 36 months of weathering in exterior. *Note* average values from six measurements

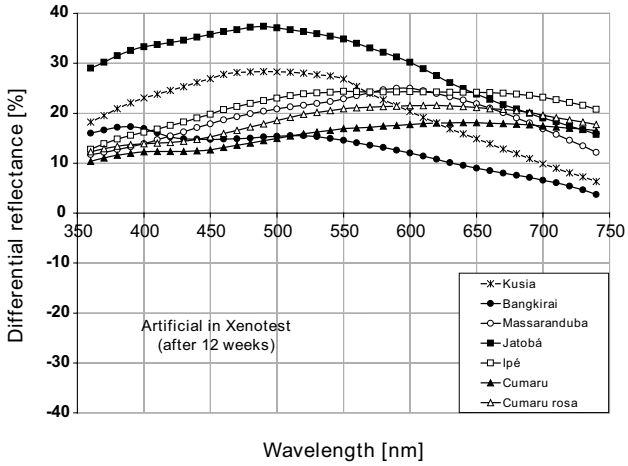

Fig. 2 Differential reflectance of tropical woods after 12 weeks of weathering in Xenotest. *Note* average values from six measurements

The DRS of the artificially weathered tropical woods (Fig. 2) were positive in the entire range of visible light, when the reflectance ranged from the minimal positive values of +4 to +16% for bangkirai (at 360–740 nm) to the maximal positive values of +30 to +38% for jatobá (at 360–490–600 nm). The courses of the positive DRS were partly different for the group of jatobá, kusia and bangkirai woods (relatively higher positive reflectance at shorter wavelengths) compared to the group of ipé, cumaru and cumaru rosa woods (relatively higher positive reflectance at longer wavelengths) (Fig. 2).

As could be expected, the DRS of the weathered tropical woods were in good accordance with the colour changes determined by the CIE-$L^*a^*b^*$ system (Fig. 3, Sect. 3.2.2), as the reflectance curves are the basis of defining chromatic coordinates and calculating the colour parameters L, a^* and b.

For example, during artificial weathering in Xenotest (1) bangkirai wood had the minimal positive DRS given in Fig. 2 and also the minimal values of $+\Delta L^*$ and ΔE^* given in Fig. 3, (2) jatobá wood had the maximal positive DRS and also the maximal values of $+\Delta L^*$ (lightening) and ΔE^*. Similar tendencies were obtained for natural weathering in exterior, when (1) kusia wood had the maximal negative DRS given in Fig. 1 and also the maximal negative values of $-\Delta L^*$ (darkening) and maximal values of ΔE^* given in Fig. 3, (2) ipé wood had the minimal negative DRS, respectively in the whole light spectra; its DRS was the most positive of all tested species—see Fig. 1, and concurrently only for ipé, $+\Delta L^*$ (lightening) together with the smallest ΔE^* were determined—see Fig. 3.

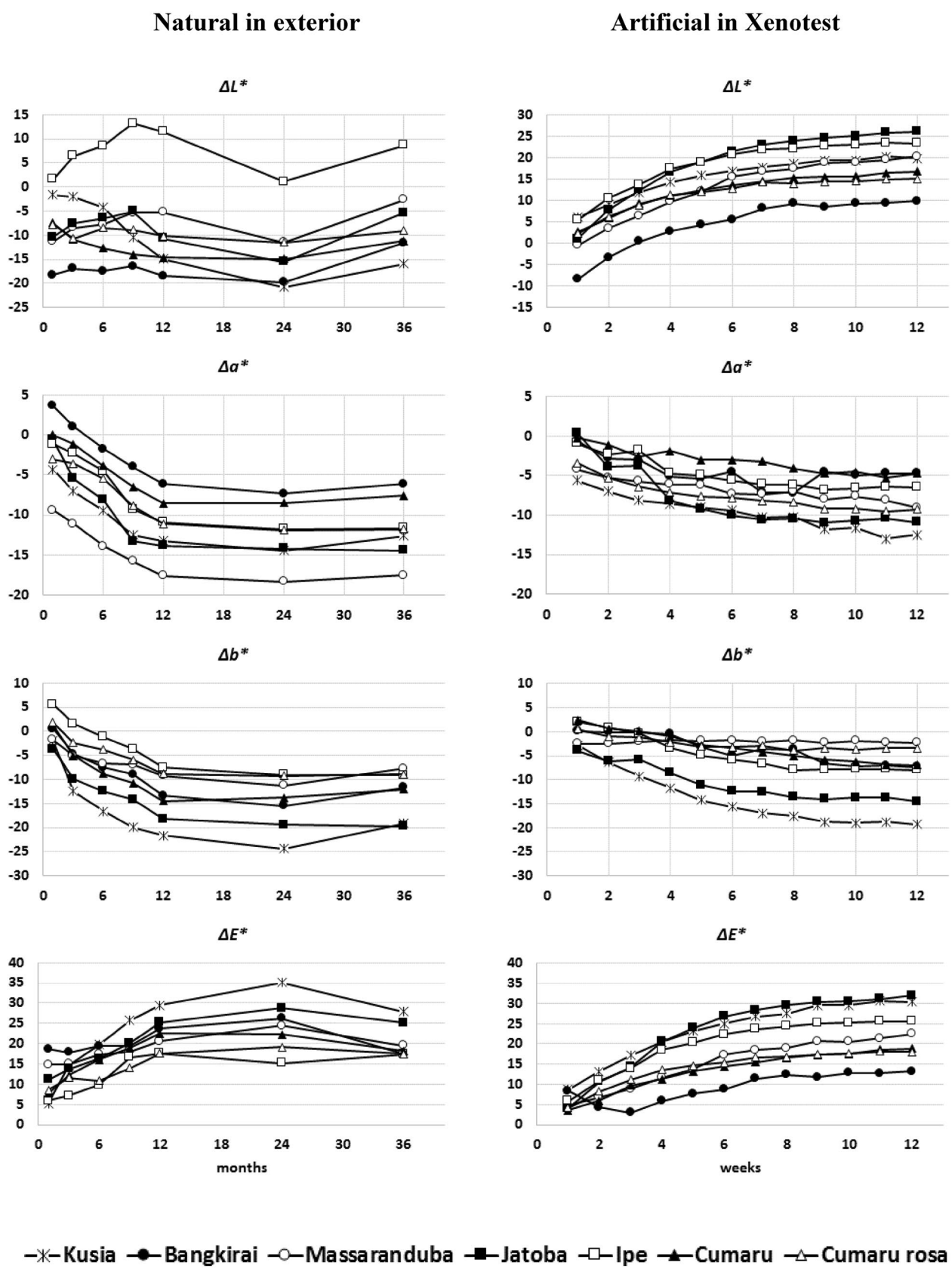

Fig. 3 Colour changes of tropical woods evaluated in the CIE-*L*a*b** colour system during weathering in exterior from 1 to 36 months and in Xenotest from 1 to 12 weeks. *Note* average values from six measurements

*3.2.2 Knowledge obtained from CIE-L*a*b* analyses*

From the seven tropical woods, the least colour stable—in both modes of weathering—were kusia and jatobá (Fig. 3—see the highest ΔE^*). These wood species in a non-weathered native state were characterised with the highest positive chromaticity coordinates (Fig. 4: $L^* = 57.9$ for kusia, and 57.6 for jatobá; $a^* = 15.6$ and 15.2; $b^* = 28.1$ and 22.5), and they also had the smallest density from all tested tropical woods (see Sect. 2.1). The worst colour stability of kusia and jatobá woods was caused mainly due to their strong greying, connected either with greening (Fig. 3—see the most negative $-\Delta a^*$, except for a higher negative value for massaranduba exposed to the exterior), and also with bluing (Fig. 3—see the most negative $-\Delta b^*$). These results confirmed that the type and content of extractives in tropical woods play an important role in their colour changes during weathering. For example, lighter woods containing a lower amount of photo-protective extractives (having higher L*) usually undergo more significant colour changes but also woods containing more easily photo-degradable and water-soluble extractives (having higher a^* and b^*). The density of wood and its surface roughness play important roles in the adsorption of impurities from the environment—for example higher colour changes can occur in woods lighter in colour after their contact with dark pollutants. According to Costa et al. (2011), jatobá wood belongs to a less colour stable species in exterior conditions. Baar and Gryc (2012) observed smaller colour stability of jatobá wood than of massaranduba wood exposed to Xenotest for 144 h without water spraying. In accordance with the present results, more expressive colour changes in outdoor weathering were described by Salas et al. (2014) for lighter woods, or Williams et al. (2001) and Kataoka et al. (2005) for less dense woods.

On the other hand, from the tested tropical woods, the most resistant to darkening in exterior, i.e. in the presence of dust particles and other impurities, were ipé and massaranduba (Fig. 3—see ΔL^*, positive for ipé or minimally negative for massaranduba), i.e. wood species with the darkest shade in a native state ($L^* = 42.1$ and 49.0), that synchronously had the highest density (see Sect. 2.1).

Bangkirai and cumaru woods, i.e. species in a native state having the lowest positive $+a^*$ chromaticity coordinate ($a^* = 8.5$ and 10.3), lost the red shade only minimally (Fig. 3—see the least negative $-\Delta a^*$ in both modes of weathering). Similarly, massaranduba and ipé woods, i.e. species in a native state having the lowest positive $+b^*$ chromaticity coordinate ($b^* = 12.2$ and 13.9), lost the yellow shade partly lesser than other tropical species (Fig. 3—see Δb^* values).

Colour changes of cumaru and cumaru rosa wood had a similar tendency in both modes of weathering, characterized by these two specifics: (1) loss of the red shade was partly stronger for cumaru rosa wood with a greater $-\Delta a^*$, (2) and loss of the yellow shade was partly stronger for cumaru wood with a greater $-\Delta b^*$(Fig. 3).

In exterior, tropical woods significantly greyed already after 3 and 6 months (Fig. 4).

Generally, the weathering processes of tropical woods were connected with their darkening in exterior ($-\Delta L^*$) and lightening in Xenotest ($+\Delta L^*$). They were parallel connected with greying as a result of greening ($-\Delta a^*$) and blueing ($-\Delta b^*$) in both modes of exposure. Similar results were achieved by Salas et al. (2014).

3.3 Changes in the lignin-polysaccharide matrix of weathered woods

FTIR (Fourier transform infrared) spectra showed that due to the natural and artificial weathering in the top surfaces of tropical woods significant changes in the lignin and cellulose occurred (Tables 3, 4; Fig. 5).

During weathering of wood surfaces, the intensity of lignin associated absorption bands at ~1510 cm^{-1} (aromatic skeletal vibration) and ~1600 cm^{-1} (aromatic skeletal vibration plus C = O stretch) decreased rapidly by about 78–99%. The peak at 1274 cm^{-1} (specific for guaiacyl lignin) also decreased very strongly, by about 48–79% for natural weathering and by about 40–70% for artificial weathering—the most for bangkirai and ipé and the least for massaranduba and jatobá. The peak at 1334 cm^{-1} (specific for syringyl lignin, and according to some researches also for cellulose) decreased milder (probably due to a negligible degradation of cellulose), by about 13–49% for natural weathering and by about 11–44% for artificial weathering—in both modes the most for bangkirai and the least for jatobá. On the basis of FTIR analyses, when the absorbance ratios A1334/A1274 always increased, it can be stated that the guaiacyl structural units were more degraded in comparison to syringyl ones in both modes of weathering (Table 3). So, comparing the degradation rates of the guaiacyl and syringyl units, the guaiacyl units were more susceptible to being affected by weathering due to action of UV and VIS light in the presence of water than the syringyl ones. This result can be explained by structural differences between these two types of lignin units, when the guaiacyl lignin has one methoxyl group in the meta-position to the phenolic hydroxyl group, whereas the syringyl lignin has two methoxyl groups both in the meta-position to the phenolic hydroxyl group (Chang et al. 2002).

The present results related to degradation of guaiacyl and syringyl units of lignin are in accordance with some other works, for example by Chang et al. (2002) who exposed maple wood to UV, or by Mitsui and Tsuchikawa (2005) who demonstrated that degradation of softwood lignin having mainly quaiacyl units is faster than of hardwood lignin

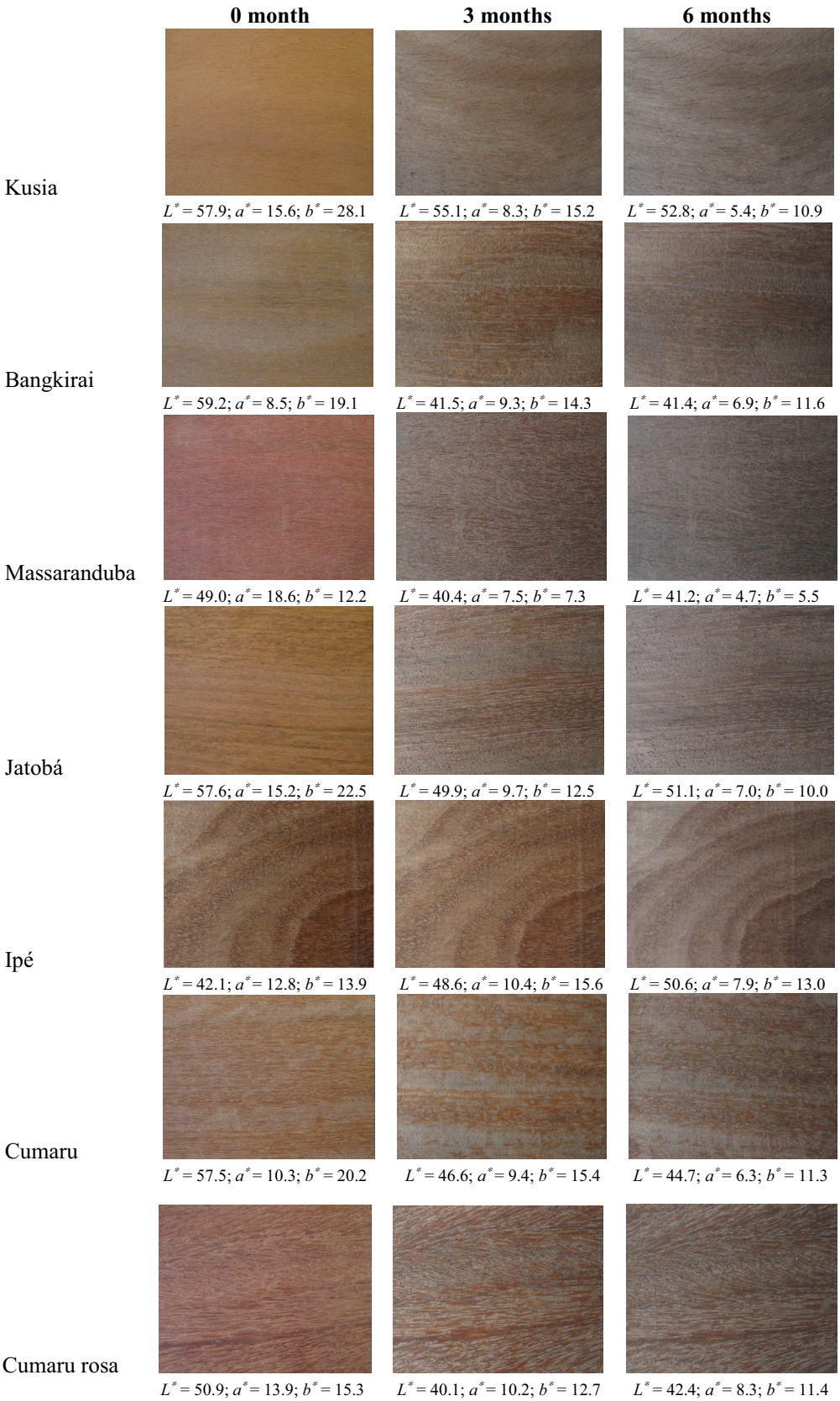

Fig. 4 Typical greying of tropical woods after 3 and 6 months of natural weathering

Table 3 FTIR spectra of the top surfaces of tropical woods before (reference) and after weathering (natural = 36 months in exterior; artificial = 12 weeks in Xenotest)

Weathering	FTIR (cm^{-1})	Intensity of FTIR spectra (normalized at 898 cm^{-1})						
		Kusia	Bangkirai	Massaranduba	Jatobá	Ipé	Cumaru	Cumaru rosa
Reference								
	1274	1.39	1.85	0.96	1.47	2.43	1.39	1.54
	1334	1.51	1.97	1.25	1.20	1.91	1.65	1.51
	1430	1.83	1.99	1.36	1.26	2.08	1.87	1.80
	1510	1.42	1.76	0.93	1.05	1.76	1.66	1.55
	1600	1.56	2.13	1.51	1.56	1.89	2.01	1.82
	1653	1.02	1.13	0.87	1.06	1.52	1.08	1.08
	1730	0.60	1.04	0.81	1.18	0.80	0.74	0.79
Natural								
	1274	0.48	0.56	0.50	0.53	0.52	0.51	0.49
	1334	0.90	1.01	0.96	1.04	1.01	0.99	0.92
	1430	0.74	0.81	0.74	0.84	0.83	0.81	0.74
	1510	0.03	0.01	0.02	0.02	0.01	0.01	0.04
	1600	0.14	0.28	0.12	0.18	0.20	0.23	0.26
	1653	0.50	0.61	0.41	0.53	0.58	0.53	0.53
	1730	0.05	0.27	0.06	0.07	0.20	0.21	0.27
Artificial								
	1274	0.66	0.56	0.57	0.56	0.92	0.57	0.60
	1334	1.18	1.11	1.11	1.06	1.56	1.07	1.14
	1430	0.92	0.94	0.85	0.85	1.36	0.82	0.86
	1510	0.01	0.02	0.01	0.01	0.01	0.00	0.02
	1600	0.33	0.25	0.15	0.22	0.42	0.22	0.27
	1653	0.63	0.63	0.51	0.52	0.89	0.49	0.59
	1730	0.41	0.29	0.29	0.32	0.57	0.28	0.35

Average values from six measurements

Table 4 Indexes *LOI* (*CI*) and *TCI* related to the cellulose crystallinity of the top surfaces of tropical woods before (reference) and after weathering (natural = 36 months in exterior; artificial = 12 weeks in Xenotest)

Weathering	Index	Kusia	Bangkirai	Massaranduba	Jatobá	Ipé	Cumaru	Cumaru rosa
Reference								
	LOI	1.83	1.99	1.37	1.27	1.44	1.88	1.80
	TCI	2.11	2.13	1.81	2.00	1.89	1.94	2.02
Natural								
	LOI	0.99	0.94	0.90	0.89	1.42	0.87	0.93
	TCI	1.97	1.69	1.70	1.84	1.62	1.81	1.61
Artificial								
	LOI	0.80	0.86	0.86	0.95	0.86	0.83	0.75
	TCI	2.06	1.89	1.98	2.05	1.77	1.81	1.88

Average values from six measurements

consisting of quaiacyl and syringyl units. In summary, for both weathering processes, the species of tropical wood had only a minor effect on the decrease of its total lignin content, and also on the decrease of its guiacyl and syringyl units (Table 3).

During the wood photodegradation, the C = O stretching band at 1740–1720 cm^{-1} increases due to oxidative reactions of lignin in the presence of UV light, which is documented by Müller et al. (2003) and Pandey (2005), who found an increase of unconjugated carbonyl groups occurring in parallel with degradation of lignin during photodegradation of wood in the absence of water. However, during weathering the C = O stretching band at 1740–1720 cm^{-1} can also decrease due to degradation of acetyl groups, which is documented by Lionetto et al. (2012) by a decrease in the absorbance value at 1735 cm^{-1} for wood artificially aged in the presence of water. Fabiyi et al. (2008) observed an increase in the concentration of two types of carbonyl

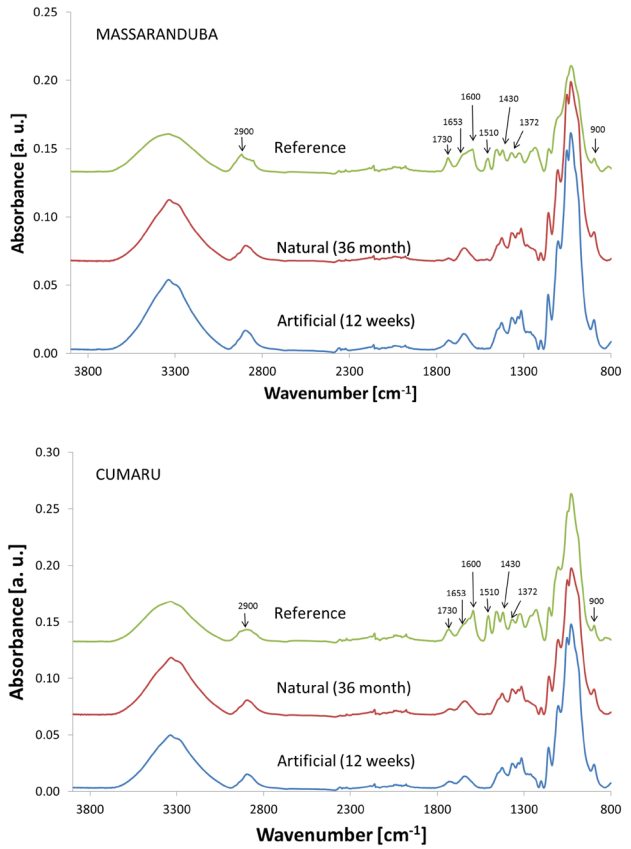

Fig. 5 FTIR spectra of massaranduba and cumaru wood before (reference) and after natural or artificial weathering. *Note* average values from six measurements

functional groups (esters at 1735 cm^{-1} and carboxylic acid at 1715 cm^{-1}) upon xenon-arc and UV weathering of wood plastic composites, while with longer exposure time the concentration of these groups began to decrease. Sandak et al. (2015), using similar types of infrared spectra (NIR and MIR), for woods exposed to exterior also determined the most intense chemical changes in lignin in the early stages of weathering.

In the present study, the bands of carbonyl groups, determined at 1730 and 1653 cm^{-1}, decreased after longer period of wood weathering, i.e. after 36 months in exterior or 12 weeks in Xenotest "UV and VIS light with water spraying" (Table 3). It is in accordance with work by Fabiyi et al. (2008) when wood-plastics were weathered for a longer time. For tested tropical woods, the peak 1653 cm^{-1} (belonging to conjugated carbonyls –C=C–C=O) decreased on average by about 56.3% during outdoor and by about 52.3% during Xenotest weathering, and the peak 1730 cm^{-1} (belonging to unconjugated carbonyls –C=O) decreased on average by about 67.9% during outdoor and by about 55.4% during Xenotest weathering (Table 3). This result indirectly points out that weathering of tropical woods had a partly lower impact on the decrease of conjugated carbonyls in comparison to unconjugated ones, both present in their surfaces. It can be explained either by different, "in this work undefined", chemical mechanisms during photo-oxidation processes in the lignin-polysaccharide matrix and extractives, and also by different water solubility of original and newly conjugated and unconjugated carbonyls during natural and artificial weathering.

On the whole, the decrease of the carbonyls was milder in comparison to the total degradation of the guaiacyl and syringyl units of lignin (Table 3). It is in accordance with knowledge that during photodegradation of wood a sharp drop of lignin can arise associated with formation of new carbonyl groups in the lignin-polysaccharide matrix (Sundqvist 2002; Ayadi et al. 2003). Photo-oxidation of cellulose and hemicelluloses results in the formation of aldehyde and ketone groups on carbon atoms C2 and C3 of the pyran or furan units, and just these carbonyls may contribute to the increase of absorbance at wavenumbers 1653 cm^{-1} and 1730 cm^{-1} (Müller et al. 2003). However, according to Pandey and Vuorinen (2008) the increased rate of carbonyl units in the photo-oxidized cellulose and hemicelluloses is much smaller than in the significantly photodegraded lignin. Therefore, the contribution of the newly created carbonyl units in the photo-oxidized polysaccharides is less important in comparison to the high loss of lignin (Table 3—see approx. 90% decrease of lignin bands at 1510 and 1600 cm^{-1}), which in a native undamaged state has several times greater number of carbonyl units. Generally, decrease of carbonyls during weathering of tropical woods, i.e. upon action of light sources and water, can be explained by two factors: (1) firstly due to the presence of higher content of extractives, which according to Chang et al. (2010, 2014), Shen et al. (2016) and other researchers can significantly inhibit wood photodegradation and creation of new carbonyl groups in lignin and other components of wood, and (2) secondly due to washing-out of water soluble polar compounds formed during photodegradation of lignin and partly of hemicelluloses as well, which contain new carbonyl and carboxyl groups (Tolvaj and Faix 1995).

Tropical woods have a relatively high amount of extractives in comparison to common European species. However, the actual loss or change in chemical structure of extractives during weathering cannot be determined by infrared spectroscopy because of their evidently lower amount in relation to greater amounts of lignin and polysaccharides (Persze and Tolvaj 2012; Tolvaj et al. 2013).

FTIR spectroscopy allows evaluating changes in cellulose, especially alterations of its crystallinity (Table 4). Absorbance at 1420–1430 cm^{-1} is assigned to aromatic skeletal vibrations and C–H plane deformations of crystallised cellulose. The band at 1372–1375 cm^{-1} (CH deformations in cellulose and hemicelluloses) and the band at

1160–1165 cm^{-1} (C–O–C asymmetric stretching vibrations in cellulose and hemicelluloses) are characteristics for saccharides. The band at 898 cm^{-1} is related to CH deformations in amorphous cellulose (Åkerholm et al. 2004; Oh et al. 2005; Poletto et al. 2014). The absorbance ratio A1430/A898 is defined as a lateral order index (*LOI*) or an empirical crystallinity index (*CI*) of cellulose, while the absorbance ratio A1372/A2900 is defined as its total crystallinity index (*TCI*) (Nelson and Connor 1964; Colom et al. 2003; Åkerholm et al. 2004).

In the process of wood outdoor weathering, the amorphous cellulose usually degrades more evidently in comparison to the crystalline cellulose. In this context, the empirical crystallinity index (*CI* identical to *LOI*) increases together with increase in the size of crystallites (Colom et al. 2003; Lionetto et al. 2012). However, in the present experiment during long-term weathering the values of *LOI* (A1430/A898) after 36 months of exterior exposure decreased less for all tropical woods (*ΔLOI* from 1.5% for ipé to ~53% for bangkirai and cumaru) than after 12 weeks of exposure in Xenotest (*ΔLOI* from 25% for jatobá to ~57% for kusia, bangkirai, cumaru and cumaru rosa) (Table 4). Similar tendencies were achieved by Chang et al. (2002) during photodegradation of softwood and hardwood species using accelerated lightfastness test.

Evolution of the *TCI* (A1372/A2900) values of tropical woods owing to weathering was not so coherent. During natural exterior weathering, the *TCI* values decreased for all tropical woods by about ~12% (i.e. from ~6.7% for kusia and cumaru to ~21% for bangkirai and cumaru rosa). However, during artificial weathering in Xenotest, the *TCI* values decreased for five species only by about ~6.7%, while for jatobá and masaranduba they even increased by about 2.5–9% (Table 4). According to Colom et al. (2003), such specific behaviour of *TCI* could be interpreted as follows: (1) the degradation process in the Xenotest chamber does not transform cellulose I into cellulose II, or (2) the *TCI* index is not valid for multi-component materials, for example also of wood, because the band at 2922 cm^{-1} is not exclusive of cellulose. Drop of the cellulose crystallinity determined by the *TCI* for more weathered woods, caused probably by an increased amount of the amorphous cellulose, may evoke an increase in their surface hydrophilicity.

3.4 Changes in the anatomical structure of weathered woods

The following typical changes in the anatomical structure of weathered tropical woods were observed by SEM analyses: (1) weakening of connections between cell elements, (2) radial micro-cracks in cell walls, (3) total degradation of parenchyma cells in medullary rays, or significant thinning of parenchyma cell walls and their extreme shrinkage, (4) a lot of transversal disruptions in libriform fibres, probably connected with significant degradation of their secondary layers, (5) degradation of pit membranes in vessels and parenchyma cells, (6) and spherical formations on the S_3 layer of cell walls produced probably from condensing compounds of degraded lignin and hemicelluloses at thermo-mechanical wrinkling.

Upon natural weathering specific changes in the anatomy of tropical woods also occurred due to an adsorption of dust particles, spores or occasionally pollen grains into empty spaces created from totally degraded medullary rays.

The above mentioned typical and specific changes in the anatomical structure of weathered tropical woods are documented for two species—massaranduba and cumaru (Figs. 6, 7).

3.5 Connections between individual analyses of weathered woods: macro-cracks, colour, molecular and anatomical structure

Regression correlations could not be applied to the evaluation of the experiments, because some analyses of weathered tropical woods were carried out before and after all defined times of weathering (cracks and colour changes by CIE-*L*a*b**), while others (chemical and anatomical changes) only before and after the end of weathering processes. Therefore, mutual relationships between performed analyses of weathered woods are documented only for the final times of their exposure—see results in Figs. 1, 2, 3, 4, 5, 6 and 7 and Tables 2, 3 and 4. The effect of specific extractives in the individual tropical woods was not reflected in these relationships, because extractives were not analysed in this work.

The creation of macro-cracks (Table 2) and micro-cracks (Figs. 6, 7) in weathered tropical woods could theoretically be caused by delignification (Table 3) and weakening of cells in the primary wall and middle lamella. However, the size and frequency of cracks were very different for the individual wood species which had a similar, approx. 90%, loss of lignin, i.e. the creation of cracks was probably connected mainly with the original anatomical structure and the definite orientation of cells on the top surfaces of tested samples.

The individual and total colour differences in surfaces of woods exposed to exterior are caused by a complex of various changes in their molecular structure. Colour changes of wood in the presence of sunlight and water are created mainly due to photodegradation and washing-out of lignin and extractives (and partly also of polysaccharides), on the whole with a relative increase in the cellulose content. On the contrary, for example colour changes of waterlogged woods are caused mainly due to hydrolysis of hemicelluloses—when, for example Solár et al. (1987), in a brown-dark 8150-year-old subfossil oak, using classical chemical analyses and IR spectra, found 50% increase

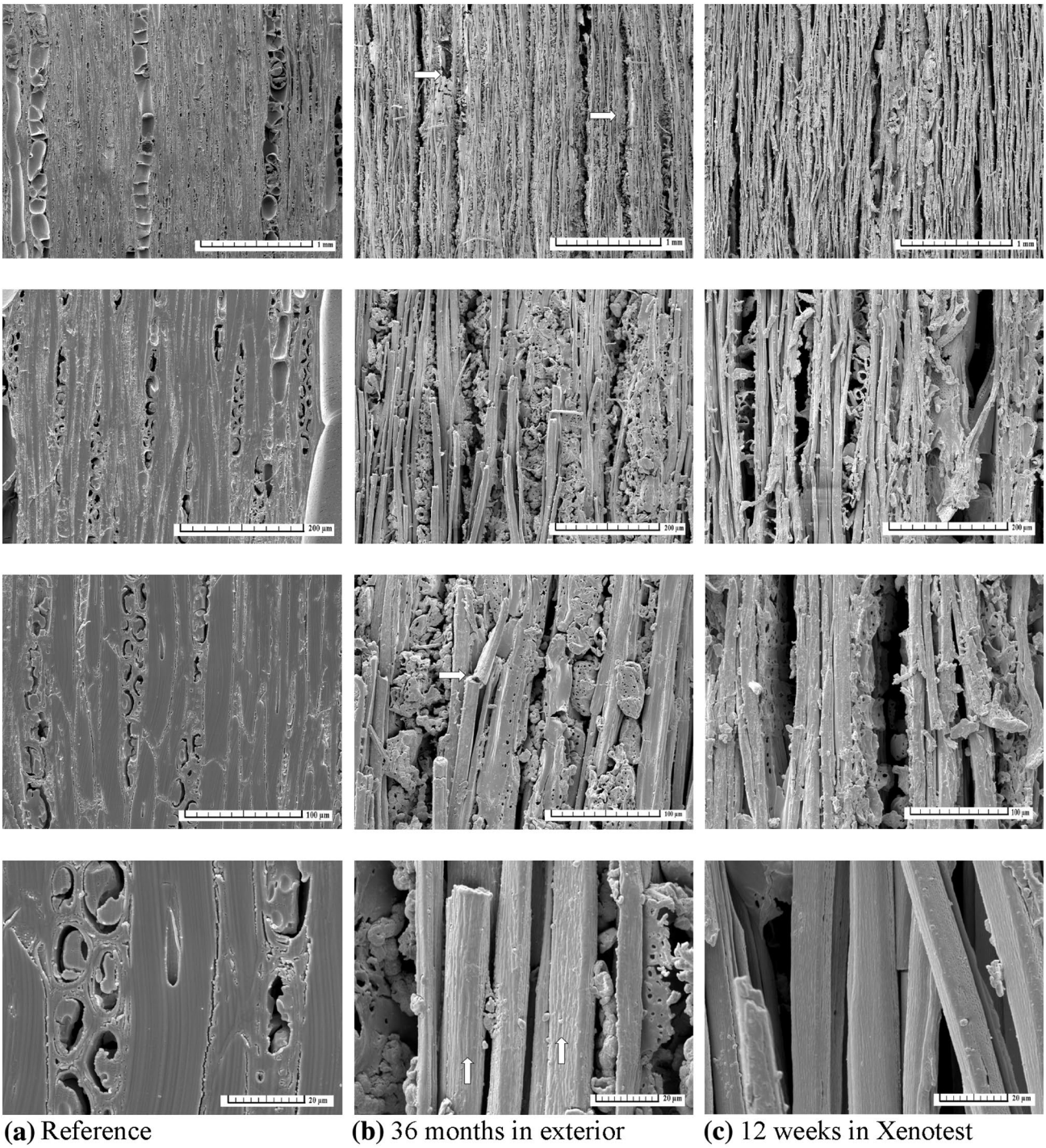

Fig. 6 Anatomical changes in the top surfaces of massaranduba wood (*Manilkara bidentata* A. Chev.) after natural (36 months) or artificial (12 weeks) weathering. *Note 1st row* magnification 100×, presents general view of sample's surfaces with documentation of weathering on the degradation of vessels (*arrows*) and the frequency of created micro-cracks, *2nd row* magnification 500×, shows the changes of ray parenchyma cells, *3rd row* magnification 1000×, shows the fragile fractures of libriform fibres (*arrow*) and the cracks in the area of rays, *4th row* magnification 8000×, shows the detailed degradation of libriform fibres in the secondary wall, e.g. also defibrillation at weathering in exterior (*arrows*)

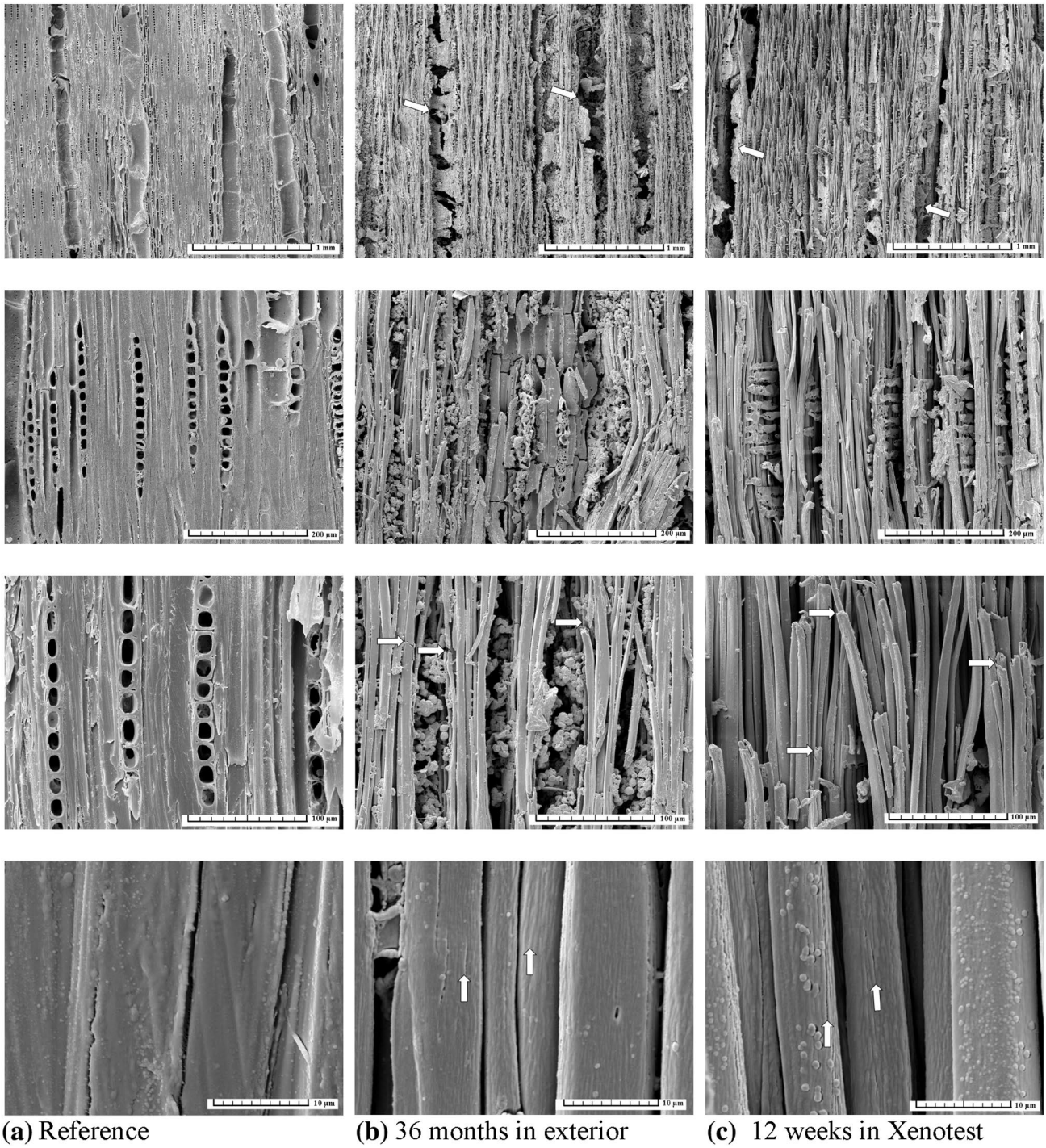

Fig. 7 Anatomical changes in the top surfaces of cumaru wood [*Dipteryx odorata* (Aubl.) Wild.] after natural (36 months) or artificial (12 weeks) weathering. *Note 1st row* magnification 100×, presents general view of sample's surfaces with documentation of weathering on the degradation of vessels (*arrows*) and the frequency of created micro-cracks, *2nd row* magnification 500×, shows the changes of ray parenchyma cells; with an extreme shrinkage of parenchyma cells (in case **c**), *3rd row* magnification 1000×, shows the fragile fractures of libriform fibres (*arrows*) and the cracks in area of rays incrusted by dust particles (in case **b**), *4th row* magnification 8000×, shows the detailed changes in the secondary wall of libriform fibres, e.g. their defibrillation (*arrows*)

in lignin-similar-compounds, 20% decrease of polysaccharides, and a partial increase of cellulose crystallinity. Liu et al. (2017) explained the darkening and other colour changes in wood exposed to 100 °C for a total period of 288 h by the help of FTIR results—i.e. with slight increase of lignin, decrease of hydroxyl groups, and increase of the unconjugated carbonyl groups. Colour changes of weathered wood may be caused as well as changes in their anatomical structure in connection with a better accessibility of their damaged surfaces to adsorption of dark pollutants. Generally, colour changes of differently aged woods are specific in relation to (1) the conditions of ageing and (2) the molecular and anatomical structure of the original wood.

In the following, two examples of the colour and the FTIR spectra are documented for weathered tropical woods determined in this experiment:

1. A tight connection between the greatest total colour difference ($\Delta E^* = +20$ until $+28$) and the greatest decrease of the unconjugated carbonyl band at 1730 cm^{-1} ($\Delta Intensity_{C=O} = \sim -92\%$) was determined for the following three naturally weathered tropical woods—kusia, jatobá and massaranduba (Table 3; Fig. 3). However, explanation of this result is not clear. According to Tolvaj et al. (2013), such connection can be generated by a similar time-dependent photodegradation of carbonyls in lignin and in some extractives. Pandey (2005), comparing the unextracted and extracted *Acacia auriculaeformis* wood, following exposure to UV irradiation, has found that the colour changes are connected mainly with photodegradation of polyphenolic extractives. In this view, the different composition and quantity of extractives in the individual tropical wood species could thus induce different colour changes during the photodegradation processes—as it is in accordance with works by Fan et al. (2010) and Chen et al. (2012).
2. A tight connection between the "unexpected" lightening ($\Delta L^* \sim +8$) and the smallest decrease of the cellulose crystallinity (determined as LOI $\sim -1.5\%$) was found for the naturally weathered ipé wood (Table 4; Fig. 3). A similar connection was also found between the smallest values of lightening ($\Delta L^* \sim +10$ until $+17$) and the highest decreases of the cellulose crystallinity (LOI $\sim -57\%$) for artificially in Xenotest weathered woods—bangkirai, cumaru rosa and cumaru (Table 4; Fig. 3).

4 Conclusion

Weathering of tropical woods—either naturally in exterior under a slope of 45° without ground contact or artificially in Xenotest with UV and VIS light and water spraying—caused the following typical changes in their structure:

- creation of longitudinal macro-cracks,
- darkening in exterior due to pollutants, except for ipé,
- lightening in Xenotest,
- greening and blueing in both weathering modes,
- very significant decrease of lignin,
- faster decrease of guaiacyl lignin than syringyl lignin,
- decrease of conjugated and unconjugated carbonyl groups,
- decrease of cellulose crystallinity,
- damaging of cell-walls by micro-cracks, their degradation and thinning.

Some of these changes were mutually compared, for example:

- in the natural or artificial modes of weathering, for tropical woods no evident connections were found between the creation of cracks or intensity of colour changes and the photodegradation of lignin—for example ipé wood evidently better resisted cracks, darkening and other colour changes than kusia wood, but the decrease of total lignin and its guaiacyl and syringyl units was comparable for both these species,
- for kusia, jatobá and massaranduba woods, in their surfaces after 36 months of natural weathering the highest decrease of the unconjugated carbonyl units was found by about 92–94%, as well as the highest total colour change ΔE^* by about 20–28%,
- for bangkirai, cumaru rosa and cumaru woods, in their surfaces after 12 weeks of artificial weathering in Xenotest the highest decrease of the cellulose crystallinity ΔLOI of about ~57%, as well as the lowest lightening (ΔL^* from $+10$ to $+17$) were determined.

However, upon these comparisons, it has to be emphasized that these changes could only be of a random nature and need to be clarified in future experiments.

On the basis of the performed weathering tests of seven tropical woods, it can be manifested that the most resistant against surface defects and colour changes was ipé wood, and the least resistant was kusia wood.

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