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THE COLOR OF BEECH WOOD MODIFIED IN AIR, PARAFFIN OR POLYETHYLENE GLYCOL, AND AFTER FOLLOWING WEATHERING IN XENOTEST

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ABSTRACT

The thermal treatment of European beech (*Fagus sylvatica* L.) wood specimens was performed in three different media – air, paraffin or polyethylene glycol 6000 (PEG 6000) – during 1, 2, 3 or 4 hours, applying either only heating at a temperature of 100 °C or modification process at the temperatures of 190 °C and 210 °C. Following, the thermally treated specimens were artificially weathered in Xenotest in an accordance with the modified EN 927-6 (2018) for 6-weeks. The color parameters L^*, a^*, and b^* of beech specimens were measured in their original state, after thermal treatment, and finally after weathering. The total color difference ΔE^*_{ab} values of the air-thermally, paraffin-thermally and PEG-thermally modified beech specimens ranged from 23.6 (for air-thermal mode 190 °C/1h) up to 55.8 (for PEG-thermal mode 210 °C/4h), evidently in connection with their apparent darkening with ΔL^* from – 22.9 up to – 54.2. Due to the following exposure of beech specimens in Xenotest, the highest total color difference ΔE^*_{ab} from 20.1 to 36.4 had the PEG-thermally modified ones, which evidently lightened with ΔL^* from 18.6 to 32.6. At weathering the PEG-thermally modified beech wood specimens were the best resistant against creation of cracks in surfaces, in contrast to the air-thermally modified specimens.

Key words: beech wood, paraffin, polyethylene glycol, thermal modification, weathering, color.

INTRODUCTION

European beech (*Fagus sylvatica* L.) is one of the commercial most used hardwoods in Central Europe. Due to its easy workability and bendability it is mainly used for the furniture, plywood, decorative veneer and floor manufacturing (KLEMENT *et al*. 2020). However, at changed weather conditions it has low dimensional stability and in its surface are created cracks. According to the Standard EN 350 (2016), beech wood belongs to non-durable species, so it can be easily attacked by decaying fungi and insects, and without convenient chemical or physical treatments it cannot be used for outdoor building structural elements.

Beech wood products are in outdoor exposures degraded also by ultraviolet (UV) radiation and other environmental factors, *e.g.*, water, oxygen and dust particles in air. The main reason of photodegradation of wood is the presence of light-absorbing chromophoric groups (a-carbonyl, biphenyl and ring conjugated double bond structures) in lignin. The absorption of light by chromoforms leads to the formation of free radicals, which react with oxygen and are responsible for the color changes of wood (HON and SHIRAISHI 2000).

The resistance of wood against aging processes can be increased by its treatment with biocides and anti-weathering coatings containing UV absorbers or pigments (REINPRECHT 2016). However, today an environmentally very acceptable method for increasing the aging resistance of wood is its thermal modification (ESTEVES and PEREIRA 2009). Due to thermal modification of wood, usually at temperatures from 160 °C to 260 °C, its molecular structure is changed in association with degradation of hemicelluloses, creation of hemicelluloses-lignin linkages, and extinction of some hydroxyl groups (TJEERDSMA *et al.* 1998, SRINIVAS and PANDLEY 2012, ANDOR and LAGAŇA 2018, CAI *et al.* 2018). These changes have a positive effect on the water resistance, dimensional stability and biological durability of the thermally modified wood. A range of changes in the molecular structure and partly also in the anatomical structure (*e.g.* composition and thickness of the individual cell wall layers) and geometry structure (*e.g.* volume and cracks) of thermally modified woods, connected with following changes in their physical, mechanical and biological properties, is related: (a) to the type of used heating medium, *e.g*. air, nitrogen, steam, plant oil, or wax; (b) to the thermal modification technology, *e.g*., regulation of the temperature, pressure, and time; (c) to the tree species used and its initial moisture content (TJEERDSMNA *et al.* 1998, HILL 2006, YILDIZ *et al.* 2006, ESTEVES and PEREIRA 2009, KOCAEFE *et al.* 2015, REINPRECHT 2016). In addition, heat treated wood has uniform dark-brown color in its entire cross-section, while more intense color changes occur due to higher modification temperatures and prolonged thermal modification time (BEKHTA and NIEMZ 2003, SRINIVAS and PANDLEY 2012, DZURENDA and DUDIAK 2020, CIRULE *et al.* 2021). Darkening of the thermally modified wood is generally attributed to the decomposition of hemicelluloses and the chemical changes in extractives (SUNDQVIST and MORÉN 2002, ESTEVES *et al*. 2008).

Thermal modification of wood can be realised in various media – *e.g.*, in air, nitrogen, natural oils, or waxes (REINPRECHT and REPÁK 2019).

Paraffin and other non-polar waxes have hydrophobic properties. They are often used to protect wood against water, as its water sorption kinetic is reduced and dimensional stability is improved (CHEN *et al.* 2020, REPÁK and REINPRECHT 2020). Combination of wax treatment and heat treatment of wood has even more significant effect on increasing its hydrophobicity (REINPRECHT and REPÁK 2019, YANG and LIU 2020, YANG *et al.* 2020, CHEN *et al.* 2020, ZHANG *et al.* 2020). The hydrophobic treatment of wood with waxes reduces its equilibrium moisture content, increases its dimensional stability and improves its resistance to creation of cracks – because waxes create a barrier in cell walls that slows down the process of absorption of water molecules to wood (WANG and COOPER 2005, AWOYEMI *et al.* 2009, LESAR and HUMAR 2011, DUBEY *et al.* 2012, REINPRECHT and REPÁK 2019). The thermal modification of wood has also a positive effect on the formation of cracks in its surfaces, when high temperatures cause depolymerization of hemicelluloses, increase in the proportion of crystalline cellulose and crosslinking of lignin – which reduces the proportion of free -OH groups in wood and the wood has a better dimensional stability.

Polyethylene glycols, in contrary to paraffin, are polar macromolecules having hydrophilic properties. They are mainly used for dimensional stabilization of archaeological waterlogged wooden artefacts (HOCKER *et al.* 2012, MAJKA *et al.* 2018).

Additional effect of the outdoor weathering on the color stability of heat-treated wood is important for practice and was examined in some previous studies (*e.g.*, AYADI *et al.* 2003, NUOPPONEN *et al.* 2004, TEMIZ *et al.* 2006, DUBEY *et al.* 2010, YILDIZ *et al.* 2011, HUANG *et al.* 2012). Thermal modification of wood increased its weathering resistance in comparison to untreated wood (AYADI *et al.* 2003, NUOPPONEN *et al.* 2004, TEMIZ *et al.* 2006, DUBEY *et al.* 2010). On contrary, some of studies showed that thermal modification of wood decreases its resistance to weathering (YILDIZ *et al.* 2011, HUANG *et al.* 2012).

The aim of the experiment was to determine the color parameters of the European beech wood after its thermal treatments in three different media – air, paraffin or polyethylene glycol 6000 (PEG 6000), and also to study the color stability and creation of cracks in the thermally treated wood after its exposition to artificial weathering in Xenotest.

MATERIALS AND METHODS

Wood

The European beech (*Fagus sylvatica* L.) wood specimens with dimension of 50 mm × 50 mm × 10 mm (longitudinal × tangential × radial), characterized with a good quality, *i.e.*, without growth anomalies, cracks or biological defects, were prepared from the sawn timber from the National Forest Centrum in Zvolen, naturally seasoned to a moisture content of 13.5 ± 2%. The specimens were dried at 103 ± 1 °C to the oven-dry state in the kiln Memmert UNB 100 (Memmert GmbH + Co.KG, Schwabach, Germany), subsequently cooled in desiccators to a temperature of 20 ± 2 °C, and weighed with an accuracy of 0.001 g (m_0).

Media for thermal treatment of wood

Three different media for the thermal treatment of beech wood specimens were used – air, paraffin and polyethylene glycol 6000 (PEG 6000).

The clear paraffin wax (MOL, Hungary) with a melting point of 61 ± 1 °C. The PEG 6000 (HiMedia, Laboratories Pvt. Ltd., Mumbia, India) with a melting point of 58 ± 3 °C, and a molecular weight from 5000 to 7000.

Thermal treatments of wood in the air, paraffin or PEG 6000

The thermal treatment of beech wood specimens was performed during 1, 2, 3 or 4 hours, either only by their heating at 100 °C or by their thermal modifications at 190 °C and 210 °C (Fig. 1). The thermal treatments were performed at atmospheric pressure in a kiln Memmert UNB 100 (Memmert GmbH + Co.KG, Schwabach, Germany), using one of the following media – (1) air, (2) paraffin, (3) PEG 6000.

The paraffin and PEG 6000 (both solid media up to app. 60 °C) were firstly melted in stainless steel containers during 1 h at a temperature of 100 °C. In the second phase, the specimens were inserted into the melt-liquid medium and impregnated 1 h at a temperature of 100 °C. In the third phase, lasting 1 h, the temperature of the air or the liquid medium was either stable 100 °C or it increased continuously to 190 °C or 210 °C. In the fourth phase, a temperature of the used modification medium was maintained at 100 °C, 190 °C or 210 °C for 1, 2, 3 or 4 hours. In the last fifth phase, the beech wood specimens were cooled directly in the used medium app. to 75 °C, then taken out from steel containers and their surfaces cleaned with filter papers from the liquid-melts of paraffin or PEG 6000, and cooled in desiccators to a temperature of 20 ± 2 °C (Fig. 1).

Beech specimens treated at temperatures of 100 °C, 190 °C or 210 °C (*i.e.*, all with a moisture content of 0%) were weighed with an accuracy of 0.001 g (m_{t0}). Then they were 14 days conditioned to a moisture content of 10 ± 2% at a temperature of 20 ± 2 °C and a relative air humidity of 60 ± 3%.

The weight percent gain **(**WPG) values of paraffin and PEG 6000 into the thermally treated beech wood specimens were determined by equation 1:

$$\mathrm{WPG} = /(m_{t0} - m_0) : m_0/ \times 100 \ \ (\%) \qquad (1)$$

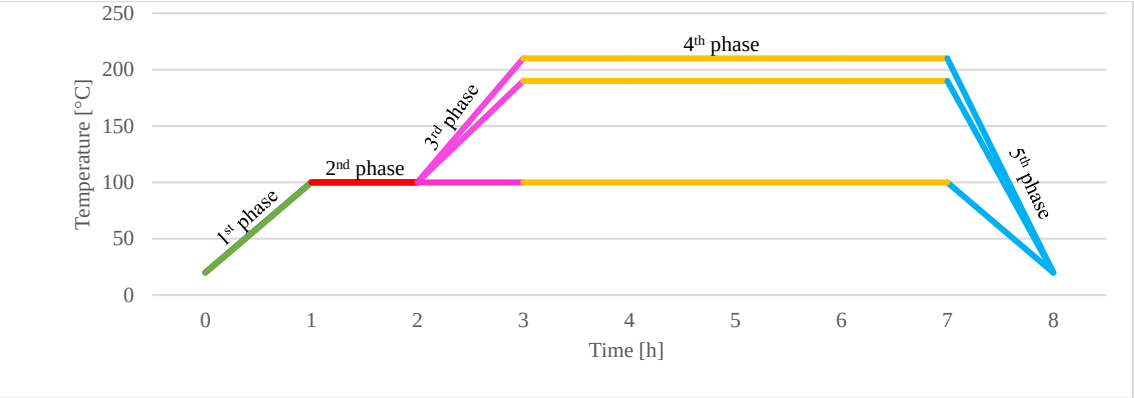

Fig. 1 Phases of the thermal treatment of beech wood in air, paraffin or PEG 6000.

Artificial weathering of wood

The artificial weathering (6 cycles, each lasting 1-week – *i.e.*, totally lasting 42 days) of all beech wood specimens (reference and thermally treated) was performed in the Q-SUN Xe-1-S Xenotest (Q-Lab Corporation, Westlake, OH, USA). It took place in accordance with the modified version of the standard EN 927-6 (2018), when each 1-week of weathering consisted from 24 h conditioning of specimens at 45 °C and then from 48 subcycle steps—each lasting 3 h (2.5 h UV-radiation and then 0.5 h water spraying). At the artificial weathering, the following modifications to the standard EN 927-6 (2018) were made: - xenon lamps instead of fluorescent UV lamps; - irradiance at 340 nm set to 0.55 $W \cdot m^{-2}.nm^{-1}$ instead of 0.89 $W \cdot m^{-2} \cdot nm^{-1}$; - the temperature on the black panel at 50 °C instead of 60 °C.

Color of wood and cracks in wood

The color analyses of beech wood specimens 50 mm × 50 mm × 10 mm were made firstly in the original state, then after thermal treatment, and finally after artificial weathering, always in the same eight places of two replicates. The color measurements were performed with the Color Reader CR-10 (Konica Minolta, Japan), having a CIE 10° standard observer, CIE standard illuminate D65, sensor head with a diameter of 8 mm (*i.e.* the measuring area was 50 mm^2), and a detector with 6 silicon photocells. The colorimetric parameters of each beech wood specimen were analysed according to the CIE$L^*a^*b^*$ color system (CIE 2007). A larger value of L^*, a^*, or b^* means a lighter, redder, or yellower colour, respectively.

From the relative color changes ΔL^*, Δa^*, and Δb^*, namely differences between color coordinates of the thermally treated and original specimens, and of the artificially weathered and thermally treated specimen, the total color difference ΔE^*_{ab} was calculated for each beech wood specimen by equation 2:

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

Cracks in wood surfaces were determined visually after the thermal treatments and also after the artificial weathering, using magnifier with 10X 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

Statistical Analyses

The statistical software STATISTICA 12 (StatSoft, Inc., Tulsa, OK, USA) was used for analysing the gathered data. Determined were the basic statistical characteristics of color parameters, *i.e.*, the arithmetic means and standard deviations. Duncan test analysed for individual color parameters the differences caused at weathering in Xenotest between the thermally treated and reference specimens, on the significance levels of: a ≥ 99.9%, b ≥ 99%, c ≥ 95%, or without significance d < 95%.

RESULTS AND DISCUSSION

Weight percent gain (WPG) values of paraffin and PEG 6000

The average WPG values of paraffin into the thermally treated beech wood specimens ranged from app. 15% for mode 210 °C/1 h up to app. 20% for several modes at 100 °C and 190 °C (Fig. 2). The PEG 6000 uptake into beech specimens was higher, and it ranged from app. 19% for mode 210 °C/4 h up to 32.4% for mode 100 °C/3h (Fig. 2). The main reason of lower WPG values determined at 210 °C are probably current significant thermal degradation processes in wood structure which are associated with decrease of its weight.

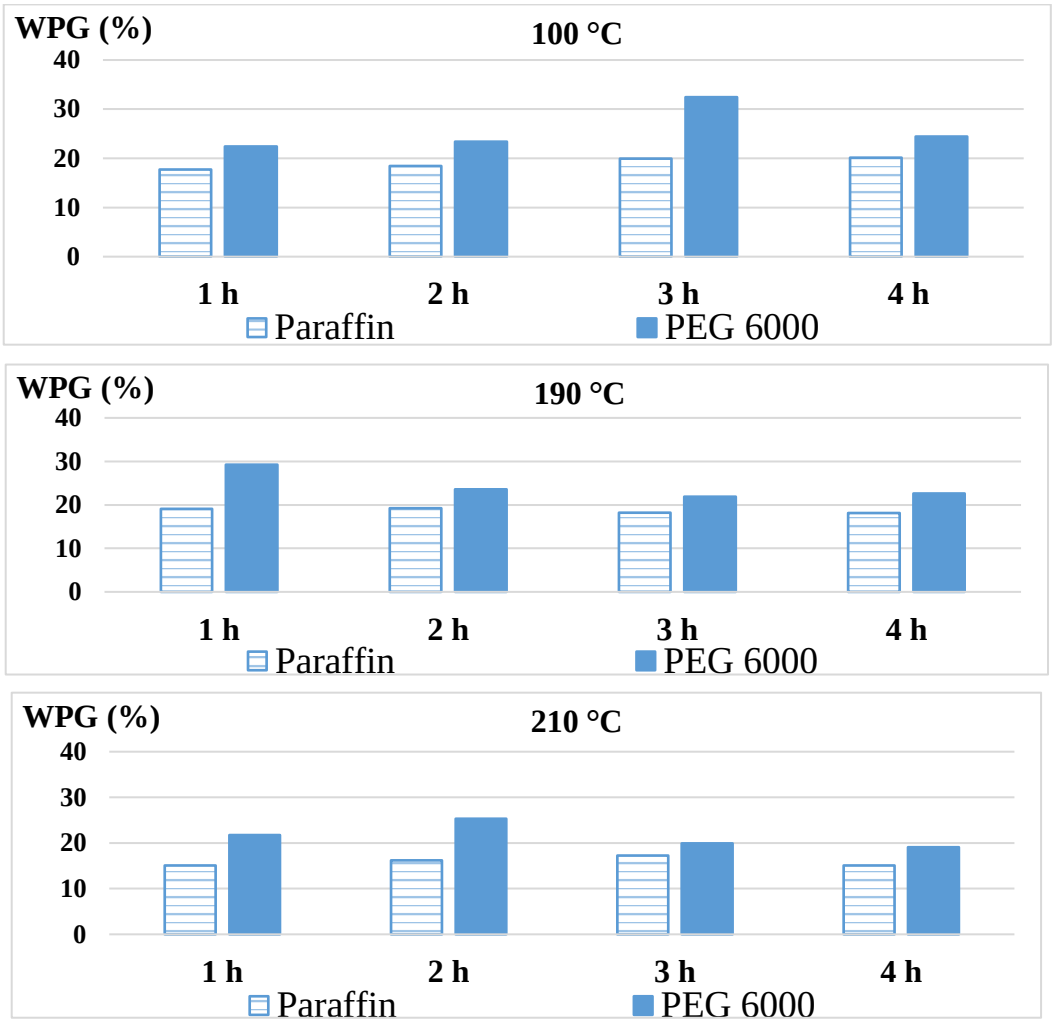

Fig. 2 The WPG values of paraffin and PEG 6000 into beech wood specimens determined after 1, 2, 3 and 4 hours of their thermal treatments at 100 °C, 190 °C and 210 °C.

Color of the thermally treated beech wood

It is generally known that color of thermally treated woods changes more intensively with increasing temperature and longer modification time (BEKHTA and NIEMZ 2003, SRINIVAS and PANDLEY 2012, CIRULE *et al.* 2021). This fact also was confirmed by the present experiments (Tab. 1, Fig. 3, Figs. 6a–8a).

Tab. 1 The color changes (ΔL*, Δa*, Δb*) of beech wood specimens due to their air-thermal, paraffin-thermal and PEG-thermal treatments.

Notes: The arithmetic means were determined from 8 values. The standard deviations are in parentheses. Average color coordinates of the reference (original) beech wood specimens: $L^* = 78.8$, $a^* = 7.7$, $b^* = 15.8$.

Mode of beech wood thermal treatment	ΔL* – Due to thermal treatment		
	In air	In paraffin	In PEG 6000
100 °C/1 h	–0.9 (0.23)	–12.6 (1.84)	–10.8 (0.68)
100 °C/2 h	–1.1 (0.18)	–11.0 (0.95)	–12.3 (0.24)
100 °C/3 h	–1.4 (0.39)	–11.3 (0.57)	–11.6 (0.86)
100 °C/4 h	–1.2 (0.39)	–12,0 (1.04)	–11.8 (0.43)
190 °C/1 h	–23.5 (0.80)	–28,5 (1.58)	–22.9 (1.39)
190 °C/2 h	–29.0 (2.62)	–29.9 (1.47)	–33.8 (1.86)
190 °C/3 h	–29.5 (0.97)	–32.2 (4.20)	–43.2 (1.20)
190 °C/4 h	–32.0 (0.61)	–39.6 (2.53)	–38.5 (1.44)
210 °C/1 h	–33.2 (0.74)	–35.4 (3.42)	–35.4 (1.70)
210 °C/2 h	–35.7 (1.01)	–34.7 (2.04)	–43.5 (2.28)
210 °C/3 h	–38.0 (1.75)	–43.3 (4.54)	–51.2 (0.41)
210 °C/4 h	–44.7 (3.04)	–45.8 (0.98)	–54.2 (0.48)

Mode of beech wood thermal treatment	Δa* – Due to thermal treatment		
	In air	In paraffin	In PEG 6000
100 °C/1 h	–0.1 (0.27)	5.9 (0.66)	5.7 (0.57)
100 °C/2 h	0.0 (0.25)	5.7 (0.54)	5.0 (3.39)
100 °C/3 h	0.3 (0.98)	5.6 (0.45)	6.2 (0.67)
100 °C/4 h	0.0 (0.26)	5.3 (0.50)	5.7 (0.50)
190 °C/1 h	1.4 (0.47)	5.7 (1.73)	5.5 (0.43)
190 °C/2 h	2.0 (1.81)	5.0 (0.63)	5.8 (1.13)
190 °C/3 h	1.9 (1.38)	6.4 (1.15)	4.0 (0.94)
190 °C/4 h	2.6 (0.97)	6.3 (1.05)	3.0 (1.23)
210 °C/1 h	–0.1 (1.05)	4.0 (0.57)	5.9 (0.55)
210 °C/2 h	0.7 (1.10)	1.6 (0.90)	4.1 (0.28)
210 °C/3 h	2.9 (0.99)	3.0 (1.05)	–1.6 (0.58)
210 °C/4 h	1.5 (0.49)	0.3 (0.93)	–3.8 (0.68)

Mode of beech wood thermal treatment	Δb* – Due to thermal treatment		
	In air	In paraffin	In PEG 6000
100 °C/1 h	–0.3 (0.14)	6.7 (0.27)	4.8 (0.17)
100 °C/2 h	–0.3 (0.23)	7.5 (0.34)	4.9 (0.28)
100 °C/3 h	–0.4 (0.15)	8.0 (0.58)	5.8 (0.52)
100 °C/4 h	–0.4 (0.18)	7.1 (0.53)	5.3 (0.53)
190 °C/1 h	1.3 (0.97)	5.0 (1.15)	5.0 (0.81)
190 °C/2 h	1.6 (0.75)	3.6 (0.54)	3.5 (0.76)
190 °C/3 h	1.1 (0.67)	4.2 (0.56)	–2.3 (0.70)
190 °C/4 h	–0.1 (0.72)	1.2 (1.19)	–4.3 (0.69)
210 °C/1 h	–1.4 (0.68)	0.8 (0.40)	2.6 (0.44)
210 °C/2 h	–3.9 (0.77)	–1.0 (0.36)	–4.3 (0.65)
210 °C/3 h	–7.6 (0.75)	–3.8 (0.82)	–11.9 (0.55)
210 °C/4 h	–7.6 (0.48)	–7.8 (0.96)	–12.9 (0.95)

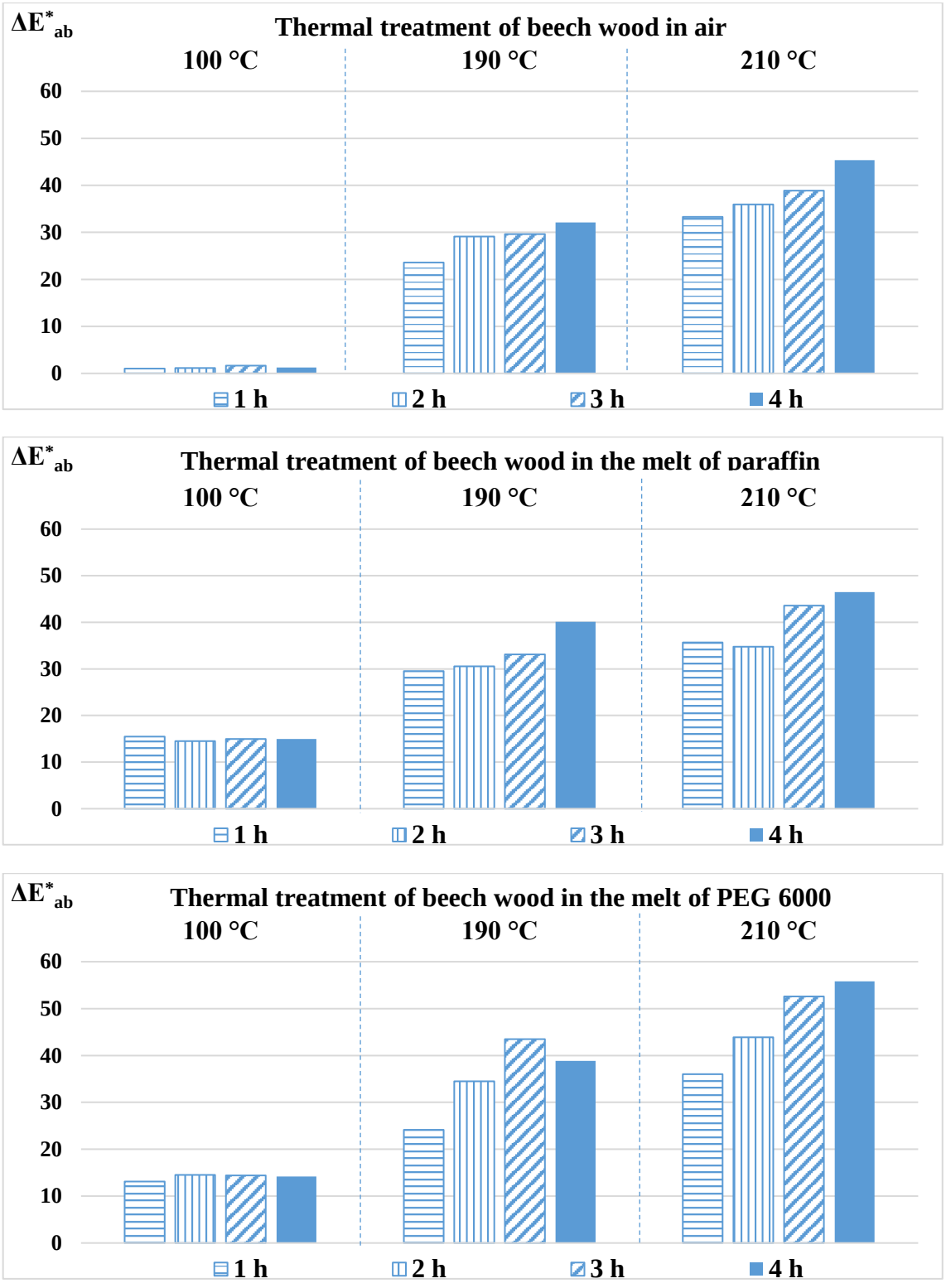

Fig. 3 The total color differences (ΔE^*_{ab}) of beech wood specimens due to their air-thermal, paraffin-thermal and PEG-thermal treatments.

The paraffin-thermal and PEG-thermal treatments of beech wood usually caused greater changes in its color comparing to the air-thermal treatment. This was typical mainly for the lower heating temperature of 100 ° C, when the total color difference (ΔE^*_{ab}) for the air-thermally treated specimens ranged only from 1 to 1.7, however, for the paraffin-thermally and PEG-thermally treated specimens from 13.1 to 15.5 (Fig. 3). It indirectly

means that paraffin and PEG 6000, both having a waxy consistency, significantly affected the color of beech wood specimens already at 100 °C in connection with their darkening, *i.e.,* without their thermal modification at 190 °C or 210 °C (Tab. 1, Figs. 7a and 8a). At using the modification temperatures of 190 °C and 210 °C, the ΔE^*_{ab} values were apparently higher from 23.6 to 55.8, however, without an evident depending on the medium (air, paraffin, or PEG 6000) used. Generally, the ΔE^*_{ab} values evidently increased with increasing the modification temperature from 190 °C to 210 °C, and with prolonging the modification time from 1 to 4 hours (Fig. 3).

Color changes of the thermally treated beech wood due to weathering

The color stability of the thermally treated wood is important for interior and mainly for outdoor exposures (REINPRECHT 2016). The color changes of beech wood specimens at the 6-weeks artificial weathering in the Xenotest were significantly influenced by the mode of thermal treatment (Tab 2, Fig. 4, Figs. 5-8).

Due to weathering, the brightness changes (ΔL*) of the air-thermally, paraffin-thermally and PEG-thermally treated beech wood specimens were specific (Tab. 2, Figs. 5-8). The reference specimens and specimens heated in paraffin at 100 °C due to weathering darkened, with ΔL* from + 1 to – 19 (Tab. 2, Figs. 5 and 7). In contrast, lighter shades after weathering obtained specimens heated at 100 °C in the melt of PEG 6000, and also specimens thermally modified at 190 °C or 210 °C in all used media. Mostly lightened specimens which were thermally modified in PEG 6000, with ΔL* from + 18.6 to + 32.6 (Tab. 2, Fig. 8).

Due to weathering, the reference and usually also the air-thermally treated beech wood specimens showed a positive change of the chromatic coordinate Δa*, *i.e.,* their shade turned to red (Tab. 2, Figs. 5 and 6). In contrast, the surfaces of paraffin-thermally modified specimens reached negative values of Δa*, *i.e.,* their shade turned to green (Tab. 2, Fig. 7). The surfaces of PEG-thermally modified specimens achieved after weathering different changes of Δa*, *i.e.,* specimens modified at 210 °C for 3 and 4 hours obtained redder shade, but the other ones changed color with a shift to green (Tab. 2, Fig. 8).

Beech wood specimens thermally modified at 190 °C or 210 °C achieved after weathering in the Xenotest a positive change of the chromatic coordinate Δb*, which means that their shade turned to yellow – the most at PEG-thermally modified specimens (Tab. 2, Figs. 6-8). In contrast, the change in Δb* was due to weathering usually negative for specimens heated at a lower temperature of 100 °C in the melt of paraffin as well as in the melt of PEG 6000 with a color shift to blue (Tab. 2, Figs. 7 and 8).

The total color difference of specimens heated at 100 °C in the melts of paraffin or PEG 6000 were due to artificial weathering usually the same (ΔE^*_{ab} approximately 15) with those of the reference ones (ΔE^*_{ab} equal 14.8) (Fig. 4). Specimens thermally modified in PEG 6000 at 190 °C or 210 °C obtained due to weathering in the Xenotest apparently higher values of ΔE^*_{ab} from 20.1 to 36.4, compared to those ones thermally modified in air with ΔE^*_{ab} from 5.6 to 13.2, and also to those ones thermally modified in paraffin with ΔE^*_{ab} from 7.2 to 15.7 (Fig. 4). This result means that beech wood thermally modified at 190 °C or 210 °C in the melt of PEG 6000 had apparently the less color stability at action of UV light and water during the artificial weathering.

Tab. 2 The color changes (ΔL*, Δa*, Δb*) of the air-thermally, paraffin-thermally and PEG-thermally treated beech wood specimens due to their 6-weeks artificial weathering in Xenotest.
Notes: Arithmetic means were determined from 8 values. Standard deviations are in parentheses. The Duncan test was performed in relation to reference specimens with significances: a = 99.9%, b = 99%, c = 95%, d < 95%.

Mode of beech wood thermal treatment	ΔL* – Due to following artificial weathering		
	Treated in air	Treated in paraffin	Treated in PEG 6000
100 °C/1 h	-13.1 (2.89) d	0.6 (1.44) a	8.3 (2.01) a
100 °C/2 h	-13.5 (3.28) d	-9.4 (1.15) c	15.1 (1.40) a
100 °C/3 h	-12.9 (3.33) d	-10.0 (1.59) c	12.1 (0.68) a
100 °C/4 h	-12.0 (3.45) d	-19.0 (1.15) b	10.4 (1.03) a
190 °C/1 h	9.7 (1.1) a	13.8 (0.60) a	18.6 (2.96) a
190 °C/2 h	11.7 (1.7) a	10.4 (2.22) a	22.5 (1.14) a
190 °C/3 h	6.1 (2.4) a	9.3 (0.77) a	30.4 (0.54) a
190 °C/4 h	3.8 (0.9) a	11.1 (1.19) a	32.6 (2.45) a
210 °C/1 h	5.2 (1.3) a	15.1 (1.12) a	20.6 (3.58) a
210 °C/2 h	3.8 (1.1) a	10.8 (0.80) a	32.3 (2.97) a
210 °C/3 h	4.2 (1.6) a	6.5 (0.98) a	25.2 (1.53) a
210 °C/4 h	9.8 (0.7) a	7.5 (2.76) a	30.1 (2.71) a
Reference	-13.1 (2.87)		

Mode of beech wood thermal treatment	Δa* – Due to following artificial weathering		
	Treated in air	Treated in paraffin	Treated in PEG 6000
100 °C/1 h	1.4 (1.03) d	-4.9 (0.51) a	-6.0 (3.19) a
100 °C/2 h	1.1 (0.93) d	-2.2 (0.52) a	-8.6 (0.16) a
100 °C/3 h	1.4 (0.78) d	-5.7 (0.48) a	-8.9 (0.32) a
100 °C/4 h	1.3 (1.11) d	-1.4 (0.38) a	-8.7 (0.08) a
190 °C/1 h	0.4 (0.83) d	-4.0 (0.47) a	-4.7 (2.08) a
190 °C/2 h	0.4 (0.79) d	-2.7 (0.84) a	-4.6 (0.60) a
190 °C/3 h	0.3 (1.14) d	-4.5 (0.29) a	-3.4 (0.19) a
190 °C/4 h	2.0 (0.25) d	-0.9 (0.19) a	-5.2 (0.76) a
210 °C/1 h	2.3 (0.75) d	-2.6 (0.34) a	-2:1 (1.06) a
210 °C/2 h	3.0 (0.47) b	-3.0 (0.59) a	-1.3 (0.90) b
210 °C/3 h	0.9 (0.58) d	-2.3 (0.46) a	4.2 (1.35) b
210 °C/4 h	-1.3 (0.46) d	0.0 (0.45) c	8.5 (0.39) a
Reference	1.2 (0.86)		

Mode of beech wood thermal treatment	Δb* – Due to following artificial weathering		
	Treated in air	Treated in paraffin	Treated in PEG 6000
100 °C/1 h	6.9 (2.29) d	-2.5 (0.60) a	1.0 (0.16) a
100 °C/2 h	6.9 (2.15) d	-5.0 (0.94) a	-1.7 (0.88) a
100 °C/3 h	7.1 (1.76) d	-10.4 (0.76) a	-7.3 (0.91) a
100 °C/4 h	6.6 (1.82) d	-4.4 (0.89) a	-5.5 (0.98) a
190 °C/1 h	5.7 (0.92) d	0.0 (0.83) a	4.1 (0.71) c
190 °C/2 h	5.0 (2.12) d	0.2 (0.57) a	3.6 (1.39) c
190 °C/3 h	1.3 (0.62) a	3.5 (0.89) b	5.0 (0.89) d
190 °C/4 h	3.5 (0.44) b	3.1 (0.55) a	6.5 (1.47) d
210 °C/1 h	6.1 (1.31) d	3.1 (0.49) a	8.1 (1.20) d
210 °C/2 h	6.5 (0.51) d	-0.8 (1.07) a	9.4 (1.10) c
210 °C/3 h	4.9 (1.29) d	2.1 (0.55) a	14.5 (0.72) a
210 °C/4 h	7.7 (0.96) d	4.5 (0.89) b	18.6 (0.57) a
Reference	6.7 (2.23)		

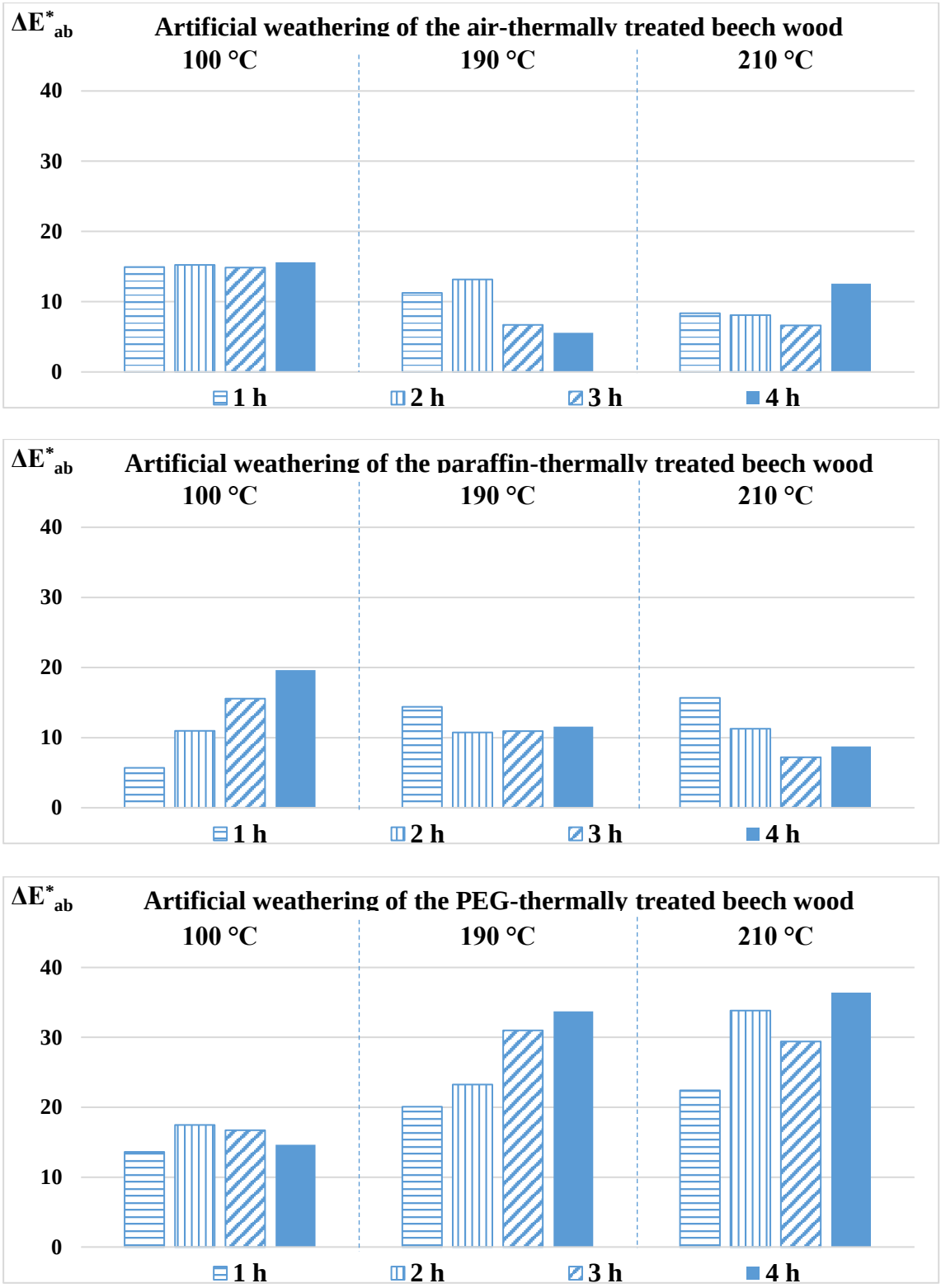

Fig. 4 The total color differences (ΔE^*_{ab}) of the air-thermally, paraffin-thermally and PEG-thermally treated beech wood specimens due to their 6-weeks artificial weathering in Xenotest.

Original beech wood Weathered beech wood

Fig. 5 The color of the original beech wood specimen (a) and the color change together with the longitudinal cracks created at the 6-weeks weathering in Xenotest (b).

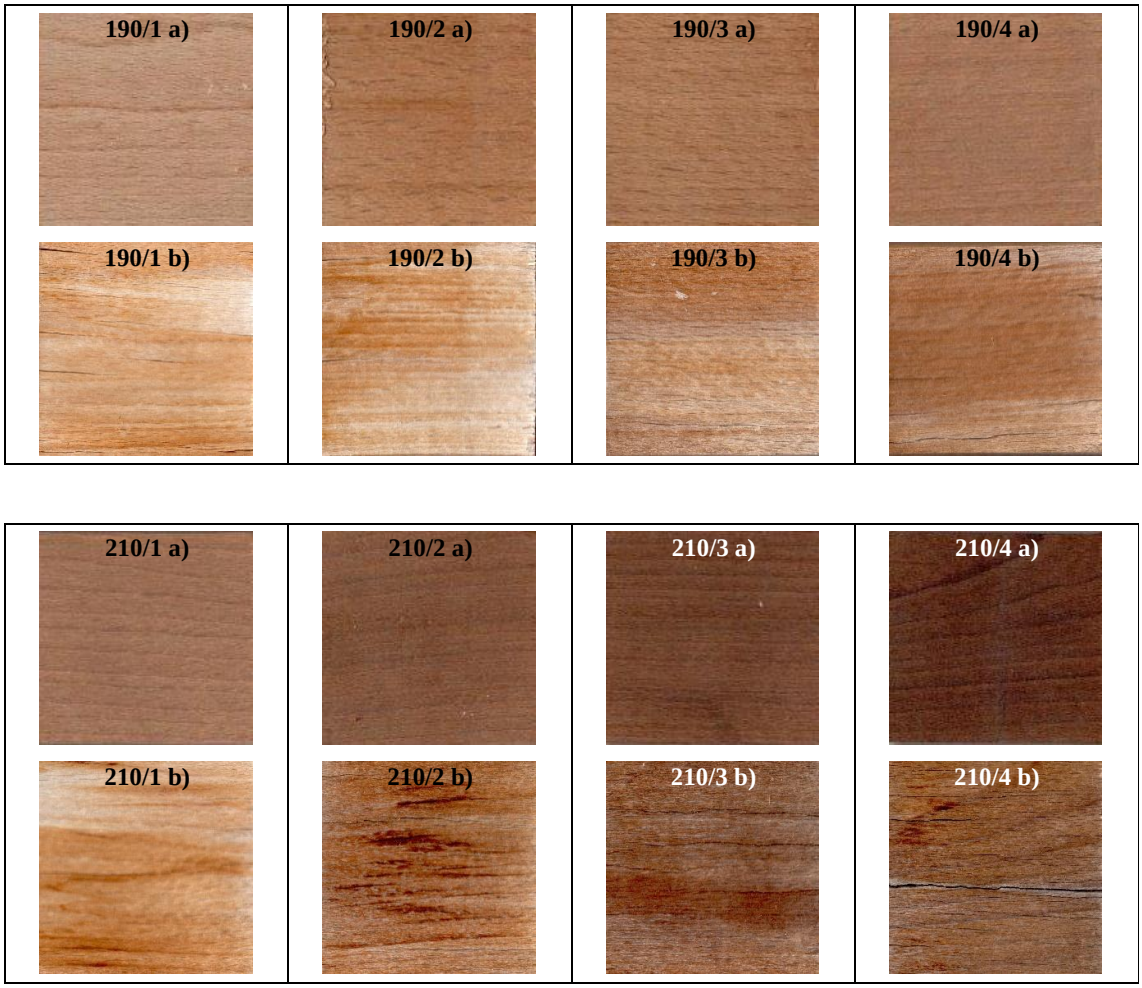

Fig. 6 The colors of the beech wood specimens thermally modified in air at 190 °C and 210 °C during 1–4 hours (a), and the color changes together with the longitudinal cracks created at the 6-weeks weathering in Xenotest (b).

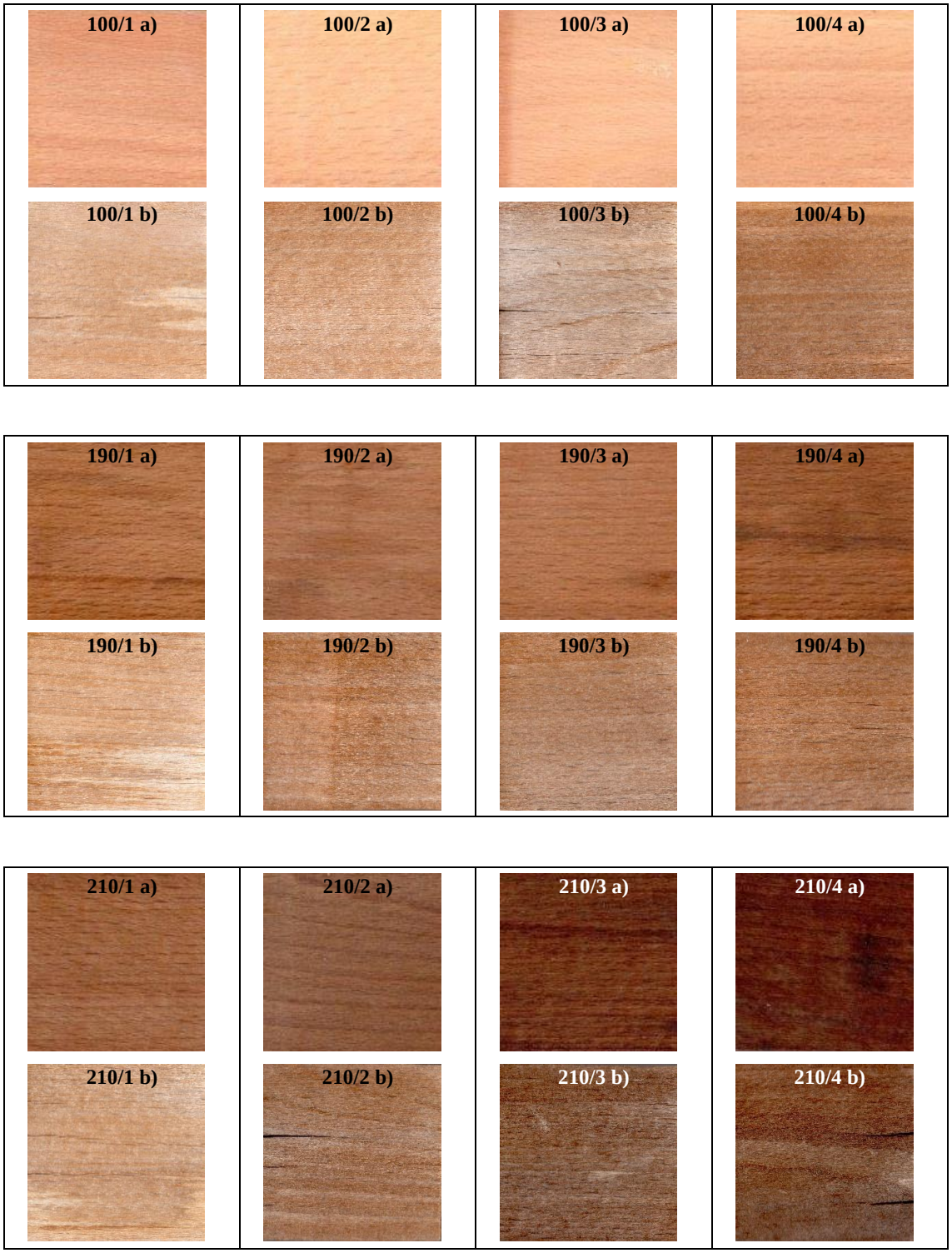

Fig. 7 The colors of the beech wood specimens thermally treated in paraffin at 100 °C, 190 °C and 210 °C during 1 – 4 hours (a), and the color changes (for the hardest modification modes "210 °C/2–4h" as well as the longitudinal cracks) created at the 6-weeks weathering in Xenotest (b).

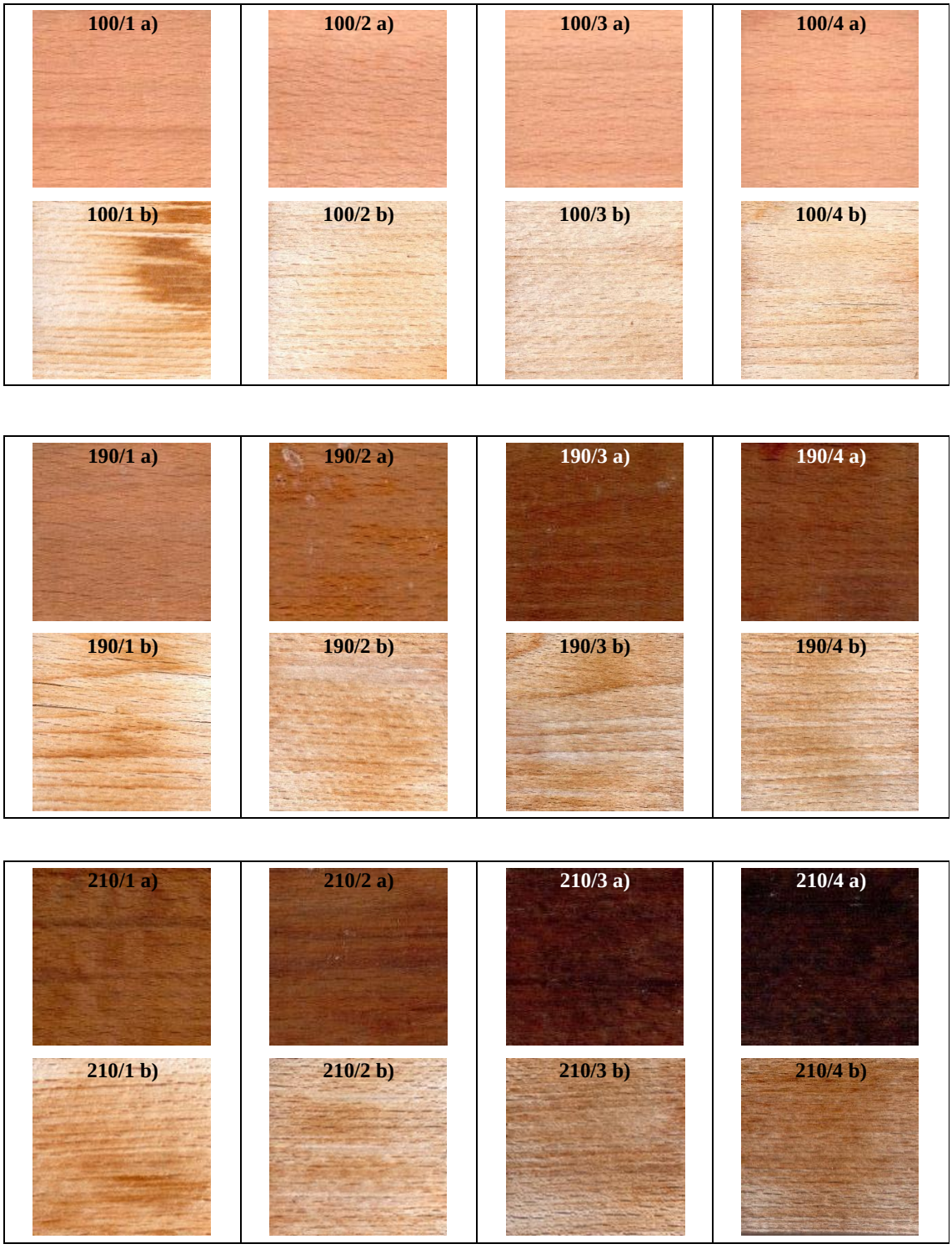

Fig. 8 The colors of the beech wood specimens thermally treated in PEG 6000 at 100 °C, 190 °C and 210 °C during 1 – 4 hours (a), and the color changes created at the 6-weeks weathering in Xenotest (b).

Cracks created in the thermally treated beech wood at weathering

The outdoor weathering of wood is often connected with creation of cracks in its surfaces. During artificial weathering in the Xenotest, the cracks formed in surfaces of the reference specimens (Tab. 3, Fig. 5b), and also in surfaces of the air-thermally and paraffin-thermally treated specimens (Tab. 3, Figs. 6b and 7b).

TIRALOVÁ and MAMOŇOVÁ (2005) found out that during thermal modification of beech wood at 205 °C were created in its surfaces only microscopically visible cracks. Similarly, in the present experiment no macroscopic cracks occurred in the thermally treated beech wood specimens (Figs. 6a–8a).

It indirectly means, that due the following cyclic action of UV radiation and water in the Xenotest the potentially created microscopic (*i.e.*, macroscopically invisible) cracks in the surfaces of the air-thermally modified beech wood and less often also in the paraffin-thermally modified beech wood specimens gradually increased and stayed visible by a human eye (Tab. 3, Figs. 6b and 7b). The paraffin-thermally modified specimens were characterized by a slightly better resistance to the formation of surface cracks than the air-thermally ones. It can be attributed to the hydrophobic nature of paraffin and an increase in the water resistance of the surface of the beech wood treated with paraffin. At the same time is valid the fact that during the thermal modification of wood in the environment of oils and waxes (*i.e.*, without the presence of air) oxidation reactions in the wood components slowdown, which also results in the reduction of cracks in the wood at its thermal modification (HILL 2006). From the point of view of the weathering effect on the creation of cracks in the paraffin-thermally modified beech wood, the modification process at 190 °C lasting for 1, 2, 3 and 4 hours appears the most optimal as no cracks were detect (Tab. 3, Fig. 7b).

Due to weathering of the PEG-thermally modified beech wood specimens no cracks formed at all. It means that PEG 6000 had an even more positive effect on the elimination of cracking the beech wood in its surfaces (Tab. 3, Fig. 8b).

Tab. 3 The cracks in the air-thermally, paraffin-thermally and PEG-thermally treated beech wood specimens due to their 6-weeks artificial weathering in Xenotest.
Note: Determined from 2 specimens.

Modes of beech wood thermal treatment	**Cracks in wood surfaces created at the artificial weathering (0-3)**		
	Treated in air	**Treated in paraffin**	**Treated in PEG 6000**
100 °C/1 h	1	1	0
100 °C/2 h	2	0	0
100 °C/3 h	1	1	0
100 °C/4 h	1	0	0
190 °C/1 h	1	0	0
190 °C/2 h	1	0	0
190 °C/3 h	1	0	0
190 °C/4 h	1	0	0
210 °C/1 h	0	1	0
210 °C/2 h	1	2	0
210 °C/3 h	1	1	0
210 °C/4 h	2	2	0
Reference	2		

CONCLUSIONS

- The thermal modification of beech wood at 190 °C and 210 °C lasting from 1 to 4 h in three different media – air, paraffin, PEG 6000 – caused always its apparent darkening when ΔL^* ranged from – 22.9 up to – 54.2.

- Following exposure of the thermally treated beech wood to artificial weathering in the Xenotest, *i.e.*, with presence of UV light and water, reflected in its different color changes. The highest total color difference ΔE^*_{ab} from 20.1 to 36.4 had the PEG-thermally modified (at 190 °C and 210 °C) beech wood, which evidently lightened with ΔL^* from 18.6 to 32.6. On contrary, darkening was determined only for air-thermally and paraffin-thermally heated (at 100 °C) beech wood.
- The PEG-thermal modification occurred as the best prevention of crack formation in beech wood surfaces.

REFERENCES

ANDOR, T., LAGAŇA, R. 2018. Selected properties of thermally treated ash wood. In Acta Facultatis Xylologiae Zvolen, 60(1): 51–60. doi: 10.17423/afx.2018.60.1.06.

AYADI, N., LEJEUNE, F., CHARRIER, F., CHARRIER, B., MERLIN, A. 2003. Colour stability of heat treated wood during artificial weathering. In Holz als Roh- und Werkstoff, 61(3): 221–226. doi: 10.1007/s00107-003-0389-2.

AWOYEMI, L., COOPER, P. A., UNG, T. Y. 2009. In-treatment cooling during thermal modification of wood in soy oil medium: soy oil uptake, wettability, water uptake and swelling properties. In European Journal of Wood and Wood Products, 67(4): 465–470. doi: 10.1007/s00107-009-0346-9.

BEKHTA P., NIEMZ P. 2003. Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. In Holzforschung. 57(5): 539–546. doi: 10.1515/HF.2003.080.

CAI, C., ANTIKAINEN, J., LUOSTARINEN, K., MONONEN, K., HERAJARVI, H. 2018. Wetting-induced changes on the surface of thermally modified Scots pine and Norway spruce wood. In Wood Science and Technology, 52(5): 1181–1193. doi:10.1007/s00226-018-1030-1.

CHEN, J., WANG, Y., CAO, J., WANG, W. 2020. Improved water repellency and dimensional stability of wood via impregnation with an epoxidized linseed oil and carnauba wax complex emulsion. In Forests, 11(3): 271–283. doi: 10.3390/f11030271.

CIE. 2007. Colorimetry - Part 4: CIE 1976 L*a*b* COLOUR SPACE. CIE DS 0144.3/E:2007, CIE Central Bureau, Vienna, Austria.

CIRULE, D., SANSONETTI, E., ANDERSONE, I., KUKA, E., ANDERSONS, B. 2021. Enhancing thermally modified wood stability against discoloration. In Coatings, 11(1): 81–93. doi: 10.3390/coatings11010081.

DUBEY, M. K., PANG, S., WALKER, J. 2010. Color and dimensional stability of oil heat treated radiata pinewood after accelerated UV weathering. In Forest Products Journal, 60(5): 453–459. doi: 10.13073/0015-7473-60.5.453.

DUBEY, M. K., PANG S., WALKER J. 2012. Changes in chemistry, color, dimensional stability and fungal resistance of *Pinus radiata* D. Don wood with oil heat-treatment. In Holzforschung, 66(1): 49–57. doi: 10.1515/HF.2011.117.

DZURENDA, L., DUDIAK, M. 2020. Changes in wood tree species *Fagus sylvatica* L. and characteristics of the thermal process of modifying its color with saturated water steam. In Advances in Ecological and Environmental Research, 5(4): 142-156. ISSN 2517-9454.

EN 350. 2016. Durability of wood and wood-based products. Testing and classification of the durability to biological agents of wood and wood-based materials. European Committee for Standardization: Brussels, Belgium.

EN 927-6. 2018. Paints and varnishes. Coating materials and coating systems for exterior wood - Exposure of wood coatings to artificial weathering using fluorescent UV lamps and water. European Committee for Standardization: Brussels, Belgium.

ESTEVES, B., DOMINGOS, I., PEREIRA, H. 2008. Pine wood modification by heat treatment in air. In BioResources, 3(1): 142-154. doi: 10.15376/biores.3.1.142-154.

ESTEVES, B., PEREIRA, H. 2009. Wood modification by heat treatment: A review. In BioResources, 4(1): 370-404. doi: 10.15376/biores.4.1.370-404.

HILL, C. A. S. 2006. Wood modification – chemical, thermal and other processes. Chichester: John Wiley & Sons, Ltd., UK, 2006, 260 p.
HOCKER, E., ALMKVIST, G., SAHLSTEDT, M. 2012. The Vasa experience with polyethylene glycol: A conservator's perspective. In Journal of Cultural Heritage, 2012, 13 (3): 175–182. doi: 10.1016/j.culher.2012.01.017.
HON, D. N. S., SHIRAISHI, N. 2000. Wood and celulosis chemistry. Boca Raton: CRC Press, LLC, Florida, USA, 928 p.
HUANG, X., KOCAEFE, D., KOCAEFE, Y., BOLUK, Y., PICHETTE, A. 2012. Study of the degradation behavior of heat-treated jack pine (*Pinus banksiana*) under artificial sunlight irradiation. In Polymer degradation and stability, 97(7): 1197–1214. doi: 10.1016/j.polymdegradstab.2012.03.022.
KLEMENT, I., VILKOVSKÝ, P., VILKOVSKÁ, T. 2020. The effect of contact-drying on physical properties of European beech (*Fagus sylvatica* L.). In Forests, 11(8): 890–900. doi: 10.3390/f11080890.
KOCAEFE, D., HUANG, X., KOCAEFE, Y. 2015. Dimensional stabilization of wood. In Current Forestry Reports, 1(3): 151-161. doi:10.1007/s40725-015-0017-5.
LESAR, B., HUMAR, M. 2011. Use of wax emulsion for improvement of wood durability and sorption properties. In European Journal of Wood and Wood Products, 69(2): 231–238. doi: 10.1007/s00107-010-0425-y.
MAJKA, J., ZBOROWSKA, M., FEJFER, M., WALISZEWSKA, B., OLEK, W. 2018. Dimensional stability and hygroscopic properties of PEG treated irregularly degraded waterlogged Scots pine wood. In Journal of Cultural Heritage, 2018, 31: 133–140. doi: 10.1016/j.culher.2017.12.002.
NUOPPONEN, M., WIKBERG, H., VUORINEN, T., SIRKKA, L. M., JÄMSÄ, S., VIITANIEMI, P. 2004. Heat-treated softwood exposed to weathering. In Journal of Applied Polymer Science, 91(4): 2128–2134. doi: 10.1002/app.13351.
REINPRECHT, L. 2016. Wood deterioration, protection and maintenance. Chichester: John Wiley & Sons, Ltd., UK, 357 p.
REINPRECHT, L., REPÁK, M. 2019. The impact of paraffin-thermal modification of beech wood on its biological, physical and mechanical properties. In Forests, 10(12): 1102–1115. doi: 10.3390/f10121102.
REPÁK, M., REINPRECHT, L. 2020. Physico-mechanical properties of thermally modified beech wood affected by its pre-treatment with polyethylene glycol. In Acta Facultatis Xylologiae Zvolen, 62(1): 67–78. doi: 10.17423/afx.2020.62.1.06.
SRINIVAS, K., PANDEY, K. K. 2012. Effect of Heat Treatment on Color Changes, Dimensional Stability, and Mechanical Properties of Wood. In Journal of Wood Chemistry and Technology, 2012, 32(4): 304–316. doi:10.1080/02773813.2012.674170.
SUNDQVIST, B., MORÉN, T. 2002. The influence of wood polymers and extractives on wood colour induced by hydrothermal treatment. In Holz als Roh- und Werkstoff, 60(5): 375–376. doi: 10.1007/s00107-002-0320-2.
TEMIZ, A., TERZIEV, N., JACOBSEN, B., EIKENES, M. 2006. Weathering, water absorption, and durability of silicon, acetylated, and heat-treated wood. In Journal of Applied Polymer Science, 102(5): 4506–4513. doi: 10.1002/app.24878.
TIRALOVÁ, Z., MAMOŇOVÁ, M. 2005. Aktivita celulózovornej huby *Gloeophyllum trabeum* na termicky upravenom dreve – mikroskopická analýza. In Drevoznehodnocujúce huby 2005, Zvolen: Technická univerzita vo Zvolene, p. 65–68. ISBN 80-228-1535-7.
TJEERDSMA, B. F., BOONSTRA, M., PIZZI, A., TEKELY, P., MILITZ, H. 1998. Characterisation of the thermally modified wood: molecular reasons for wood performance improvement. In Holz als Roh- und Werkstof, 56(3): 149–153. doi: 10.1007/s001070050287.
YANG, L., LIU, H. -H. 2020. Effect of a Combination of moderate-temperature heat treatment and subsequent wax impregnation on wood hygroscopicity, dimensional stability, and mechanical properties. In Forests, 11(9): 920–928. doi: 10.3390/f11090920.
YANG, L., HAN, T., FU, Y. 2020. Effect of heat treatment and wax impregnation on dimensional stability of *Pterocarpus macrocarpus* wood. In Wood Research, 65(6): 963–974. doi: http://doi.org/10.37763/wr.1336-4561/65.6.963974.

YILDIZ, S., GEZERB, D., YILDIZ, C. 2006. Mechanical and chemical behaviour of spruce wood modified by heat. In Building and Environment, 41(12): 1762–1766. doi:10.1016/j.buildenv.2005.07.017.
YILDIZ, S., YILDIZ, U. C., TOMAK MAIL, E. D. 2011. The effects of natural weathering on the properties of heat-treated alder wood. In BioResources, 6(3): 2504–2521.
WANG, J. Y., AND COOPER, P. A. 2005. Effect of oil type, temperature and time on moisture properties of hot oil-treated wood. In Holz als Roh- und Werkstoff, 63(6): 417–422. doi: 10.1007/s00107-005-0033-4.
ZHANG, J. -W., LIU, H.,-H., YANG, L., HAN, T. -Q., YIN, Q. 2020. Effect of moderate temperature thermal modification combined with wax impregnation on wood properties. In Applied Sciences, 10(22): 8231–8242. doi: 10.3390/app10228231.

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