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ORIGINAL ARTICLE

Natural weathering of soft- and hardwoods modified by contact and flame charring methods

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Abstract

Exterior cladding boards benefit from a known service life that makes planning of maintenance and replacement procedures easier. Among the different wood modification methods, surface charring of wood is expected to increase the lifespan of wooden elements in building façades. This paper reports the properties of surface charred Norway spruce, Scots pine and Silver birch in Southern Finnish climate over a natural weathering period of one year. Several modifications were examined, namely variants of contact and flame charring. These also included oiled and brushed surfaces. The flame charred samples of spruce and birch withstood the weathering well, with some minor flaking and cracking. The thick pine samples cracked extensively regardless of modification, raising questions on suitable density and thickness of wood destined for a charring modification. Contact charring did not seem suitable for outside uses at least in direct sunlight, as the colors faded, and surfaces cracked within all examined groups. The spectroscopical methods employed also revealed degradation of contact charred wood lignin, whereas the flame charred surface consisted mostly of recalcitrant carbon structures rather inert towards weathering. This highlights the importance of sufficient structural degradation of wood components in creating a weathering resistant surface, and also shows that a thicker thermally modified layer does not necessarily improve the weatherability in contact charred wood.

1 Introduction

Wooden exteriors have been shown to have a lower environmental impact than other common construction materials such as concrete (Hill 2019). Improving energy efficiency of buildings reduces the use phase emissions but highlights the durability of applied materials. All products, also façade boards, benefit from predictability, as a known service life will help assess the environmental and economical loads of buildings more accurately. Coatings are by far the most common treatment for wood surfaces (Sandak et al. 2019). Coated wooden façade elements require upkeeping with repeated cleaning, recoating and replacement to retain visual appearance and structural protection. Although modern coatings have progressively become greener (e.g., solvent to waterborne formulations), the environmental profile of wooden components would benefit from using no coating at all. However, leaving wood untreated will expose it to weathering that may change its appearance to a point of "aesthetic instability", that necessitates replacement even if other functions are still fulfilled (Sandak et al. 2021). The UV-radiation, in combination with water and heat, causes degradation of wood components, leading to erosion, dimensional distortion, increased roughness, discoloration and increased friability (Feist and Hon 1984). Wood surfaces can be protected using, for example, UV-stabilizers or enzymatic treatments, and modifications such as acetylation may increase surface resistance (Sandak et al. 2019). However, weathering damages are characteristic also for thermally and chemically modified wood and in the course of time the surfaces become eroded and unevenly washed out (Jämsä et al. 2000; Evans 2009; Sandak et al. 2019). In general, these modification methods are also relatively cost-intensive which limits common use. Surface charring of wood is a potentially cost-effective and low-maintenance option. This type of modification method (similar to the Japanese yakisugi) has seen a rise in popularity in recent years (Hasburgh et al. 2021). It is a one-sided modification method that targets only the exposed surface. Thus, in contrast to traditional thermal

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modification, the process is rather fast and leaves most of the wood in its natural state. The result is a fully organic, natural “coating”. The surface is, in essence, black, but different appearances can be created with different methods (i.e., contact vs. flame charring, modification duration) and further processing (brushing, oiling, coating) to suit multiple preferences, needs and services.

Although some peer-reviewed research papers have been published in recent years, the data on the exact behavior of charred surfaces during weathering are very limited. In general, charring induces thermolysis of components that results in a carbonaceous residue. The composition of the char depends on the used method, but to simplify, the further the thermolysis proceeds, the more inert the surface will be. Kampe and Pfriem (2018) and Kymäläinen et al. (2020) have published results on natural weathering of Norway spruce charred with experimental devices—one with gas flames and one utilizing a continuous contact heating method. Both reported rather good weatherability when assessed visually but noted changes in the modified lignin component that indicates photodegradation. The protective function of the char was speculated to be connected to thickness of the char layer, and not so much to the thermally degraded lignin component. The char layer thickness, as well as several other properties of the char, depend heavily on the technique used, namely temperature and modification time. Similarly, wood species has a great effect since the cell structure of char is similar to the original unmodified wood (Zicherman and Williamson 1981), meaning that pores and cells retain their shape and size. For example, spruce still shows pit aspiration that reduces the permeability compared to, for example, Scots pine (Kymäläinen et al. 2017).

The aim of this paper is to compare surfaces created with two different charring techniques: a contact heating method with controlled temperature and time that maximizes the thickness of the char and pyrolysis layers, and a flame charring method that leaves the surface heavily degraded in a short time. The goal is to compare the weathering characteristics of the charred surfaces of different wood species in Southern Finnish climate during a period of 12 months. Norway spruce and Scots pine were used to represent common softwoods. To accommodate comparison of soft- and hardwood surfaces and evaluate the weatherability of a species not currently used for exterior claddings, Silver birch was also included in the test regime. A standard method was used to assess surface changes such as color and molding, and spectroscopical means were employed to evaluate the behavior of chemical components, mainly the lignin, in different cases.

2 Materials and methods

2.1 Material preparation

The materials used in this study were mature Norway spruce (*Picea abies* (L.) H. Karst), Scots pine (*Pinus sylvestris* L.) and Silver birch (*Betula pendula* L.) sapwood sourced from Southern Finland. The thicknesses of the tangentially cut boards were 24, 25 and 25 mm, respectively, and average air-dry densities were 410, 590 and 680 kg/m^3, respectively. The boards were planed on pith side, which was always the surface exposed to modification. The samples for contact charring were cut to 100 × 100 mm, which were also the dimensions of the hot plate. Flame charring was implemented on 1-m-long boards, which were subsequentially cut to 100 × 100 mm. The starting moisture content (MC) was 8–12%.

The temperature of the hot plate was set to 320 °C, and the modification duration was 30 min. The conditions were chosen on the basis of preliminary testing, with the goal of minimizing surface cracking while maintaining a high enough temperature to induce sufficient thermolysis of components (over 300 °C), as well as forming a thick thermally modified layer beneath the surface (long holding time) (Kymäläinen et al. 2018). The char layer thickness was about 1–2 mm and 4–5 mm when including the dark-brown transition zone. A weight was used on top of the sample to ensure even connection throughout the entire specimen surface. Flame charring was executed outdoors with a butane torch, held appr. 20 cm above the surface. The torch was moved slowly along the length of the board until a consistent crack pattern formed. This generally took 2.5 to 3 min for one board. Half of the boards were brushed to investigate the contribution of the cracked char layer to weatherability. The char layer thickness (including the transition zone) was about 1.0–1.3 mm for all unbrushed samples.

Unmodified and painted references were used. The paint was a common water-soluble black acrylate exterior wood paint (Pika-Teho, Tikkurila OYJ, Vantaa, Finland). The samples were lightly sanded and painted once with an acrylate primer (Ultra Primer, Tikkurila OYJ, Vantaa, Finland), followed by two coats of paint as instructed by the manufacturer. A flame charred surface is sooty and staining, and western manufacturers often choose to seal the surface with oils or waxes. To investigate the contribution of a simple, organic, low-cost coating and to determine whether the char layer would become more stable against wear, doubles were coated with cold-pressed linseed oil. The oil was applied liberally with a brush, let dry and then applied again as instructed by the manufacturer (Woodcare. guide, Rakennuskemia, Finland). Excess oil was blotted with a paper towel. The sides of all samples were sealed once with a solvent-soluble alkyd paint (Miranol, Tikkurila OYJ, Vantaa, Finland). The transverse sides were sealed with a double layer. The backs of the samples were not treated in any way. Table 1 explains the codes used to identify the samples. Four samples per modification were used, of which one was left as the inside reference and three subjected to weathering.

2.2 Natural weathering setup and analysis

The weathering test followed the standard procedure SFS-EN 927-3 (2019) for a duration of 12 months. General appearance, color change, flaking, mold growth and cracking were evaluated on a scale of 0 to 5, where 0 stands for no visible defects and 5 for dense pattern of defects. The size of the samples was smaller than dictated by the standard because of the hot plate dimensions. CIELab color space was measured with Spectrolino color analyzer (X-Rite GmbH, Switzerland) and recorded with accompanying software Keywizard v2.5 from five points per sample. The points were situated on each corner and the center and values averaged without separating early- and latewood. The viewing angle was 10°, calibrated against paper white, with D65 illumination. After initial measurements, a weathering rack was placed on an open, unshaded area facing South with the samples at an inclination of 45°. About 0.5 cm from the top and bottom of samples was left unexposed because of rack fastenings. After one year of weathering the color measurements were repeated and differences in values L^*, a^* and b^* were calculated as determined by SFS-EN ISO/CIE 11664-4 (2019). The CIELab color difference ΔE^*_{ab} was calculated as

$$\Delta \mathrm{E}^*_{ab} = \sqrt{\left(L^*_2 - L^*_1\right)^2 + \left(a^*_2 - a^*_1\right)^2 + \left(b^*_2 - b^*_1\right)^2} \qquad (1)$$

A Spectrum Watchdog Series 1450 (Spectrum Technologies, Aurora, IL, USA) was used to log temperature, relative humidity and rainfall at the site (Otaniemi, Espoo, Finland). The color values were analyzed within species between modifications and within modification between species using one-way ANOVA and post hoc testing by Tukey–Kramer method.

Table 1 Codes used for sample identification

Modification	Code
Unmodified reference	Ref
Oiled reference	Ref-O
Painted reference	Paint
Contact charred	320
Contact charred, oiled	320-O
Flame charred	F
Flame charred, oiled	F-O
Flame charred, brushed	FB
Flame charred, brushed, oiled	FB-O

2.3 ATR-FTIR

ATR-FTIR was used to evaluate changes in the surface functional groups after the weathering. Thin surface shavings were extracted with a razor blade from a weathered sample and the reference stored indoors. The shavings were dried to 0% MC, placed in a Spectrum Two ATR-FTIR (Perkin Elmer, Waltham MA), and three to four spectra were recorded with a resolution of 0.5 cm^{-1} in the wavelength range 4000–500 cm^{-1}. Ten scans per measurement were obtained and the spectra were automatically baseline corrected with the software Spectrum IR. The spectra were further processed by using the i-baseline function to facilitate comparison, setting the lowest valley to zero. Afterwards the spectra were normalized to highest peak (= 1). Difference spectra were calculated between inside stored reference and weathered sample averages. From FTIR, the effect of weathering in the three different species was analyzed by a ratio of lignin and carbohydrate absorbances ($I_{\mathrm{lig}}/I_{\mathrm{carb}}$) (Živković et al. 2016). The lignin aromatic band at ~ 1510 cm^{-1} for softwoods, 1504 cm^{-1} for hardwoods (Barker and Owen 1999) and the polysaccharide band at 1374 cm^{-1}, were selected to assess the lignin degradation due to the weathering. The peak for carbohydrate at 1374 cm^{-1} was selected due to its least variability among species.

2.4 Raman spectroscopy

The flame charred surface had deteriorated to a point that made comparison of peaks using the FTIR impossible. Therefore, to further elucidate the changes taking place in contact and flame charred wood surfaces, Raman spectroscopy was included. The measurements were performed with a 532 nm excitation laser (inVia™ Qontor, Renishaw, UK). The spectra were recorded at the surface of modified samples. Each spectrum was collected with 30 accumulations, 10% of laser power and 0.3 of exposure time. The high-resolution spectra were collected at 2400 l/mm grating and centered at 1400 cm^{-1}. WiRE5 software was applied for baseline correction at polynomial order of 2. A ratio between intensities~1350 cm^{-1} and~1580 cm^{-1} corresponding to D and G bands, respectively, was calculated. This ratio of peaks leads to a self-normalization and enables an overall comparison among samples.

3 Results and discussion

3.1 Weathering details

The relative humidity, average monthly temperature and cumulative rainfall logged on site are shown in Fig. 1. Monthly average temperatures ranged from – 6.9 to 17.1 °C, with a low in February and high in June. The winter had an average monthly snow cover of 150–284 mm between January and March, during which time the rainfall measuring bucket was blocked with snow. For this period, the bottom rows of samples were also blanketed with wind-blown piles of snow. No visually detectable differences dependent on the placing were seen between the rows, thus this detail was omitted from the further analysis.

3.2 Visual evaluation after natural weathering

3.2.1 General appearance and molding of the samples

References were extensively grayed and worn, and loose fibers were easily detected. The birch references were especially damaged by the weathering and hosted more mold in comparison to softwood references. This was not surprising, as untreated birch is not generally recommended for outside use because of a tendency for molding. Thermally modified birch wood can, however, also be used in exteriors (International ThermoWood Association 2021). The weathering damages of oiled references (Ref-O; all species) were worse than those of unoiled ones, especially in the context of molding. All discoloring fungal growth was counted as mold, i.e., possible blue stain was not separated. The general appearance of the contact charred samples was worn, cracked and faded, and the flame charred and brushed samples (FB and FB–O) showed similar changes. In contrast, the flame charred, unbrushed samples (F and F–O) withstood weathering well. There was no visible mold, very limited surface cracking and hardly any flaking. Leaching was not directly measured, but no visible deposits had accumulated beneath the samples and erosion of flame charred surfaces was modest. Detailed information on measured defects can be found in Supplementary Information Table S1.

The oiling mainly caused more problems than benefits. Cold-pressed linseed oil is easily absorbed into the wood and increases hydrophobicity. As a natural wood protective coating it is recommended by several manufacturers also for outside use, but it may also increase molding. It is often found in natural oil paints in boiled form. The oiled surfaces gathered more dirt (e.g., pollen) than unoiled samples, which may explain the more extensive molding. However, the flame charred and oiled samples seemed to have fared the best out of all the samples. The oil was quickly absorbed into the porous surface and clearly contributed to binding the char. The F–O samples showed less flaking, and the surface was less sooty to touch.

3.2.2 Cracking and flaking

Flaking was recorded from charred and painted samples by assessing the defect quantity per sample area, as well as estimating the surface area affected by the flaking in

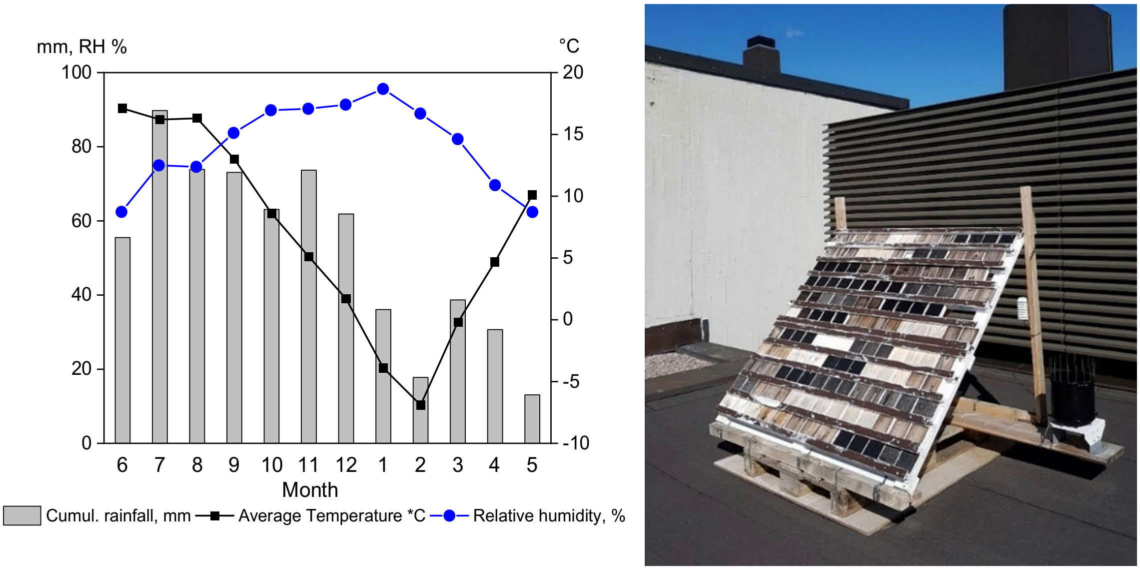

Fig. 1 Left: Relative humidity (%), monthly rainfall (mm) and averages of monthly temperature (°C); Right: The weathering rack after three months of weathering in September 2020

percentages. Cracking was evaluated visually based on the quantity of cracks (0–5), size of largest cracks (0–5), as well as number of largest cracks. The depth of deepest cracks was evaluated on a scale of 1 to 3 where 1 = checking, 2 = penetrates topcoat, 3 = penetrates whole system. Topcoat is here considered equal to char layer and whole system as char plus transition layer. Detailed data on both flaking and cracking is found in Table S1. The cracking (quantity of defects), evaluated on a scale of 0 to 5, is shown Fig. 2a–c to give a visual overview on the effect of treatment and species on cracking behavior.

The pine samples cracked heavily almost regardless of modification—only the painted references showed negligible cracking. The material used was mature pine sapwood with a density of about 590 kg/m^3. This is above the usually quoted range for Finnish-grown Scots pine (370–550 kg/m^3; Puuinfo 2020). The total number of cracks was about the same as for weathered spruce, but they were deeper: some of the samples had cracked halfway through the entire specimen (Fig. 3). Thick boards are recommended for exterior claddings, and the basic recommendation in Finland is minimum 23 mm (RT 82-10829 2004). The higher mass helps reduce moisture-driven dimensional changes as the moisture has a larger volume to distribute over. Thickness was therefore prioritized when choosing boards for this experiment. Although higher density woods tend to erode slower than lower density woods (Sell and Feist 1986), Sjökvist et al. (2019) reported that high-density spruce wood suffered from more cracks, and the sorption differences between low- and high-density samples were more connected to the coating performance. Because the painted pine references remained intact, it may be concluded that the wood was not too dense for outside use, rather too dense for one-sided charring. It is likely the dense material accumulated more stresses during modification, which then released during weathering and resulted in severe cracking. One-sided charring creates sharp temperature and moisture gradients causing strong shrinkage and swelling stresses and, consequently, microcracking of the wood. These microcracks then easily transform into macrocracks due to cyclic drying and wetting and concomitant contraction and swelling. Contact charring attempts to avoid some of these problems by reducing the modification temperature and prolonging the modification time, but it seems this slower regime does not serve to reduce the cracking but rather increases it. Moreover, thermally modified wood has been reported to crack, even more than unmodified wood, when exposed to cyclic humidity conditions, despite the lower hydrophilicity (Altgen et al. 2017). This is likely a result of the more brittle nature of the wood. Additionally, existing microcracks caused by wood anisotropy, annual ring structure, etc., and originating from kiln-drying, contribute to cracking of wood (Bucur 2011; Altgen et al. 2017).

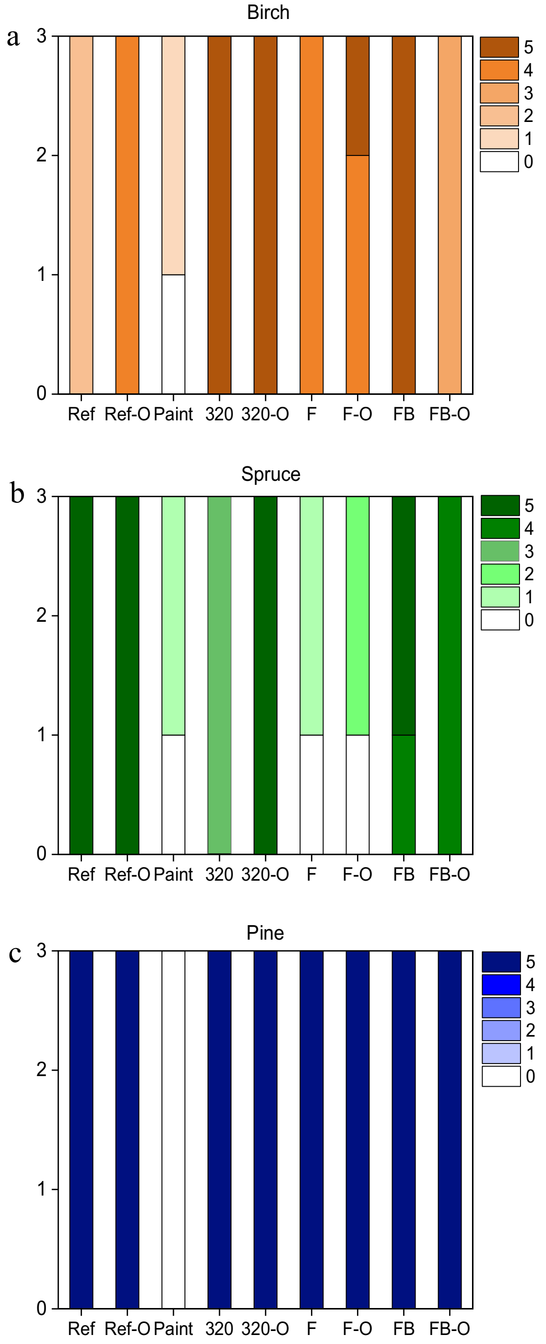

Fig. 2 Surface cracking evaluated visually on a scale of 0–5, where 0 = no defects, and 5 = dense pattern of defects on weathered samples, with the number of samples on y-axis; Birch (**a**), spruce (**b**), and pine (**c**)

Birch exhibited a higher total number of cracks (Table S1), but they were generally shallower than those in the two softwoods. However, several birch samples had severe internal cracks visible from the transverse ends (data

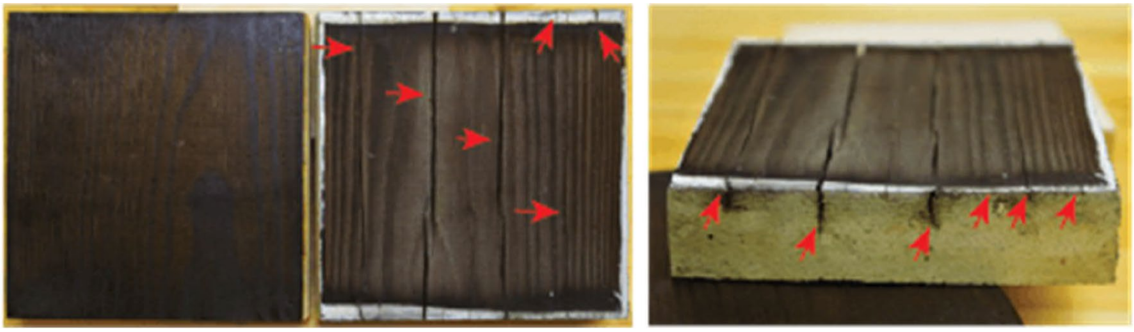

Fig. 3 A heavily cracked sample of contact charred pine (P320; middle and right) next to the practically flawless inside stored reference (left). The cracking for this sample is evaluated as 5 (dense pattern of defects), with depth of deepest cracks as 3 (penetrates whole system), and number of deepest cracks is 6, indicated by arrows. Flaked area is 0%, and cracked area 20% (includes also smaller cracks scaled as 1 and 2)

not shown). The exact effect of this honeycombing remains to be determined, as in non-structural use the relevance of internal cracks is case specific. The reference surfaces showed extensive defibrillation and breakage of fibers which was recorded as flaking. In contrast, the flame charred variants showed very little flaking, and in terms of surface stability evaluated by cracking, birch clearly benefitted from flame charring, although brushing gave mixed results (Fig. 2a). Hardwoods are, in general, more sensitive towards thermolysis (Atreya 1983; Windeisen and Wegener 2008) and the formed char layer is thicker than on softwoods. Because of the wood structure, the formed char is also compact and resistant to mechanical wear in a natural setting.

Spruce is an excellent material for exterior claddings, as it generally exhibits little dimensional changes. As an impermeable species, it is however susceptible to radial cracking (Boonstra et al. 2006). References and contact charred samples cracked heavily, but the flame charred samples performed adequately. The flame charred (F and F–O) samples stand out with least defects, with F–O presenting less flaked area and a smaller number of cracks (Table S1). Painted spruce samples also showed some mild surface cracking/flaking, but this is most likely related to the placement of the samples in the rack. Usually, it is recommended to orient tangentially cut cladding boards so that the ring pattern points down. One of the painted references was oriented the opposite way, with the ring pattern pointing up, resulting in characteristic peeling of earlywood and latewood sections on the tangential surface. Although tangentially cut boards were chosen for this study, radially cut surfaces have been shown to crack less in outside use (Sandberg 1999; Kaila and Heikkinen 2020). The use of radially cut boards remains limited due to a higher price (larger waste percentage in cutting) but could still be an interesting subject for further studies. For example, Machova et al. (2021) reported higher fire resistance and lower surface roughness on radial vs. tangential samples of beech modified with a contact charring method.

Traditionally, it is recommended to expose the pith side to weathering as it cups away from the center growth ring, thus preventing excess loosening of fastenings and seams. Because of the before-mentioned temperature gradient the charred side cups inward regardless of direction (i.e., pith or sap side of a board) (Ebner et al. 2021). A steeper temperature gradient could mean higher cracking, but only a few, if any, of the cracks penetrated through the entire system (class 3) in flame charred spruce and birch. Less recorded cracking could in part be related to the surface structure of the flame charred samples: in contrast to the hard, smooth surface created by contact charring, the char is porous and heavily cracked to begin with, and therefore less stressed than an intact contact charred surface would be. Because of very limited adsorption of water vapor (Kymäläinen et al. 2015, 2018), the water that penetrates is mostly in liquid form. It is possible the porosity allows also faster desorption, speeding up the evaporation of absorbed water and thus reducing moisture-induced dimensional changes. The overall rigidity of the material would also contribute to less swelling/shrinking (Kymäläinen et al. 2015). The structural degradation taking place at the contact charring regime may not be severe enough to limit adsorption, but allows moisture ingress, facilitates some degree of adsorption, and thus contributes to swelling/shrinking stresses. The modest cracking of the brushed samples also indicates that the treatment time can have an effect: the short exposure time during flame charring creates a negligible transition zone in comparison to long duration of contact charring. Despite removal of the protective char layer, the brushed samples exhibited less cracks than contact charred samples (spruce, birch). Therefore, contrary to the hypothesis of the importance of a thicker thermally modified transition layer discussed by Okamura et al. (2017) and Kymäläinen et al. (2020), the thicker transition zone may in fact be detrimental to durability in weathering. The original hypothesis was that the thermally modified layer would further decrease ingress of moisture and thus increase dimensional stability. Instead, a stressed transition layer is formed, as discussed in Zicherman and Williamson (1981), where the origin of surface cracks was traced to the pyrolysis zone beneath the char surface where evaporation and cooling change drastically over few cell layers.

As a result of the visual evaluation, it was clear that contact charring at 320 °C did not result in sufficient protection against weathering. Moreover, the flame charred brushed samples (FB and FB–O) cannot be recommended for outside use, at least in direct sunlight, because of extensive fading of color. The black char layer should obviously remain intact to provide enough protection against UV-radiation and rain. Overall, the brushed surfaces were still more intact than the contact charred ones.

3.3 Color change

All reference samples turned from beige to gray during the exposure. The oiled references were darker in color, some of the oiled birch references had even turned black from extensive weathering and molding. Contact charred samples retained their dark color in the latewood sections, but not in earlywood sections—the overall color change ΔE was in the range 13–26 (Fig. 4). As mentioned, the point values were averaged and no separation between early- and latewood was made other than in visual evaluation. This was due to the fact that it was impossible to separate the different wood types in flame charred samples (and contact charred birch). The L^*, a^* and b^* values increased, i.e., these surfaces became lighter and more red and yellow. Modified birch and pine samples showed less total color change than spruce, but the color change was less than for references in all cases. Flame charred samples remained black with relatively little flaking. Some of the original sheen was lost, but otherwise the samples showed little change in appearance during the weathering period. Color measurements verify the observation, with ΔE remaining below 2.1 in all cases. Oiling somewhat dulls the sheen but brings out a bluish hue on the char surfaces at certain viewing angles, which was visible still after 1 year. L^* is the most sensitive and easily visualized parameter for wood surface quality during wood thermal modification, as well as weathering. Lightening of the color is related to degradation of lignin and extractives, that bring out the light-colored cellulose (Huang et al. 2012). The increase in L^* (Fig. 4) was seen in all samples but only a very small difference was measured for painted, F and F–O samples (all species). Flame charred and brushed samples (FB and FB–O) of spruce and pine went through similar change in appearance to the contact charred samples: the latewood sections remained dark, but earlywood sections were badly weathered (Fig. 5). Gray tones were detected and ΔE was of similar magnitude to those of contact charred samples. Birch FB samples showed less changes. This is related to the char layer properties, as the surface of this denser material is less prone to abrasion and was less affected by brushing. Therefore, more black char remained on the surface instead of the thermally modified transition layer that was revealed

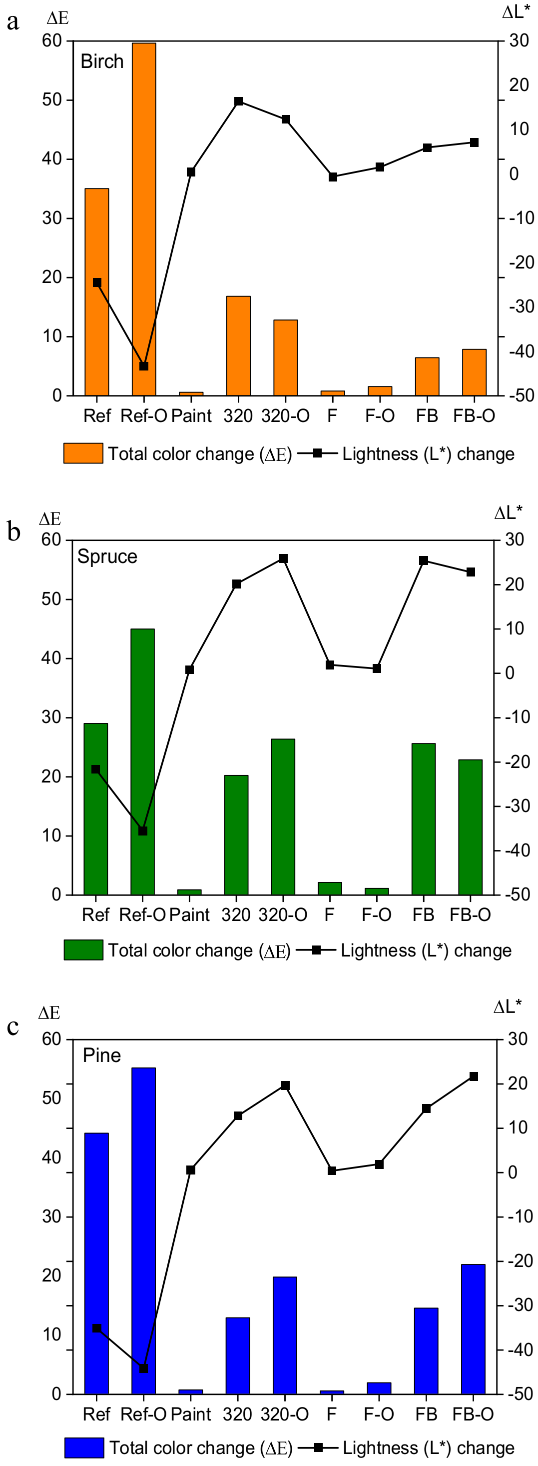

Fig. 4 Total color change (ΔE) and change in lightness (L^*) after natural weathering of birch (**a**), spruce (**b**), and pine (**c**)

Fig. 5 A selection of inside stored spruce references (left) and weathered specimens (right). From top to bottom: unmodified reference (Ref), contact charred (320), flame charred (F), flame charred and brushed (FB)

in softwoods. The char layer obviously protects the wood effectively against weathering damage, again highlighting the relevance of char layer thickness. All in all, the modified birch samples exhibited lowest values of ΔE. This suggests that birch also benefited from the contact charring, though it is possible that mold affected the darker surfaces. To reveal the effect of mold, the modified samples should be examined further, preferably by chemical methods. One-way ANOVA showed that all groups (modifications) differed from each other both before and after the weathering. Further post hoc testing was applied to color values measured from modified surfaces (excluding Ref and Ref–O). The Q critical value was significant between modifications on all species with some differences: For spruce, the oiling did not affect color changes. For pine, the P320 L^* did not differ from FB and FB–O, meaning that in terms of lightness values the contact charring was equal to flame charring combined with brushing. Oiling did, however, affect the other relations (a^* and b^*). For birch, all modifications differed from each other significantly in terms of color values after weathering. Between species (within modification), the one-way ANOVA showed significant differences after weathering between all modifications except for paint (L^* and a^*), and between 320-O, F, FB and FB–O (b^*). The painted surface was thus unchanged during weathering, and contact charring combined with oiling experienced similar changes, color wise, to the flame charred variants. It has already been shown by several researchers, that thermally modified wood discolors less than unmodified wood during weathering (Ayadi et al. 2003; Baysal et al. 2014; Tomak et al. 2014). The authors attribute this to lignin condensation and increased phenol and antioxidant contents that limit photodegradation. Thermal modification is of course different from the methods used in this paper, but some similarities occur. The thermolysis is taken further in charring, causing more structural degradation and modifications in the lignin component. This is discussed in more detail in the chapters below. The table describing the detailed color values may be found in Table S2 in Supplementary Information.

3.4 Chemical changes of modified and weathered wood surfaces analyzed by FTIR and Raman spectroscopy

3.4.1 ATR-FTIR spectroscopy

Chemical changes in the wood surfaces of unmodified and contact charred samples were assessed by FTIR (Fig. 6). However, the method was found to be unsuitable for flame charring modification due to the high degree of carbonization, which made calculation of peak ratios impossible. In this case, Raman spectroscopy was used (Fig. 7). Contact

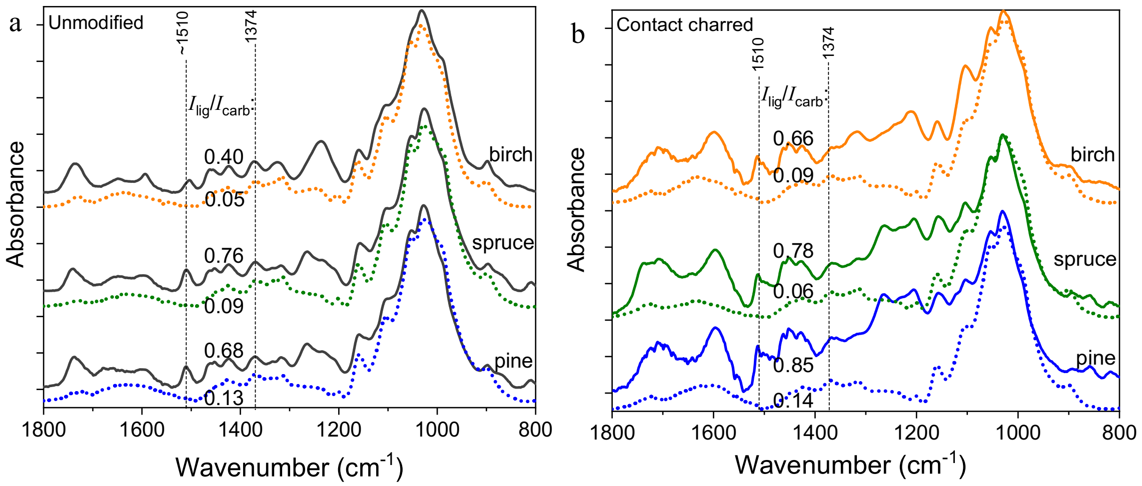

Fig. 6 Infrared spectra of unmodified (**a**) and contact charred birch, spruce and pine wood (**b**). Solid line stands for samples before weathering and dotted line for samples after weathering

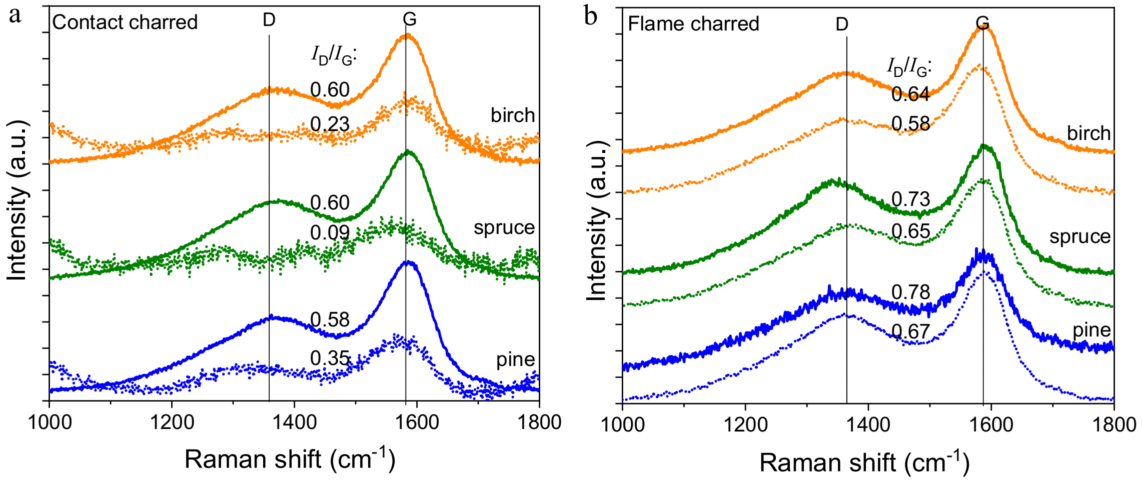

Fig. 7 Raman spectra from the surface of contact-charred wood (**a**) and flame charred (**b**), before weathering (solid line) and after weathering (dotted line)

charred samples were also characterized by Raman for comparison. The relevance of surface chemistry in weathering of wood stems from the photodegradation of wood components. Especially lignin strongly absorbs UV-light, then degrades through a set of complex radical reactions (Feist and Hon 1984; Evans 2009). Cellulose remains, as is visible in Fig. 6b, where, after weathering, the contact charred samples more or less regain the spectrum shape of unmodified samples due to degradation and leaching of lignin, as can also be seen in the color results. In addition to revealing the cellulose, hemicelluloses solubilize providing easily accessible sustenance for mold and decaying fungi. Roughened surfaces also gather dirt and moisture, further promoting the growth of fungi. However, the hypothesis behind longer service life of surface charred wood is that the lignin component is less susceptible to photodegradation. This has been discussed previously in connection to color stability of thermally modified wood (Huang et al. 2012; Ayadi et al. 2003; Cui and Matsumura 2019). Kampe and Pfriem (2018) investigated flame charred spruce subjected to artificial weathering. Based on peaks for C–O stretching of cellulose (1050 cm^{-1}) and stretching vibration, aromatic ring of lignin (1595 cm^{-1}), the authors concluded that decomposition of lignin took place, but it was slower than in unmodified samples. The surface temperature was not reported, so drawing conclusions on the char quality is difficult. Reporting on contact charred spruce, Kymäläinen et al. (2020) noted formation of oxidized lignin structures and new carbonyl groups as well as degradation of the aromatic C=C band at around 1729 and 1508 cm^{-1} after two years of natural weathering. The temperatures used in said study remained below 500 °C and the formed char layer was very thin. It is likely the components were not degraded far enough to hinder weathering.

In general, all the examined wood species undergo similar changes during the modifications (Fig. S3 in Supplementary Information). The carbohydrate peaks at around 1734, 1375, 1158, and 898 cm^{-1} degrade and diminish, while the lignin reference peaks at around 1510, 1462, 1269/1330 and 1225/1122 cm^{-1} (softwood/hardwood, Pandey and Pitman 2004) intensify. To reach a self-normalization allowing a reasonable comparison among species, avoiding effects such as sample preparation, a ratio of intensities between lignin aromatic band against holocellulose (I_{lig}/I_{carb}) was assessed. As can be observed in Fig. 6a, the unmodified samples of pine and spruce presented a higher I_{lig}/I_{carb} ratio compared to birch wood. This higher ratio is in fact expected for softwoods (Barker and Owen 1999). The I_{lig}/I_{carb} ratio of contact charred samples, before weathering (Fig. 6b), increased when compared to its unmodified form before weathering (Fig. 6a), mostly due to the degradation of carbohydrates as a consequence of the charring treatment. This observation is less evident for spruce wood. The difference is small but is possibly connected to the higher amounts of extractives in pine, that may again increase the charring rate and therefore degradation of components especially at the lower end of the temperature range. In the unmodified weathered samples (Fig. 6a), the I_{lig}/I_{carb} ratio is near zero for all species, indicating heavy degradation of lignin during natural weathering. In the contact charred weathered samples (Fig. 6b), it is possible to observe a similar pattern, with I_{lig}/I_{carb} ratio reaching zero and indicating extensive deterioration of lignin. In both cases, the I_{lig}/I_{carb} ratio for pine after weathering is slightly higher than the other two species, meaning that pine may be more resistant to weathering. This can be related to its slightly higher amount of lignin and higher density (Sell and Feist 1986; Sandberg 1999).

3.4.2 Raman spectroscopy

Raman spectroscopy allowed for a more detailed comparison between contact and flame charring treatments, where analysis of the *D* and *G* bands further elucidated the compositional changes. These bands are the most prominent signals and commonly investigated in carbon materials (Bengtsson et al. 2020). The intensity ratio of *D* and *G* (I_D/I_G) can provide information about the carbon structure of the material, where G is known as the graphite band with a vibrational frequency at ~ 1580 cm^{-1} due to the sp^2 bonded carbon in planar sheets, and *D* (~1350 cm^{-1}) is known as a defect-induced band indicating the presence of some disorder. Thus, comparing the I_D/I_G values between contact (Fig. 7a) and flame (Fig. 7b) charred samples, before weathering (solid lines), it is possible to observe ratios of 7, 22 and 50% higher in flame charring for birch, spruce and pine, respectively. This is mostly associated with a higher intensity of the defect-induced *D* band, as *G* band presented similar shape and intensities in both treatments (Fig. S4 in Supplementary Information). These values infer a higher graphitization of flame-charred samples. In fact, when analyzing the modified samples after weathering, the *D* and *G* intensities almost disappear for contact charred samples (except for pine, supporting the observations of higher weathering resistance from FTIR, Fig. 6), while the flame-charred samples presented only a slight decrease (9, 11 and 14% for birch, spruce and pine, respectively) in the intensities after weathering. These results confirm a strong surface change after flame charring, conserved after weathering, similarly for all species.

It is clear the contact charring temperature is not high enough to form a stable char, that would resist the compositional changes caused by weathering. The temperature/modification time was chosen based on earlier research by Kymäläinen et al. (2015, 2017, 2018) where higher hydrophobicity and dimensional stability were seen in samples modified between 300 and 350 °C for 10 to 30 min. The aim was to create a high enough structural degradation by moving from endothermic to exothermic region (above 280 °C; Browne 1958), pass the char line at about 290 °C (Schaffer 1967) and to pass the transition in degradation of cellulose (around 310 °C; Shafizadeh 1982) releasing tar, to induce sufficient hydrophobicity but to remain below the threshold for substantial surface cracking. Breaking the crystalline cellulose structure would increase cracking, but substantial preliminary testing using our device showed that surface stability was at its highest at this chosen temperature. Below, the sorption properties would diminish and above, surface cracking would increase. However, based on these results, the structural degradation should be taken even further to preserve the surface during exterior use. The flame charring modification, on the other hand, produces a highly degraded char with a more organized structure, which can be translated as “quality”. This kind of char is rather inert in weathering, as can be concluded from the visual evaluation, color measurements as well as the Raman results. As to the differences between wood species, flame charred pine seemed most resistant to weathering when using spectroscopical measures. It also showed slightly higher color stability compared to spruce, but also more and deeper cracks, raising questions on suitable thickness/density.

4 Conclusion

After one year of natural weathering of spruce, pine and birch modified by contact and flame charring, it became clear that the modification method has a great effect on the surface durability. Although the flame charred surface is porous and rather friable, it resists weathering well because of compositional changes, measured by spectroscopical methods, that lead to a more ordered, graphitized carbon structure that is hardly reactive towards photodegradation. Flame charred birch presented rather good weathering resistance with good color stability and a hard surface with little flaking. Spruce showed the best overall performance, evaluated with visual, colorimetric and spectroscopic means. The flame charred spruce showed slightly higher flaking percentages in comparison to birch, but oiling was found to improve the visually determined appearance, although statistically, oiling did not affect the color changes. Color wise, pine and birch benefitted also from oiling. When comparing the weatherability of flame charred and brushed samples to contact charred ones, it was shown that they crack less than contact charred samples, indicating that the thicker transition zone may not be desirable after all. It is likely that this zone is highly stressed and tends to crack in the presence of fluctuating humidity and other environmental factors. The contact charred samples also presented inadequate color stability. The cracking seems to be the defining problem of charred wood exteriors, but it should be investigated whether this is a consequence of the thermal/moisture stresses, or the initial wood density. Flame charring, however, seems to be a viable option to modify exterior cladding boards, although further investigation with full sized specimens is needed to reveal the stability in use.

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Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

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