Spectral Sensitivity of Thermally Modified and Unmodified Wood

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The chemical structure of wood changes significantly during thermal modification, significantly influencing the behaviour of wood during weathering. In this study, the effect of different wavelength ranges on thermally modified and unmodified aspen (*Populus tremula* L.) wood during solar irradiation was investigated. Irradiation was performed by exposing wood to natural solar irradiation under filters transmitting different wavelength ranges. For both woods, the magnitude of characteristic change (discolouration, changes in reflectance, and chemical composition) clearly depended on the solar wavelength bands, but the trends of the changes differed. For unmodified wood, the magnitude of the characteristic changes increased as the portion of short-wavelength radiation in the light increased. However, UV radiation was not found to be the dominant factor influencing changes in thermally modified wood during solar irradiation. The colour and chemical structure of thermally modified wood changed substantially for all studied irradiation conditions.

Keywords: Thermally modified wood; Solar irradiation; Photosensitivity; Chemical change; Discolouration; Weathering

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INTRODUCTION

Thermal treatment is a wood modification method that improves wood’s dimensional stability, reduces hygroscopicity, and enhances resistance to microbiological attacks without using any harmful chemicals (Hill 2006). Additionally, thermal modification can create new application areas for wood species that would have no proper commercial value otherwise. The production of thermally modified (TM) wood has increased during the last few decades. As a result of thermal treatment, wood appearance is altered, as wood acquires lighter or darker brown colour, which is a result of the chemical changes in wood components during the process (Sundqvist and Morén 2002; Bekhta and Niemz 2003; Müller et al. 2003; Boonstra and Tjeerdsma 2006). Preference is often given to TM wood exactly because of its altered colour, and occasionally it is even used as an alternative to tropical woods (Esteves et al. 2008; Tuong and Li 2010; Mklečić et al. 2011). Because of a substantial loss in strength, TM wood is mostly recommended for non-structural usage. Therefore, the main application areas of TM wood are garden furniture, flooring, building facades, and decking for terraces (Schnabel et al. 2007). In all these applications, wood serves as a functional and decorative material. Accordingly, wood’s aesthetic appearance and its stability are of great importance.
Many factors are responsible for wood weathering, such as solar irradiation, moisture, temperature, biological agents, and air pollutants (Williams 2005). Among them, solar irradiation has been found to be the most damaging factor for wood degradation (Pandey and Khali 1998; Tolvaj and Varga 2012). Moreover, discolouration is recognised to be the first sign of wood degradation, as light irradiation and colour change is more pronounced than other indicators during the initial phase of exposure (Tolvaj and Mitsui 2010; Auclair et al. 2011; Srínivas and Pandey 2012). Therefore, the evaluation of colour changes has been recognised and widely used as an effective tool to analyse the peculiarities of wood weathering features, typically applying the CIELAB colour model. Likewise, Fourier transform infrared (FTIR) absorption spectra are extensively used to monitor alterations in the wood chemical structure due to irradiation.

The UV portion (295 to 400 nm) of the solar radiation is regarded as the dominant factor causing wood discolouration and degradation during sunlight exposure (Hon 2001; Tolvaj and Mitsui 2010; Teacă et al. 2013). Therefore, artificial weathering with UV irradiation is often applied to imitate and study the changes caused by solar radiation exposure for both unmodified and TM wood (Ayadi et al. 2003; Müller et al. 2003; Miklečić et al. 2011; Srínivas and Pandey 2012; Hauptmann et al. 2014; Tolvaj et al. 2014). However, thermal modification, which results in a changed chemical structure of wood (including the formation of new chromophores), can significantly influence the behaviour of wood during weathering. It is well established that thermal modification does not induce resistance against UV radiation (Ayadi et al. 2003; Deka et al. 2008; Miklečić et al. 2011; Srínivas and Pandey 2012, Tolvaj et al. 2014). It has been also reported that the weathering process for TM wood, because of its changed chemical structure, differs from that of unmodified wood (Ayadi et al. 2003). However, there is little information regarding the photosensitivity of TM wood concerning the full solar spectrum, and the light wavelength ranges able to cause photodegradation.

The objective of the present study was to investigate the effect of different wavelengths of solar radiation on TM wood during outdoor exposure. European aspen (Populus tremula L.) was used for the experiment as it is a fast-growing species with inadequate commercial value and thermal modification is regarded as a potential way to increase its market share (Karlsson et al. 2011). For comparison purposes, changes in unmodified wood were also investigated. The data on wood spectral sensitivity are an important element to develop efficient compositions for wood protection from the undesirable effects of weathering, during both indoor and outdoor applications, in places where it is reached by solar radiation.

**EXPERIMENTAL**

**Materials**

Aspen (Populus tremula L.) wood was used for this experiment. Defect-free boards measuring 1000x100x25 mm were subjected to hydrothermal modification in a WTT (Wood Treatment Technology, Denmark) experimental wood modification device, in a water vapour medium, under elevated pressure (0.6 MPa) at 170 °C, for an effective treatment time of 1 h. After modification, the boards were conditioned for a month in an atmosphere of 20 °C and 65% relative humidity. The surfaces of TM and unmodified boards were planed before exposing to irradiation.
Natural Sunlight Irradiation

The natural sunlight irradiation was conducted via outdoor exposure between May and August in Riga (56°58’N 24°11’E). Wood was exposed outdoors only during sunny hours, when the flux density of the total UV radiation (290 to 390 nm) was above 10 W m⁻². During the exposure, the average flux density of UV radiation was 33 W m⁻² and the average total solar radiation density was 610 W m⁻². During the experiment, the air temperature at the specimens’ surface varied from 25 to 41 °C, and the relative humidity ranged from 15% to 35%. The total exposure time was 100 h. The wood samples were stored indoors in the dark, when they were not exposed outdoors. The shielding of wood with four glass filters (F2 – F5) transmitting different wavebands, as well as exposure to full solar irradiation (F1), were applied to study the effect of the spectral composition of the incident light on wood.

The spectral transmittance of the filters in the wavelength range from 290 to 900 nm, are presented in Fig. 1. The characteristic wavelength transmittance of the filters, in which more than 1% of radiation in the range of 290 to 900 nm is transmitted by the filter, are given in parentheses in the legend box.

![Transmittance spectra of filters with wavelengths ranging from 290 to 900 nm](image)

**Fig. 1.** Transmittance spectra of filters with wavelengths ranging from 290 to 900 nm

The F2 filter was a band-pass filter, transmitting only the UV portion of the solar radiation, thus providing information about the effects of solitary solar UV radiation on wood. The three others were cut-off filters (F3, F4, F5), which exhibited a typical cut-off of different shorter waveband ranges of the solar radiation.

One board was used for a set of filters, which ensured similar wood surface for all irradiation conditions. Constructions, consisting of top plywood with apertures (ø – 35 mm) shielded by the filters and a holder underneath for a wood board to be installed and fixed in a horizontal position, were designed for the experiment. Two boards of each wood, TM and unmodified, were exposed to irradiation.

Measurements of Reflectance Spectra and Colour

A portable spectrophotometer CM-2500d Konica Minolta, Japan (standard illuminant D65, d/8° measuring geometry, 10° standard observer, measuring area Ø 8 mm) was used for wood reflectance spectra and colour measurements. Reflectance spectra were recorded for wavelengths ranging from 360 to 740 nm, using a scanning interval of 10 nm. Colour was expressed in accordance with the CIELAB colour model (Commission Internationale de l’Eclairage 1976) as colour parameters L*, a*, b*. The total colour change
(\(\Delta E_{ab}\)) was calculated from the colour parameter differences between the initial and resulting values \(\Delta L^*\), \(\Delta a^*\), \(\Delta b^*\) according to the formula:

\[
\Delta E_{ab} = \left( (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right)^{\frac{1}{2}}
\]

(1)

Spectrophotometric measurements were performed before and at the end of the experiment. Both times two measurements were recorded at the same three marked points for each irradiation system and average values were calculated for colour representation.

**FTIR Spectroscopy**

FTIR spectra were acquired by applying a Perkin-Elmer (USA) Spectrum One FTIR spectrometer, equipped with a Perkin Elmer Universal Attenuated Total Reflection (ATR) Sampling Accessory with a Diamond/ZnSe crystal. The spectra were recorded directly at the surface, using a spectral resolution of 4 cm\(^{-1}\). In total, 64 scans were obtained and averaged. FTIR spectra were recorded for both unirradiated and irradiated wood at the end of the experiment. Spectra of three replicate specimens for each irradiation system were recorded and averaged. For final semiquantitative evaluation of absorption changes, the spectra were baseline corrected and normalized to 1.5 absorbance units for the highest absorption peak around 1030 cm\(^{-1}\) (because of CO stretching in cellulose and hemicelluloses).

**RESULTS AND DISCUSSION**

**Colour Changes**

At the end of the experiment (100 h of exposure), colour changes were detected for all studied irradiation systems for both unmodified and TM wood (Fig. 2).

![Fig. 2. Colour change \(\Delta E_{ab}\) of unmodified and TM wood subjected to various irradiation systems](chart.png)

It is apparent that the extent of the colour change depended on the solar wavelength bands contacting the wood. This finding agrees with the results of Kataoka et al. (2007) and Živković et al. (2014), who investigated the behaviour of unmodified wood exposed to light of different wavelength ranges. However, the effect of different spectral regions on wood discoloration differed for unmodified and TM wood. Exposure of TM wood to the full solar spectrum (F1) resulted in less discoloration in comparison to unmodified wood with colour change \(\Delta E_{ab}\) values of 12.6 and 19.5 units, respectively. Several researchers have reported better colour stability for TM wood during exposure to UV radiation, as well as natural weathering (Ayadi et al. 2003; Nuopponen et al. 2004; Deka and Petrič 2008; Yildiz et al. 2011; Tolvaj et al. 2014). The phenomena is attributed to an increase in lignin...
stability, due to condensation and the appearance of antioxidant compounds during the wood thermal treatment process (Ayadi et al. 2003). However, Srinivas and Pandey (2012) reported differing results, finding that the thermal treatment of wood resulted in more discoloration during artificial weathering.

The least discoloration among all irradiation systems was observed for the unmodified wood shielded by the filters transmitting exclusively the visible range of solar radiation, namely F5 (light above 600 nm) and F4 (light above 515 nm), with corresponding color changes $\Delta E_{ab}$ of 2.5 and 2.3 units, respectively. Accordingly, exposure to light with wavelengths ranging above 515 nm caused some transformations in the chromophores of unmodified wood. However, the chromophore transformations did not result in noticeable aesthetic changes, as the limiting value of color change ($\Delta E_{ ab}$), which can be distinguished by the naked eye, is approximately 3 units (Hon and Minemura 2001). Likewise, the most intense color change ($\Delta E_{ab}$ = 23.8) was also detected for unmodified wood, namely, under the filter F2 transmitting solely in the UV region below 400 nm. Moreover, unmodified wood subjected to full solar irradiation (F1) discoloured even less ($\Delta E_{ab}$ = 19.5). Hon and Minemura (2001) have reported similar results, showing that photo-induced discoloration in wood specimens under a filter transmitting only UV light was superior to the color changes of the specimens subjected to full sunlight. This phenomenon may be a result of the diverse color transformations resulting from exposure to different wavelength ranges, as demonstrated by Kataoka et al. (2007). They found that exposure of wood to different wavebands caused dissimilar and in some cases inverse color changes. In the present study, the extent of color changes in unmodified wood increased with the growth of the short wavelength light portion reaching the wood surface under the filters. These results agree with the statement that UV radiation is of major importance for unmodified wood discoloration (Tolvaj and Mitsui 2010; Teacă et al. 2013).

In contrast to unmodified wood, TM wood discoloured noticeably under the F4 and F5 filters, transmitting solely visible light. At the end of the experiment, the color change ($\Delta E_{ab}$) for TM wood shielded by the filters F4 and F5 reached 7.6 and 3.8 units, respectively. The brown color of the TM wood indicates the presence of chromophores absorbing a considerable part of the visible light. The results of the present study suggest that the absorbed visible light, regardless of its relatively low photon energy, is able to provoke substantial transformations in TM wood chromophores. Moreover, exposing TM wood solely to UV radiation under the filter F2 resulted in a relatively small color change ($\Delta E_{ab}$) of 5.3 units. This phenomenon could be explained by the fact that the UV spectrum only represents approximately 5% of the total solar energy reaching the earth’s surface (Deka et al. 2008). In general, these results imply that the UV portion (below 400 nm) of solar radiation did not show the dominant effect on discoloration of TM wood and the solar radiation of longer wavelength range had a noteworthy effect on TM wood discoloration. Moreover, the amplitude of the $\Delta E_{ab}$ variation for wood shielded from different wavelength ranges of sunlight via filters was more than twice as small for TM wood (3.8 to 12.6) than unmodified wood (2.3 to 23.8). These results imply that, in regards to discoloration, TM wood is less sensitive than unmodified wood to the spectral composition of the incident light, and a broader spectral range of solar radiation can provoke discoloration of similar magnitude in TM wood.
Changes in Reflectance Spectra

Reflectance spectra characterise wood chromophores and changes in their concentration (Pandey and Vuorinen 2008). Difference reflectance spectra (Fig. 3) were calculated by subtracting the reflectance spectrum of the unirradiated from the irradiated wood.

The difference reflectance spectra of unmodified and TM wood were substantially different in pattern and extent. Difference reflectance curves were located on the opposite sides of the zero axis for unmodified and TM woods, which agrees with the lightness changes in the opposite directions of the two wood types. Unmodified wood darkened while TM wood became lighter, due to irradiation under all studied conditions.

A pronounced band of difference in reflectance appeared in the wavelength region from 400 to 560 nm for unmodified wood (Fig. 3b). This area is typically associated with the formation of quinone structures (Pandey and Vuorinen 2008). Only a slight decrease in reflectance but still at the same wavelength band (from 400 to 560 nm) was observed for wood exposed to longer wavelengths of the solar radiation under the filters F4 and F5. These results indicate that chromophoric groups with a similar characteristic absorbance range in the shorter wavelength region of visible light were formed in unmodified wood under all investigated irradiation systems. Decrement in reflectivity at a similar wavelength range was observed for rubberwood exposed to xenon arc light (Pandey and Vuorinen 2008) and western hemlock exposed to fluorescent lamps (Chang and Chang 2001).

In contrast to unmodified wood, no distinct maxima in the difference reflectance-spectra were observed for TM wood (Fig. 3a). The difference reflectance spectra of TM wood were fairly even over the whole wavelength range, exhibiting slightly greater changes in the wavelength region beyond 500 nm. Moreover, unique patterns of the difference reflectance spectra can be discerned for TM wood depending on the irradiation system. Difference reflectance spectra were red-shifted for specimens shielded by the solely visible light transmitting filters F4 and F5. Only minimal changes in the reflectance below 450 nm and 550 nm were detected for TM wood shielded by the filters F4 and F5, respectively. The reflectance changed almost equally over the whole wavelength range, with only a slight increase in the longer wavelength part for TM wood shielded by the filter F2, transmitting solely the UV light below 400 nm. However, the exposure to the broader light ranges (F1 and F3) caused the greatest reflectance change for TM wood. Additionally, for the TM wood under the filters F1 and F3, changes in reflectance, similar to those under the F2 filter, were detected in the short wavelength region, along with a more pronounced
reflectance increase in the longer wavelength range. These results suggest that TM wood contains a variety of chromophores, which are transformed during solar irradiation. Moreover, these chromophores differ in spectral sensitivity ranges.

To compare the changes in reflectance, the extent of the change in reflectance was quantified by expressing it as the area below/above the corresponding difference reflectance curve, and presented as relative units in Table 1.

Table 1. Changes in Reflectance of Unmodified and TM Wood Subjected to Various Irradiation Systems for 100 h (Relative Units)

<table>
<thead>
<tr>
<th>Irradiation system</th>
<th>F1 (nm)</th>
<th>F2 (nm)</th>
<th>F3 (nm)</th>
<th>F4 (nm)</th>
<th>F5 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure range</td>
<td>Solar radiation</td>
<td>295-400</td>
<td>360-900</td>
<td>5150-900</td>
<td>600-900</td>
</tr>
<tr>
<td>Unmodified wood</td>
<td>679 (36)</td>
<td>708 (24)</td>
<td>355 (42)</td>
<td>43 (22)</td>
<td>44 (23)</td>
</tr>
<tr>
<td>TM wood</td>
<td>311 (31)</td>
<td>120 (12)</td>
<td>259 (39)</td>
<td>122 (33)</td>
<td>50 (24)</td>
</tr>
</tbody>
</table>

Values in parenthesis are standard deviations.

It can be seen that the reflectance changes for unmodified wood prevailed for most irradiation systems, excluding the filters transmitting visible light F4 and F5, when only slight changes were detected. These results could be explained by the lower content of chromophores in TM wood, apt to undergo transformation due to irradiation. On the other hand, TM wood contains a relatively high quantity of chromophores, liable to the changes initiated by irradiation with wavelengths above 515 nm (F4).

**Chemical Changes**

In the present study, absorbance difference spectra were calculated to clearly depict the changes in absorption, as the difference spectra reveal only the bands that are altered by irradiation, with positive peaks representing an increase and negative peaks a decrease in absorption. A variety of absorption peaks are used for analysing the chemical transformations in wood due to weathering, though the major spectral changes in wood caused by light irradiation have been reported at approximately 1510 and 1600 cm⁻¹ as a result of the photodegradation of lignin and near 1730 cm⁻¹ resulting from the formation of non-conjugated carbonyl groups (Colom et al. 2003; Miklečić et al. 2011; Srinivas and Pandey 2012; Tolvaj and Varga 2012). The difference FTIR spectra of unmodified and TM aspen wood exposed to irradiation are presented in Fig. 4, showing only the region of the most important absorption changes, between 1800 and 1450 cm⁻¹.

![Fig. 4. Difference FTIR spectra of wood subjected to various irradiation systems: a) TM wood and b) unmodified wood.](image)

It is apparent that irradiation noticeably influenced the chemical structure of both unmodified and TM wood. Moreover, the changes in absorbance were dominant at similar wavebands for both wood types. This agrees with the results of Deka and Petrič (2008) and Miklečić et al. (2011), who reported similar changes in FTIR spectra of unmodified and TM wood as a result of weathering. A characteristic feature for almost all irradiation systems was reduction of bands at approximately 1510 and 1600 cm\(^{-1}\) because of the photodegradation of lignin, accompanied by an increment of the carbonyl band around 1730 cm\(^{-1}\). However, the extent of the changes in the spectra depended on the wavelength range of irradiation for both unmodified and TM wood.

Figure 5 shows changes in the absorbance relative values at the more characteristic wavebands. The absorbance band near 1510 cm\(^{-1}\) had disappeared for both unmodified and TM wood after exposure to full solar irradiation (F1). Accordingly, the corresponding difference values on the charts represent the utmost changes for this waveband. The rapid disappearance of the absorption band near 1510 cm\(^{-1}\) agrees with the findings of previous research (Pandey and Khali 1998; Huang et al. 2012; Srinivas and Pandey 2012).

**Fig. 5.** Changes in absorbance relative units at the wavebands 1510, 1600, and 1730 cm\(^{-1}\) for wood subjected to various irradiation systems: a) TM wood and b) unmodified wood

In general, greater changes in IR spectra were observed for TM wood compared to unmodified wood for all analysed wavebands and irradiation systems, which suggests that TM wood was more chemically transformed by irradiation. This finding disagrees with the results reported by Miklečić et al. (2011) and Deka et al. (2008), who observed fewer changes in the TM wood FTIR spectra as a result of weathering. On the other hand, Huang et al. (2012) reported a faster decrease in the lignin band at 1510 cm\(^{-1}\) for TM wood. Srinivas and Pandey (2012) also detected a greater extent of changes in the FTIR spectra for TM wood compared to unmodified wood.

Regarding unmodified wood, changes in the analysed absorption bands increased as the portion of the shorter-wavelength radiation transmitted by the shielding filters increased, suggesting that light of shorter wavelength was the principal cause of photodegradation of the unmodified wood. Moreover, hardly any changes in IR absorbance were found for unmodified wood shielded by the filters F4 and F5, which only transmit visible light (Fig. 4b and 5b), agreeing with the results of Kataoka et al. (2007), who used the absorption intensities at 1730 cm\(^{-1}\) to assess the irradiation effect on wood and found that the light above 434 nm did not cause any detectable chemical changes in wood.

A reduction in absorbance at 1510 cm\(^{-1}\) (Fig. 4a and 5a) was detected for the TM wood shielded by all filters, except those transmitting solely visible light (F4 and F5). This reduction corresponded to the near entire disappearance of this band, assigned to lignin. Moreover, a rather low increase in the absorbance at 1730 cm\(^{-1}\) was detected for the TM

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wood shielded by the filter transmitting exclusively the UV portion of sunlight (F2). On the other hand, irradiation of TM wood for light with a waveband above 515 nm (F4) caused a substantial decrease in the intensity of lignin-related absorption bands around 1510 cm\(^{-1}\) and 1600 cm\(^{-1}\), as well as a marked increase in the carbonyl absorption band at 1730 cm\(^{-1}\). These results suggest that exposure of TM wood to visible light (up to 600 nm) caused not only substantial discolouration, but also provoked a considerable chemical transformation, including serious lignin degradation. Accordingly, an efficient coating formulation for TM wood preservation should provide shielding from the light up to 600 nm.

CONCLUSIONS

1. The exposure of thermally modified (TM) and unmodified aspen wood to specific wavelength ranges of solar radiation showed that, for both woods, the extent of the changes in colour and chemical composition clearly depended on the incident wavelength range. However, the effects of different spectral regions differed for unmodified and TM wood. For unmodified wood, the magnitude of changes in colour and chemical composition increased with an increase in the UV light portion in the irradiation system. Colour changes in TM wood exposed to irradiation above 515 nm (F2) prevailed over those caused by UV irradiation below 400 nm (F4). These results suggest that light with relatively low photon energy can provoke substantial colour transformations in TM wood.

2. An analysis of changes in the reflectance spectra showed that TM and unmodified wood differ in chromophores involved in the discolouration process. TM wood contains a lower content of chromophores apt to undergo transformation with irradiation, but it contains relatively more chromophores liable to change initiated by irradiation with light in the wavelength range above 515 nm (F2). Additionally, TM wood contains chromophores with diverse spectral sensitivity.

3. A similar course of the most pronounced changes (near 1510, 1600, and 1730 cm\(^{-1}\)) in the FTIR spectra was found for both unmodified and TM wood. Greater relative changes in the FTIR spectra were detected for TM wood under all the studied irradiation conditions, which indicates a more severe chemical transformation in TM wood.

4. Noticeable discolouration and chemical transformation in TM wood shielded by the filter transmitting light above 600 nm, suggests that coating formulations, containing substances that can reduce the amount of light reaching the wood surface by at least up to 600 nm, are important for efficient protection of TM wood exposed to weathering.

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