THE INFLUENCE OF ACETYLATION ON THE COLOUR AND PHOTOSTABILITY OF COMMON HORNBEAM WOOD (Carpinus betulus L.)

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Abstract:
The aim of our research was to study the effect of acetylation and boiled linseed oil-coating on the photodegradation of common hornbeam wood (Carpinus betulus L.). For this study, a 200-hour-long mercury vapour lamp irradiation test was carried out. The tests were done on 4 different types of wood materials: native hornbeam, acetylated hornbeam, boiled linseed oil-coated hornbeam and boiled linseed oil-coated, acetylated hornbeam samples.

According to the results, the change of colour coordinates and the colour difference compared to the original colour was determined as well as conclusions were drawn on the photodegradation process according to the Fourier Transform Infrared spectra.

Key words: hornbeam; acetylation; photodegradation; colour; FTIR.

INTRODUCTION
The aesthetic appearance of wooden products are greatly influenced by their colour. This is why their colour stability is expected by users whether it is an indoor furniture or an outdoor decking. The colour of wood changes if it is exposed to ultraviolet (UV) light or thermal impact. The colour can be objectively determined with various methods. In this work CIELAB colour system was used where L* defines lightness (0 is black and 100 is white), a* denotes red/green hue (positive values for red and negative values for green), and b* denotes yellow/blue hue (positive values for yellow and negative for blue). The colour change of wooden products can be determined by calculating the change in colour components (∆L*, ∆a*, ∆b*) and then the total colour difference (∆E*). According to Terziev and Boutelje (1998), and Mononen et al. (2002) the difference can be seen by the naked eye if ∆E* is 2 or more. Jirouš and Ljuljka (1999) determined the levels of colour differences for paper but these can be used for wood also (Straže and Gorišek 2008). It should be noted that the difference between wooden surfaces cannot be noticed just because of the colour change but also of the inhomogeneity of wood itself (vessels, tyloses, ray flecks, grain structure, early and latewood transition).

If the wood is exposed to natural weather, the colour change is affected by the temperature, sunny hours, precipitation, rate of UV-A and UV-B radiation, etc. The surface starts to grey after months because of the leaching of lignin, thus a* and b* decrease significantly (Tolvaj and Papp 1999, Tolvaj and Mitsui 2005). The advantage of artificial ageing is the reproducibility of the measurements, the constant settings and the short testing time. In these test, artificial light sources are used like xenon lamp, mercury-vapour lamp, etc. Only photodegradation occurs unlike in case of weather exposure.

The colour of objects is determined by the conjugated double bonds in their chemical structure. These bonds are present in lignin and extractives. The colour of wood is mainly defined by the quantity and quality of extractives. The changes in the chemical structure can be examined by Fourier Transform Infrared (FTIR) spectroscopy. Here the reflectance spectra can be converted to absorbance spectra with Kubelka-Munk (K-M) theory. The changes are better evaluated on differential spectra as the bands are clearly visible (Tolvaj 2013).

In the past decades, many researchers reported in the topic of photodegradation using mercury-vapour lamp (Ohkoshi 2002, Colom et al. 2003, Tolvaj et al. 2011, Tolvaj 2013). After UV exposure, the reduction in absorption of guaiacyl lignin (1510cm-1) and syringyl lignin (1600cm-1) indicates the
degradation of lignin aromatic ring. The absorption of conjugated carbonyl groups initially decreases then increases. At 1765 and 1708cm⁻¹ band the absorption of unconjugated carbonyl groups increase.

Acetylation is a chemical wood modification method, which improves the durability, dimensional stability and strength of wood without being toxic to the environment (Hill 2006). In the process, the wood is impregnated with a liquid reagent using vacuum and pressure, so that it becomes integrated in the wood modifying its chemical structure and properties. On industrial level, acetic anhydride is used (Accsys Technologies, the Netherlands). When acetic anhydride reacts with the hydroxyl (OH) groups in the cell wall, acetyl groups form. These are bigger molecules than OH groups which results in a denser and heavier wood material. The properties of acetylated wood is generally given according to its WPG (Weight Percentage Gain) as the physical and mechanical properties usually improve by increasing the WPG.

The colour of wood does not necessarily change significantly after acetylation unlike in case of thermal modification, as it is done at lower temperatures. Broadleaved species usually darken at a higher rate than coniferous species, and dark-coloured species usually become brighter while light-coloured species usually darken (Rowell 2013, Mitsui 2010, Fodor 2015, Dong et al. 2016).

After acetylation, the absorption of carbonyl groups (174cm⁻¹) and methine (CH), methylene (CH₂), methyl (CH₃) groups (297 cm⁻¹) increase while the absorption of the functional groups of lignin decrease (Mohebby and Radjihassani 2008, Fodor et al. 2017).

In this work mercury-vapour lamp was used for the irradiation of wood. It results in a stronger colour change in a shorter time than xenon lamp or natural sunlight. This is because the mercury-vapour lamp has different wavelength emission. Unlike xenon lamp, it emits light in all UV regions. 80% of its emission is UV light, from which 31% is UV-A (380-315nm) region, 24% is UV-B (315-280nm) region and 25% is UV-C (>280nm) region. It cannot imitate the irradiation of natural sunlight but the progress of photodegradation can be observed in a short time (Tolvaj and Persze 2011).

OBJECTIVE
The aim was to examine the effect of acetylation on the photostability of hornbeam wood. The samples were to artificial irradiation (mercury-vapour lamp). The rate of photodegradation was evaluated according to the change of colour components and FTIR differential spectra.

MATERIAL, METHOD, EQUIPMENT
Edged and air-dry hornbeam boards were ordered from a Hungarian sawmill (BOPAÁR Ltd.). The dimensions were 27×160×2500mm (thickness × width × length). Half of the boards were left untreated and the other half was sent to Accsys Technologies to be acetylated under industrial conditions. The average WPG was 15%.

For the tests, half of the samples were coated with boiled linseed oil as it is of reasonable price, does not hide the grain pattern of wood and is of natural origin. It was layered two times. The artificial ageing was carried out in a Sapratin ageing machine, at the Institute of Physics and Electronics at the University of Sopron. There were two mercury-vapour lamps used (800 Watt) which were 64cm above the samples. The temperature of the equipment was set to 50°C.

The samples  were of 20×45×140mm (thickness × width × length) with planed, smooth, tangential surface. There were five circles marked on each sample for colour measurement. There were 10 hornbeam (marked H), 10 acetylated hornbeam (A), 10 boiled linseed oil-coated hornbeam and 10 boiled linseed oil-coated and acetylated hornbeam samples.

The colour was expressed in CIE L*a*b* colour space with X-Rite SP60 Portable Colorimeter and Color iControl program. The colorimeter's sensor head was 8mm. The colour was measured and calculated based on the D65 illuminant and 10° standard observer.

The samples for FTIR spectroscopy were of 5×10×30mm (thickness × width × length) with planed, smooth, radial surface. For the measurements JASCO FT/IR-6300 spectrometer and Spectra Manager program was used. The final spectra of each sample was the average of 45 measurements.

The colour and FTIR measurement was determined after 0-5-10-20-30-60-120-200 hours of irradiation.

RESULTS AND DISCUSSION
As a result of acetylation the colour of hornbeam became darker, greyish brown. The ray flecks became darker, the wavy grain has become more prominent to the naked eye. The modification process affected the whole cross section. The outer layer of wood (2-3mm) is darker but it disappears after further processing.

After 5 hours of mercury-vapour lamp irradiation, the colour changed remarkably, especially in case of boiled linseed oil-coated acetylated hornbeam. The rate of colour change decreased over time (Fig. 1.).
During irradiation, hornbeam’s light colour became darker yellow. The brightness decreased while the red and yellow hue increased (Table 1 and Fig. 1.). Fig. 2. shows the shifting of the yellow and red hue. The colour of hornbeam coated with boiled linseed oil changed similarly, the brightness decreased, the red hue increased, while the yellow hue initially (in the first 5 hours) decreased then increased. Coating hornbeam wood with boiled linseed oil improved its colour stability. (Fig. 3.).

Acetylated hornbeam’s dark greyish brown colour brightened heavily as a result of mercury lamp irradiation. The biggest colour change was measured in the first 5 hours. The brightness increased, the red hue decreased, the yellow hue initially decreased then increased (Table 1 and Fig. 1.). The biggest total colour change was in case of boiled linseed oil-coated, acetylated hornbeam. (Fig. 1.). The change of its colour components were similar to acetylated hornbeam but the shifting of red and yellow hue was more prominent (Fig. 2.).

### Table 1

| Colour coordinates of hornbeam samples before and after exposed to mercury-vapour lamp for 200 hours | Before irradiation | After irradiation (200 hour) |
|---|---|---|---|
| L* | a* | b* | L* | a* | b* |
| Hornbeam | 80,71 | 2,93 | 18,92 | 72,64 | 7,77 | 33,10 |
| Acetylated hornbeam | 52,97 | 6,61 | 20,59 | 67,99 | 3,40 | 18,23 |
| Boiled linseed oil-coated hornbeam | 72,17 | 6,39 | 34,94 | 64,69 | 11,17 | 38,24 |
| Boiled linseed oil-coated acetylated hornbeam | 28,19 | 15,44 | 41,55 | 55,65 | 8,18 | 27,05 |

**Fig. 1.**

Change of colour coordinates during mercury-vapour lamp irradiation (L*: lightness, a*: red hue, b*: yellow hue, ΔE*: colour difference of the actual and the original colour, H: hornbeam, A: acetylated hornbeam, untreated or BLO: coated with boiled linseed oil).
Fig. 2. Change of red ($a^*$) and yellow ($b^*$) colour points during mercury-vapour lamp irradiation. The points marked with triangle represent the colour points of the original sample, then it is followed by the colours measured in the 5th, 10th, etc. hours (H: hornbeam, A: acetylated hornbeam, untreated or BLO: coated with boiled linseed oil).

Fig. 3. Box diagram of the colour changes ($\Delta E^*$) caused by 200 hour-long mercury-vapour lamp irradiation compared to the original colour (H: hornbeam, A: acetylated hornbeam, untreated or BLO: coated with boiled linseed oil).

Fig. 4. Photos of hornbeam samples before and after being exposed to 200 hour-long mercury-vapour lamp irradiation: a - untreated hornbeam, b - acetylated hornbeam, c - boiled linseed oil-coated hornbeam, d - boiled linseed oil-coated, acetylated hornbeam.

Fig. 4. shows the scans of one sample from each type before and after 200 hour-long irradiation. The yellowing of hornbeam and brightening of acetylated hornbeam is visible to the naked eye.

The FTIR spectra on Fig. 6. was measured before irradiation. After each phase (5-10-20-30-60-120-200 hours) the FTIR spectra was measured again. The changes were determined according to differential spectra, which was calculated by subtracting the initial (non-irradiated) spectra from the irradiated spectra.
In each spectrum the peaks and absorption bands were determined (Table 2) and marked with numbers on each diagram and in the text.

According to previous studies (Fodor 2015), the moisture content of hornbeam is greatly reduced due to the bulking of the cell wall during acetylation. As the cell wall’s OH groups were replaced by acetyl groups, the weight increased by 15% (WPG). During UV irradiation the hydrogen bonds were broken, the OH groups changed and rearranged in the system which is indicated by the positive and negative peaks in the spectra (1). There are bigger peaks (differences) in the differential spectrum of acetylated hornbeam than untreated hornbeam.

The absorption of methylene (CH), methylene (CH2) and methanol (CH3) groups increased after UV-B and UV-C irradiation except for acetylated hornbeam. This band is usually not affected by photodegradation. The reason for this absorption change can be due to the fact that this band cannot be separated from the band of OH stretching (Tolvaj and Faix 1995). Acetylated hornbeam has a bigger proportion of these groups than untreated hornbeam.

Cellulose is a rigid chain, linear polymer which is mostly crystalline in wood with some amorphous parts. The content and structure of cellulose is directly related to wood strength properties (Winandy and Rowell 1984). A previous research proved that there was no significant degradation in the cellulose of hornbeam after acetylation (Fodor et al. 2017). As a result of UV irradiation, the aromatic rings of lignin rupture, carboxyl groups and/or lactones form, thus the absorption of carbonyl groups increase (Tolvaj and Faix 1995). The unconjugated carbonyl region has two distinct wavenumber ranges at 1800-1760cm^-1 and 1740-1700cm^-1 (3). In case of acetylated hornbeam the absorption at 1743cm^-1 is higher than at 1793cm^-1. The absorption of hornbeam is smaller at 1698cm^-1 than at 1773cm^-1. In every case, the absorption of conjugated carbonyl groups decreased (4). These peaks are less prominent in case of boiled linseed oil-coated samples. After acetylation the amount of carbonyl groups increased, thus the rate of photodegradation was higher. In case of non-acetylated samples, the thermally unstable acetyl groups degraded which indicates the reduction of carbonyl groups. There are positive and negative peaks as well in C-H deformation (8), C-O stretching (11), asymmetric C-O-C stretching (12) and symmetric C-O-C stretching (13) in hemicellulose, this can be due to the rupture of etheric bonds and reformation in the system.

### Table 2

<table>
<thead>
<tr>
<th>Band number</th>
<th>Wavenumber (1/cm)</th>
<th>Functional group</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3677-3152</td>
<td>Hydroxyl group (OH) stretching</td>
<td>Cellulose, hemicellulose, lignin</td>
</tr>
<tr>
<td>2</td>
<td>2983-2844</td>
<td>CH stretching</td>
<td>Methine (CH), methylene (CH2), methyl (CH3) groups</td>
</tr>
<tr>
<td>3</td>
<td>1804-1773, 1745-1698</td>
<td>Unconjugated C=O (carbonyl group) stretching</td>
<td>Xylan</td>
</tr>
<tr>
<td>4</td>
<td>1675-1658</td>
<td>Conjugated C=O (carbonyl group) stretching</td>
<td>Xylan</td>
</tr>
<tr>
<td>5</td>
<td>1604-1596</td>
<td>Aromatic skeletal vibration</td>
<td>Syringyl lignin</td>
</tr>
<tr>
<td>6</td>
<td>1514-1495</td>
<td>Aromatic skeletal vibration</td>
<td>Guaiacyl lignin</td>
</tr>
<tr>
<td>7</td>
<td>1476-1411</td>
<td>Asymmetric C-H deformation</td>
<td>Lignin, carbohydrates</td>
</tr>
<tr>
<td>8</td>
<td>1397-1383</td>
<td>Symmetric C-H deformation</td>
<td>Cellulose and hemicellulose</td>
</tr>
<tr>
<td>9</td>
<td>1372-1309</td>
<td>C-H deformation</td>
<td>Cellulose</td>
</tr>
<tr>
<td>10</td>
<td>1279-1266</td>
<td>Ring vibration</td>
<td>Guaiacyl lignin</td>
</tr>
<tr>
<td>11</td>
<td>1219-1215</td>
<td>C-O stretch</td>
<td>Xylan</td>
</tr>
<tr>
<td>12</td>
<td>1176-1159</td>
<td>Asymmetric C-O-C stretching</td>
<td>Cellulose and hemicellulose</td>
</tr>
<tr>
<td>13</td>
<td>1146-1117</td>
<td>Symmetric C-O-C stretching</td>
<td>Cellulose and hemicellulose</td>
</tr>
<tr>
<td>14</td>
<td>1102-1067</td>
<td>C-O vibration</td>
<td>Cellulose and hemicellulose</td>
</tr>
</tbody>
</table>

(Fig. 5.).
Fig. 5.
Change of hornbeam samples’ FTIR difference spectra during 200 hour-long mercury-vapour lamp irradiation (BLO: boiled linseed-oil).
Lignin is responsible for retaining the wood strength and stiffness in case wood is contacted to moisture as lignin is the most hydrophobic component of the wood and it can limit the access of water (Winandy and Rowell 1984). During acetylation, in the acidic medium some parts of lignin can dissolve (Rowell 2005). The structural change and degradation of lignin was indicated by low absorption of aromatic functional groups (Fodor et al. 2017). As a result of mercury lamp irradiation the aromatic rings of lignin ruptured, which is indicated by lower absorptions in syringyl (5) and guaiacyl (6) lignin, asymmetric C-H deformation in lignin at 1476-1470 cm^{-1} (7), ring vibration in guaiacyl lignin (10) and aromatic C-H skeletal vibration (13). The absorption reduction in boiled linseed oil-coated samples is less notable.

Alterations of the lignin structure can also account for the slightly darker, walnut-like colour of acetylated hornbeam. These changes can include the oxidation of phenolic skeletal system as an effect of heat and acidic medium, as well as the reaction of lignin with evolving furfural in strong acidic medium (Dongre et al. 2015, Fodor et al. 2017) which results in not only structural changes of lignin, but also alterations in the colour of wood. However, the strength and stiffness properties of acetylated hornbeam increased (Fodor 2015) which indicate the degradation of lignin was not significant. The brightening of acetylated hornbeam during mercury lamp irradiation is probably associated with the extractive content. After acetylation, the extractive content of hornbeam increased (Fodor et al. 2017) which transformed during UV irradiation thus influence the colour. This effect was somewhat eased by coating with boiled linseed oil.

**CONCLUSIONS**

The aim of this work was to examine the effect of acetylation and boiled linseed oil coating on the photodegradation of hornbeam wood. 200 hour-long mercury-vapour lamp irradiation was carried out on hornbeam, acetylated hornbeam, boiled linseed oil-coated hornbeam and boiled linseed oil-coated, acetylated hornbeam samples.

According to our results, during UV irradiation hornbeam yellowed, the red hue (a^*) and yellow hue (b^*) increased. The dark, greyish brown colour of acetylated hornbeam brightened during UV irradiation because of the transformation of extractives. Unlike hornbeam, its brightness increased while the red and yellow hue decreased. Coating the samples with boiled linseed oil decreased the rate of colour change.

According to the FTIR spectra, lignin did degrade during mercury-vapour lamp irradiation. The absorption of functional groups in lignin decreased which led to the increase of methane, methylene, methyl and carbonyl groups. The rate of degradation and structural changes were highest in case of acetylated samples, but the strengthening polymers did not degrade notably.

In the future, other sealants and varnishes are to be tested on acetylated hornbeam that are natural, non-toxic and pigmented.

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