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ACETYLATION OF EUROPEAN HORNBEAM (*CARPINUS BETULUS* L.) WOOD FOR OUTDOOR APPLICATIONS

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Abstract

Many European wood species have low natural durability which makes them unable to be used for exterior applications without additional protection. In this work, European hornbeam wood (*Carpinus betulus* L.) was industrially acetylated in order to improve its properties and widen its usage.

Thorough literature research was made on the availability and future of European hornbeam wood, from forestry and wood industry point of view. Then, the current state of research was explained regarding the modification of this species. Previous work of my master thesis on acetylated hornbeam discussed improved dimensional stability, mechanical properties, durability against fungi in laboratory conditions, and aesthetical color.

In order to understand the changes in product-related properties after acetylation, chemical analysis was carried out to determine the chemical components, pH, buffering capacity, and content of organic extractives. These findings were evaluated by Fourier-transform infrared spectroscopy (FTIR) and high-performance liquid chromatography (HPLC). After acetylation, changes in microscopic structure were examined by bright-field microscopy and scanning electron microscopy.

In a six-year-long test in soil, acetylated hornbeam showed no signs of fungal decay or insect damage, except for one stake, that was locally attacked by brown rot after 1.5 years. The decayed area was less acetylated compared to the good performing stakes, proven by FTIR analysis.

Acetylated hornbeam is more hydrophobic, having increased contact angle and lower surface energy. This influences its bonding and coating properties. Compared to untreated hornbeam, the shear strength was reduced in dry conditions, but showed enhanced strength when soaked in cold or boiling water. The same was experienced in the bonding strength results with polyvinyl acetate and polyurethane adhesives.

When exposed to ultraviolet light, acetylated hornbeam fades and grays similarly to untreated hornbeam, based on test results of natural irradiation (2 years) and artificial (200 hours) irradiation. Besides getting a patina, it remains intact, without cracking or warping, like untreated hornbeam. For the case when photostability is desired, various coatings were tested, among which three dark pigmented stains showed the best results.

According to these results, use classes, product groups, market share of acetylated hornbeam were determined, supplemented by SWOT analysis and related literature, in order to give a full picture of it as a product.

Kivonat

Számos európai fafaj alacsony tartóssági osztályba tartozik, ezért nem alkalmasak kültérben való felhasználásra további védelem nélkül. Ebben a kutatásban közönséges gyertyán (*Carpinus betulus* L.) acetilezésére került sor ipari körülmények között, tulajdonságainak javítása és felhasználásának bővítése céljából.

Alapos szakirodalmi kutatás történt a gyertyán elérhetőségéről és jövőjéről, erdészeti és faipari szempontból. Ezután a gyertyán modifikálásával kapcsolatos kutatások jelenlegi állása került ismertetésre. Korábbi kutatásaink az acetilezett gyertyán jobb dimenzióstabilitásáról, mechanikai tulajdonságairól, laboratóriumi gombaállóságáról és esztétikus színéről számoltak be.

Az acetilezés okozta termékspecifikus tulajdonságok változásának megértése érdekében kémiai vizsgálatokra került sor a kémiai összetevők, pH, pufferkapacitás és szerves extraktumok tartalmának meghatározására. Ezek az eredmények Fourier transzformációs infravörös spektroszkópiával (FTIR) és nagy teljesítményű folyadékkromatográfiával (HPLC) is alá lettek támasztva. A mikroszkópos szerkezet acetilezés utáni változásai világos látóterű mikroszkóppal és pásztázó elektronmikroszkóppal kimutathatóak voltak.

6 év tartóssági vizsgálat során az acetilezett gyertyán nem mutatta korhadás vagy rovarkárosítás jeleit talajjal való érintkezés esetén, kivéve az egyik mintatestet, amelyen 1,5 év után barna korhadás jelei mutatkoztak meg. A korhadt résznek alacsonyabb volt az acetiltartalma, melyet FTIR vizsgálatok igazoltak.

Az acetilezés növelte a gyertyán víztaszító tulajdonságait, peremszögét, és csökkentette a felületi energiáját. Ez befolyásolja a ragaszthatóságot és felületkezelhetőséget. A kezeletlen gyertyánhoz képest a nyírószilárdság csökkent száraz körülmények között, de fokozott szilárdságot mutatott vízben való áztatás vagy főzés után. Ugyanez volt a tapasztalat a polivinil-acetát és poliuretán ragasztók ragasztási szilárdsági eredményeinél is.

UV sugárzásnak kitéve az acetilezett gyertyán hasonlóképpen elhalványul és elszürkül, mint a kezeletlen gyertyán, természetes öregítés (2 év) és mesterséges (200 óra) öregítés vizsgálati eredményei alapján. A patinásodás ellenére ép marad, repedés vagy vetemedés nem alakul ki, mint a kezeletlen gyertyánnál. Elvárt színtartósság esetére különböző felületkezelő anyagok is a vizsgálat tárgyát képezték, amelyek közül három sötét színű lazúr mutatta a legjobb eredményt.

Ezen eredmények alapján az acetilezett gyertyán felhasználási osztályai, termékcsoportjai, piaci részesedése meghatározásra kerültek, kiegészítve GYELV elemzéssel és a kapcsolódó szakirodalommal, hogy teljes képet kapjunk róla, mint termékről.

This dissertation is dedicated
in loving memory of
my father and grandfathers.

Chapter 1. Literature review

1.1. About sustainability and wood

In the past decades, there has been an increased awareness of the fragility of the environment. Our present patterns of consumption are not sustainable in the long term. Mankind uses non-renewables (material, energy) but their reserves are finite and exhaustible. For a better future, there are many solutions for reducing greenhouse gas emissions which include, but are not limited to: use renewable materials (explained below), renewable energies (wind energy, solar power, water/hydropower), develop sustainable technologies, reduce CO_2 emissions, capture, utilize and store carbon, reduce cattle farming and consume less meat, decrease the rate of transportation (cars, planes), use energy-efficient (energy-saving) household items, use modern data centers instead of single computers (cloud computing services and platforms), etc.

A renewable material is a material, which is made of natural resources, and it can be replenished, generation after generation. These include wood, bamboo, agrifibers, cork, corn (corn ethanol instead of petroleum, poly-lactic acid instead of plastic), and cotton (instead of plastic textiles, wool, and silk). Wood has been utilized since the beginning of humankind for various applications like fuel, shelter, weapons, tools, and furniture. It is a favored resource for its easy workability, sustainability, renewability, aesthetics and its important characteristic: being able to store carbon as a tree, wood, wood-based panel and paper as well. Humans also adapted to its weaknesses: it has different properties in three anatomical directions (inhomogeneous); it can be degraded by many microorganisms; it burns, and it is decomposed by ultraviolet radiation (Stamm, 1964; Rowell, 1983). Wood, including wood fibers and particles, can be altered to meet expectations like strength as great as steel, or flexibility as plastic, or even transparency as glass or plastic film.

In the wood industry, sustainability can be promoted by processing domestic wood species. There are over 8000 tree species which have become restricted and endangered due to habitat destruction or degradation and unsustainable timber production, and illegal logging. These species are listed by the Convention on International Trade of Endangered Species (CITES, categories listed as Appendix I – endangered, II – at risk in the wild, III – at risk in certain countries) and the International Union for Conservation of Nature (IUCN, categories listed as critically endangered, endangered, and vulnerable).

The use of timber and wood-based products in construction help meet the sustainable development goals set by the United Nations (UN) and complies with the Green Deal of the European Union (EU). Now, glue laminated timber (GLT, glulam) and cross laminated timber (CLT) are established engineered wood products (EWPs) and are critical assets in green timber building constructions. Although they are mainly based on softwoods, they could be made from hardwoods as a type of green innovation. Hardwoods can be a more efficient, sustainable raw material for plywood, veneer and strand based LVL, laminated strand lumber (LSL), and I-joists as well (van Acker, 2021).

As the need for wood material as well as for bioenergy is constantly growing, it will inevitably lead to higher competition for the same resource and can evolve into a critical shortage. Vertical integration in addition to better tree and wood quality should lead to a more structured approach, and in the end, produce green energy based on woody biomass. In order to increase the use of wood products for the building sector, there is a need to include engineered wood products based on hardwoods, having properties comparable with those used in building and in the construction sector. In this way, sustainable strategies can be developed for green building over the coming decades. The raw material can also easily come from forest plantations based on fast growing hardwood species (van Acker, 2021).

For many years, the output of roundwood in the EU has been dominated by coniferous trees. In the course of climate change, the increasing temperature, temperature extremes, and drought need to be taken into account and adapt to it during forest management. In order to enhance the provision of ecosystem services, the plantation and use of hardwood species need to be increased. Hardwood forests are Europe's largest overlooked renewable resource. Today, they are mainly used inefficiently for energy generation. It is essential to connect the forestry chain with the processing industries and the final customers. Hardwoods represent the primary opportunity to foster a long-term strategic pathway for sustainable development of the emerging forest-based circular bio-economy and thus respond to major key societal and environmental global challenges (van Acker, 2021).

Innovative and sustainable ideas in the building industry:

- replace solid softwood with beech, birch, fast-growing hybrid poplar or willow;
- produce CLT out of hardwood (disadvantage: higher density, longer pressing time, lower availability compared to softwood);
- make glulam out of white ash, yellow birch, white oak, beech, poplar;
- LVL from beech, aspen, poplar;
- manufacture combined glulam – hardwood outer lamella, softwood inner lamella;
- use modified wood for glulam beams, plywood, OSB, LSL, LVL production in order to increase durability and dimensional stability;
- and use adhesive-free technologies (van Acker, 2021).

Engineered wooden products contribute to the main advantages of building with wood: they are fast (short building time), light (very good strength to stiffness ratio), and green (sustainable, bioenergy). A greater use of hardwoods in the building sector will underpin sustainability and environmental objectives related to greenhouse gas emission and significantly contribute to the circular economy in particular through the improvement of a better vertical integration between cultivation and the wood industry as part of the future bio economy (van Acker, 2021).

1.2. About wood modification

For decades, wood was made to last longer in the environment by treating it with preservatives. Here, toxicity was the mechanism to prevent decay. Various waterborne salt formulations and combinations of chromium copper and arsenic, borates, pentachlorophenol, and oil type formulations (creosote) were used as wood preservatives, but these have been banned in many countries or only allowed with limited use. Their toxic mechanism involves denaturation of proteins, inactivation of enzymes, cell membrane disruption, inhibition of respiration and inhibition of protein synthesis (Rowell, 2005). There are two types of wood preservation processes: non-pressure (dipping, brushing, diffusion, vacuum), and pressure processes (full cell, modified empty cell and empty cell).

Today, non-toxic methods are preferred for wood preservation (Rowell, 2020). These include, but are not limited to: oil coating (linseed oil, tung oil), extractives purified from durable species, burying in mud, charring (e.g. yakisugi), and wood modification techniques. *"Wood modification involves the action of a chemical, biological or physical agent upon the material, resulting in a desired property enhancement during the service life of the modified wood. The modified wood should itself be non-toxic under service conditions, and furthermore, there should be no release of any toxic substances during service, or at end of life, following disposal or recycling of the modified wood. If the modification is intended for improved resistance to biological attack, then the mode of action should be non-biocidal"* (Hill, 2006).

Wood modification processes can be divided into two groups: active modification, which changes the chemical structure of wood, and passive modification, which does not change it, while improving the wood properties.

Most active modification processes involve the chemical reaction with the hydroxyl (-OH) groups of wood polymers (Rowell, 2005). They are the most reactive sites and are responsible for the dimensional stability of wood through their hydrogen bonding to water. In moist wood, water molecules form hydrogen bonds between OH groups and individual water molecules, the number of which changes during shrinkage and swelling.

Several wood-treatment interaction mechanisms can occur at the same time during wood modification. These are responsible for new wood properties like increased strength, improved durability, and better dimensional stability, etc. These mechanisms are illustrated in Figure 1.

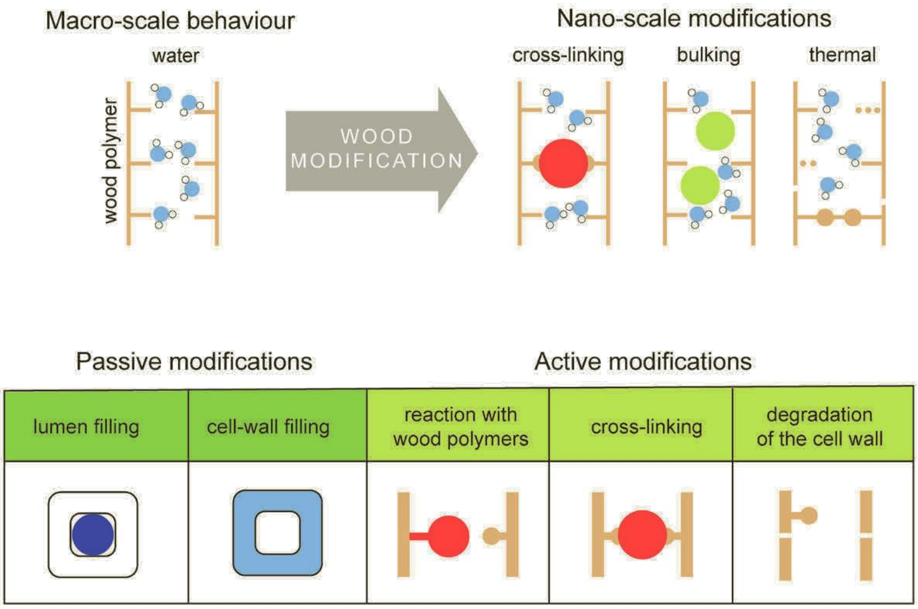

Figure 1. Schematic diagram illustrating the effect of active and passive modifications (Sandberg et al., 2017, 2021).

Most of the wood modification processes are based on the work of Alfred Stamm (Stamm, 1964), but there was an early attempt to use chemical modification by the Nobel family. In the 1840s, they used ferric sulphate and an acid to impregnate wheel hubs for better durability and dimensional stability (Carlberg, 2019).

Modification processes can be divided to four main types: chemical treatment, thermally-based treatment, EPL processes (treatment with the use of electromagnetic irradiation, plasma or a laser), and other types of treatment (Figure A64, see Figure A… in Appendices).

Thermally-based processes involve the combined use of temperature and moisture (thermo-hydro processes, TH), through which force can be applied (thermo-hydro-mechanical processes, THM) to change the wood properties or to shape it (Navi and Sandberg, 2012). Impregnation or gluing to lock a shape can also be included in these processes.

Wood is capable of absorbing a large amount of electromagnetic energy at high moisture content, which is used during electromagnetic treatment processes. These processes also include changing the wood surfaces by a laser or plasma treatment, abbreviating them as EPL processes. There are also other processes which have been or may be of interest for wood modification, but have not been further developed or are not used industrially or at least on a larger scale (Figure A64) (Sandberg et al., 2021).

Chemical modification is a process of bonding a reactive, stable, less hydrophilic, simple chemical to a reactive part (OH group) of a wood polymeric constituent (lignin, hemicelluloses, cellulose), with or without catalyst, to form a covalent bond between the two (Rowell, 1983). These can be ethers, acetals, and esters (Larsson-Brelid, 1998; Rowell, 2006). Since it alters the cell-wall macromolecules, it is regarded as an active modification process. Chemical modification has been used historically to 1) isolate various cell wall components; 2) study differences in properties as a result of changing the chemistry; and 3) improve the performance properties of wood. Many chemical reaction systems have been published for the modification of wood and the systems have been reviewed in the literature. The reagent does not need to be environmentally friendly itself, but the process and the final product must be. An important indicator of successful modification is the weight percentage gain (WPG), which is defined as the dry weight increase of wood after the treatment. In this work, chemical modification, specifically acetylation with acetic anhydride will be discussed.

1.3. About acetylation

Cellulose acetate was one of the first plastic materials (1865) produced by mixing cellulose with acetic anhydride, and it has been used in many products, like cigarette filters and photographic films (Sandberg et al., 2021).

The first experiment in the acetylation of wood was done by Walter Fuchs, who acetylated pine to isolate lignin using acetic anhydride and sulfuric acid as catalysts (Fuchs, 1928). The weight percentage gain was 40%. Similarly, Otto Horn acetylated beech to remove hemicelluloses (Horn, 1928). In the same year, powdered beech and pine was acetylated using pyridine or dimethylaniline as a catalyst to yield an acetyl weight gain of 30-35% after 15 to 35 days at 100 °C (Suida and Titsch, 1928). The first patent on wood acetylation was filed by Hermann Suida a few years later (Suida, 1930). Harold Tarkow and his colleagues acetylated balsa for decay resistance (Tarkow and Moses, 1945), and one year later for dimensional stability (Tarkow et al. 1946). They documented the improvement of physical, mechanical, durability and photostability properties of several wood species after acetylation. Another patent was filed on acetylation of lignocellulosic board materials a year later (Stamm and Tarkow, 1947). Further reports, which were part of the pioneering work of the Forest Products Laboratory are detailed in recent review (Ibach and Rowell, 2021). Since then, many laboratories have performed acetylation on various wood species and agricultural resources: beech, Norway spruce, Scots pine, poplar, Radiata pine, black locust, Southern yellow pine, ponderosa pine, red oak, sugar maple, walnut, elm, cativo, eucalyptus, rubberwood, willow, OSB, bamboo, bagasse fiber, jute, kenaf, wheat straw, pennywort, water hyacinth, etc (Sandberg et al., 2021).

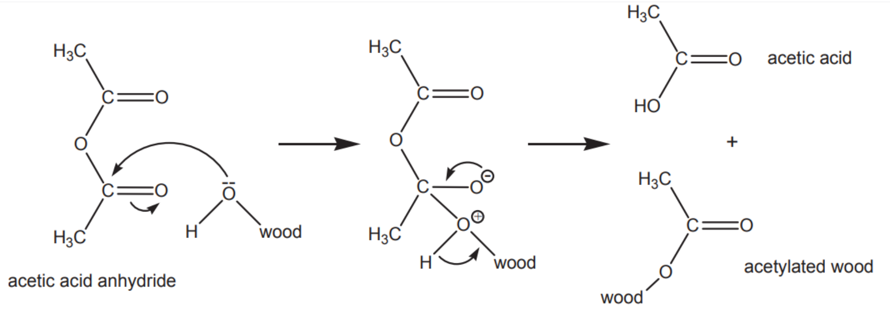

Figure 2. General scheme for the acetylation of wood by reaction with acetic acid anhydride (Schwanninger et al., 2011).

The reaction of acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall, with the formation of the by-product acetic acid (Figure 2).

The by-product acid must be removed from the product as the human nose is quite sensitive to the odor of acetic acid. While this is easily done with wood particles and fiber, it is somewhat difficult to do in solid wood. Acetylation is a single-addition reaction, which means that one acetyl group is on one hydroxyl group with no polymerization.

Presently, acetylated wood is industrially produced by Accsys Technologies in Arnhem, the Netherlands. This acetylation process is protected by patent (Girotra, 2009). It is marketed today under the commercial name Accoya®, utilizing predominantly radiata pine wood (*Pinus radiata* D. Don), and to a lesser extent, beech (*Fagus sylvatica* L.) and alder (*Alnus* sp.), having a 20% acetyl weight gain on the average. The basic properties of Accoya® are listed in Table A22 (see Table A… in Appendices).

In the past century, various wood species have been subjected to acetylation, both in laboratory as well as on a (semi)commercial scale. Those wood species may be successfully acetylated, which are easy to dry, to impregnate, and which have a low to intermediate density (300 to 700 kg/m^3). Other, product-related characteristics are important as well, like available volume, dimensions, quality, price, properties, acetylation economics and potential markets (Bongers et al., 2008). Non-uniform acetylation results were confirmed in spruce and Douglas fir, having large dimensions, with wood quality problems such as distortions and cracking, and low performance. There have been issues with the presence of different qualities within a board of highly permeable wood species, like sapwood, heartwood, reaction wood, knots, and resin canals, which can all lead to uneven acetylation and lower quality (Bongers and Uphill, 2019). Several other wood species were tested as well, which showed promising results, like masson pine (Bongers and Uphill, 2019), tauari vermelho (Bongers et al., 2008), beech, alder, lime, maple (Bollmus et al., 2015), Scots pine (Larsson-Brelid and Tillman, 1989), Corsican pine (Hill and Jones, 1996), aspen, poplar (Beckers and Militz, 1994), and Southern yellow pines (Goldstein et al., 1961).

Nowadays, Accoya® wood is available worldwide, and its main uses are typically in the outdoors, above or in ground contact (Mantanis, 2017). According to the companies’ annual reports, Accoya® sales were 25, 34, 34, 40, 43, 50, 58 and 61 thousand m^3 per year between 2014-2021. The company has a production capacity goal of 200,000 m^3 annually for 2025 (Accsys PLC, 2021). Because of its cost, it is mainly used in value-added products in transportation, sports equipment, military, and construction. It has been utilized as exterior doors and windows, residential decking, sidings, outdoor furniture, musical instruments, wet rooms, greenhouses, bridges, outdoor sculptures, etc (Mantanis, 2017; Sandberg et al., 2017).

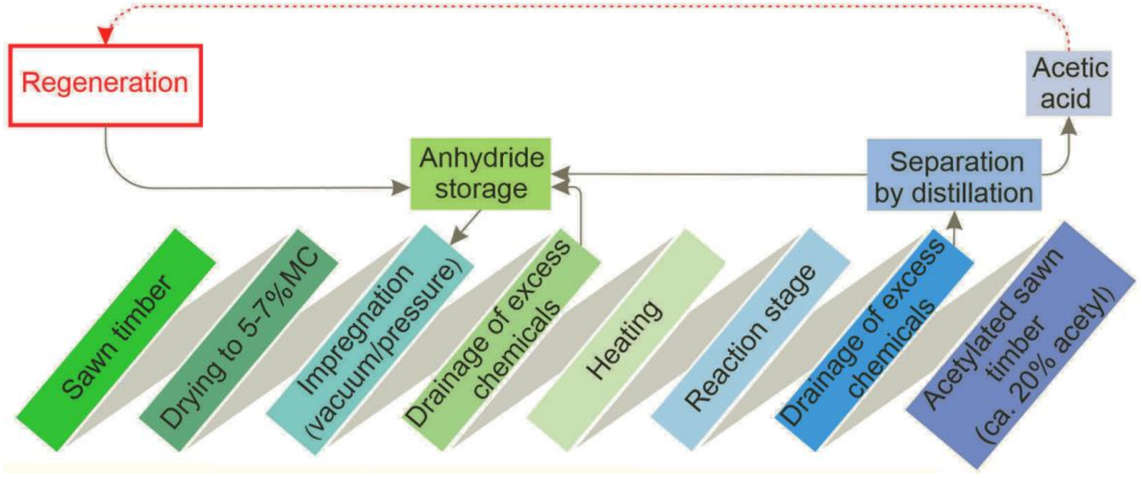

Figure 3. Scheme of the acetylation process (Larsson-Brelid, 2013).

In the Accoya® process, the wood is dried at high temperature and then conditioned to a moisture content of 5-7% before the acetylation. The wood is impregnated in a pressurized autoclave, so that the reagent penetrates through the wood and into the cell walls. It is heated approximately at 120-140°C allowing the reagent to react with hydroxyl groups in the wood (Larsson-Brelid, 2013). At present, acetic acid is not upgraded to anhydride in the industrial process, they sell it to chemical and food industry. As the value of WPG cannot be precisely calculated from its dry weight for industrially treated wood, the maximum degree of acetylation and acetyl content is determined with chemical analysis methods such as high-performance liquid chromatography (HPLC), gas chromatography–mass spectrometry (GCMS), Fourier-transform infrared spectroscopy (FTIR) and near-infrared spectroscopy (NIR) (Beckers et al., 2003).

In 2022, the price of wood strongly depended on the wood quality and dimensions. The prices were also very high due to the increased demand for wood supply worldwide. Accsys technologies is standardized using a 4-sides clear and 3-sides clear quality. According to the company, in the spring of 2022, the typical price ranges of raw material used for acetylation were (cost, insurance and freight, CIF for short) 650 – 700 EUR/m^3 for Radiata pine (from New Zealand), 700 – 850 EUR/m^3 for beech (from Germany), and 950 – 1200 EUR/m^3 for alder (from the USA). At the same time, the commercial price of Accoya® was approximately 3,000 EUR/m^3 in the Netherlands, and ± 200 EUR/m^3 in other European countries (according to webshops and information from industrial workers).

1.4. Position of modified wood in the market

As researchers, policy makers and end-users became more aware of the importance of the bioeconomy in the future, the need for more environmentally-acceptable treatments increased. In Europe, the highest annual production among modified products is of thermally modified wood (535,000 m^3) and acetylated wood (120,000 m^3). The estimated annual production of densified wood is approximately 2,000 m^3, and it is 45,000 m^3 for furfurylated wood (Mantanis, 2017; Sandberg et al., 2017; Jones and Sandberg, 2020) (Table 1).

Table 1. Overall estimated global production of modified wood (Jones et al., 2019; Jones and Sandberg, 2020).

Modification	Europe	China	North America	Oceania/Japan	Other
Thermally modified timber	695,000	250,000	140,000	15,000	10,000
Densified wood	2,000	<1,000		<1,000	
Acetylation	120,000				
Furfurylation	45,000				
Other methods	35,000	290,000		5,000	To be determined

The national production of thermally modified wood has become popular as it can be commercialized on a small scale. There are at least 27 countries which produce thermally modified timber, and 12 of them had commercial production over 10,000 m^3/year according to a questionnaire (Jones et al., 2019). Acetylated wood is industrially produced only in the Netherlands by Accsys Technologies, while in the UK, a new plant is under development.

On the global market, thermally modified wood (China, USA, Canada, New Zealand, Brazil), resin impregnated wood (China, Malaysia, India), and DMDHEU modified wood (New Zealand) has been widely developed (Sandberg et al., 2017; Jones and Sandberg, 2020). The overall estimated global production is approximately 1,608,000 m^3 per year, which is predicted to increase in the following years due to the increasing consumer demand and the relative ease of producing thermally modified timber (Table 1).

The product applications of modified wood are defined by the Durability Class, and the Use Class defined by EN 335: 2013. The Wood Protection Association created a specification manual (WPA, 2012), which categorized various product ranges according to the typical Use Classes (Table A23, Table A24). Table A25 shows how different wood modification methods can be applied to these product ranges and use classes (Jones and Sandberg, 2020). Acetylated wood can be used in most of the Use Classes. Research studies indicated that it is suitable even in Use Class 5 where it is continuously exposed to seawater.

1.5. About hornbeam trees from the forestry point of view

European hornbeam (*Carpinus betulus* L.) (Figure 4) can be found all over Europe, except for the Mediterranean. Besides Hungary, hornbeam can be found in fair amounts in various countries: Slovakia, Ukraine, Germany, Poland, Croatia, Bulgaria, Serbia, Slovenia and Austria. There are many hornbeam forests found in France, Romania, and Iran.

Figure 4. Hornbeam tree (left) and log (right) (Molnár, 2010).

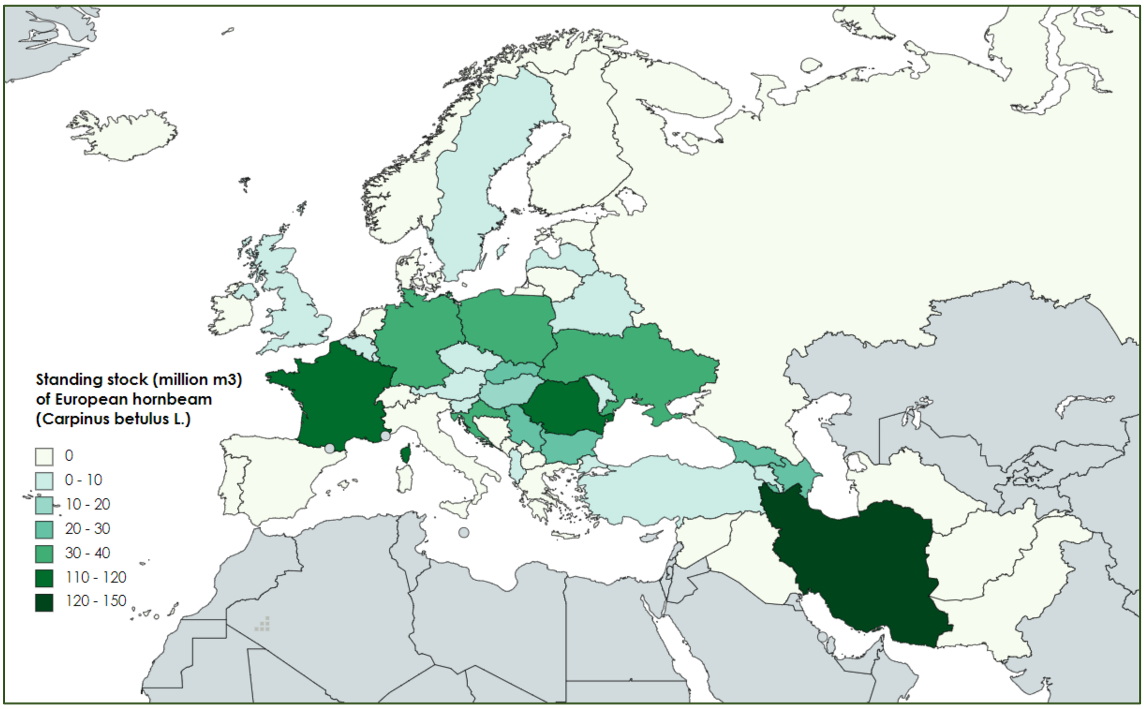

Figure 5. Standing stock (million m^3) of hornbeam (Carpinus betulus L.) in the world according to forest inventories in the last decade.

Some important data about the availability of European hornbeam wood has been collected according to the results of own survey to experts, as well as forest inventories and national reports. The results are summarized in Table A26, and illustrated using the webpage www.mapchart.net (Figure 5).

There are some countries which have optimal conditions for the growth of hornbeam, or overlap with the actual area of hornbeam, but are not listed in the table because they have non-significant amount of hornbeam (Bosnia, Denmark, Greece, Iraq, Ireland, Kosovo, Lithuania, Montenegro, Russia, Switzerland, and outliers), there is less than 5 million m^3 standing stock of hornbeam (Albania, Armenia, Belarus, Belgium, Latvia, Luxembourg, Republic of Moldova, United Kingdom), or only different species of hornbeam grow there, like *Ostrya carpinifolia* or *Carpinus orientalis* (Italy, North Macedonia).

Hornbeam has a controversial role in Hungarian silviculture. Where there are old seed trees in the area, it regenerates naturally from seed, but despite its ecologic end economic benefits, it is seldom planted artificially. It never had great economic importance, in regeneration stage most of the time it is necessary to limit its growth in favor of the main species (usually sessile oak) (Solymos, 1993; Szalacsi et al., 2015). In case of inadequate silvicultural practice, hornbeam can suppress oaks, forming pure hornbeam stands with lower increment, standing volume and economic as well as ecologic value compared to mixed oak stand. These pure stands should be restored to mixed oak forests at the end of the rotation period (Béky, 1970).

Hungarian forests cover 1,875,926 ha, which comprise mainly of deciduous tree species, covering 90% (1,696,915 ha) of the forest area, while coniferous species cover only 10% (179,011 ha). From the wood species, black locust accounts for the largest area with 24%, which is followed by oak having 21%, and Turkey oak having 12%. Hornbeam accounts for 5% (97,231 ha) (NFK, 2021).

The gross standing volume of the Hungarian forests is 404 million m^3 (2021), which has been continuously increasing since 1980's. The reason is that there are considerably less felling than wood increment. The standing volume of hornbeam was 18,278 K m^3 in 2021, and shows an increasing tendency since the mid-2000s (Figure A66) (NFK, 2021).

Looking at the felling statistics of 2021, the species with the greatest harvested timber volume were black locust (1,210 K m^3), hybrid poplars (1,112 K 000 m^3), oaks (753 K m^3), Turkey oak (650 K m^3) and beech (514 K m^3). Felling of hornbeam was 168 K m^3 in 2021, showing a decreasing trend in the past 25 years (Figure A67) (NFK, 2021).

Hornbeam trees are of medium height (15–25m) and usually grow in hill and mountain forests as there are favorable climatic conditions for it. If there is optimal climate, it can also grow on planes, e.g. in Germany. They can also be found in parks and gardens as hedges. The stems are often crooked, buttressed, fluted, and twisted. There are also populations with smooth, cylindrical, straight trunks, but these require more planning and work (Figure 4, Figure 6). In beech hornbeam mixed forests, beech has more shade which forces hornbeam to grow straight upwards, which enables long, straight, clear, cylindrical trunks to develop. On the other hand, in oak hornbeam mixed forests, hornbeam receives more light at the understory level which makes it grow expansively, growing branches at lower levels, and developing curvy, fluted stems.

Although hornbeam can grow a more desirable trunk, as it is usually a secondary species mostly in oak-hornbeam stands, it is not a sylvicultural goal to have quality hornbeam logs, and hornbeam is cut back several times during the regeneration process.

Boles clear for about half the height of the tree (usually not more than 6 m long), but in unfavorable conditions they may branch low down. They have diameters around 35–50 cm, rarely up to 90 cm. The bark is only 1–2cm thick, smooth, dark gray, and composing about 7% of the volume (Molnár and Bariska, 2002).

Figure 6. Disks made from fluted (left) and cylindrical (right) hornbeam logs.

It is a very hardy species and tolerates cold winters well. It prefers moist and humid climatic conditions, but not hot and dry weather. It is sensitive to air pollution. It has good shade tolerance, so it is an important supplementary or subsidiary species in sessile and pedunculate oak and beech forests, where it is repressed during reforestation and first thinning to allow beech or oak to develop (Béky, 1970; Solymos, 1993; Sikkema et al., 2016). Initially, it sprouts well and grows fast compared to oaks. Later its growth slows down. The branches are thin and attached at a sharp angle to the trunk. It is the most common understory species in the Hungarian forests, which heavily shades the forest floor.

Its life span is about 120-150 years, and it is harvested mainly at 80-100 years, depending on the site and it is usually adjusted to the felling of the main species like oak or beech (Molnár and Bariska, 2002). The felling age of oak has been recently lengthened (Kottek et al., 2023) so hornbeam will also be felled accordingly. Due to climate change, its territory will shift to northern areas, or from plains to higher altitudes, where soil conditions do not limit its spread (Varol et al., 2022).

Even if more favorable climate scenarios are considered, its potential habitat will decrease in southern territories of its area, including Hungary. Hornbeam has a definite need for humid climate, and it is the indicator species of the so-called hornbeam-oak climate category. Earlier, areas with a relative air humidity higher than 53% at 2 pm in July were considered the potential range of hornbeam in Hungary. Hornbeam-oak climate is found in areas with a forestry aridity index (FAI) of 4.75 to 6 (Führer et al., 2011). Based on this, in Hungary hornbeam is primarily the species of the colline and sub-mountain zone, but it can also be found on plains with a high enough annual participation. In Hungary, based on meteorological data, the potential area of hornbeam decreased from 29% to 21% between 1960 and 2010 (Führer, 2018) and is likely to decrease to 16% between 2020-2050 and to 4% between 2040 and 2070 (Gálos and Führer, 2018). It will probably completely disappear from the plains and in the long term, it may only survive on the northern slope of mountains and on the western parts of Hungary.

On the other hand, its overall standing stock can still increase in the short-term depending on forest political decisions, forest management changes, as current trend in the short or medium-long term aims to increase the ratio of mixed species forests, which favors hornbeam. Unexpected events, like new wood pests which attack the main species can also increase the share of hornbeam.

In the future, hornbeam will be a good option as mix species in regions where its area will grow. It favors deep, moist and well-drained soils from sub-acid to calcareous, wet heavy clay to light dry sandy soils as well, and tolerates a wide range of soil types as long as its climatic needs are met (Béky, 1970). It is one of the few strongly shade-tolerant native trees in Europe. It can be used as a secondary species, as an understory tree. In mixed forests, it can suppress the main species by regenerating better and faster. It will appear in the areas of beech, spruce and fir forests, which will need to be exchanged to oak hornbeam mixed forests due to climate change-induced drought and dry climate (Sikkema et al., 2016) (Figure A65).

1.6. About hornbeam wood from the engineering point of view

The growth ring boundaries of hornbeam wood are distinct, often with an undulating course as seen on the transverse section. Its heartwood is basically white or gray, and sapwood is similar to the heartwood color (Figure 7). Its average color can be identified in CIELAB system, having lightness of 82.20, redness of 3.99, and yellowness of 18.20 (Tolvaj et al., 2013). It is dull white to grayish throughout, turning dirty yellowish under prolonged exposure, and the core is often brownish in older trees. It has narrow, 1-2 cell wide rays, which are invisible. On the other hand, the longitudinal surfaces have darker grayish streaks (tangential) and flecks (radial) due to the few broad and several cm high (aggregate) rays. Vessels are so small that it is not visible to the unaided eye, and they are evenly distributed, giving rise to fine and even texture. Pith flecks quite common, producing prominent dark markings particularly on tangential faces. There is no interlocked grain. Hornbeam wood is commonly somewhat cross-grained or wavy due to the irregular (fluted) trunk (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

Figure 7. Transverse section (left, ca. 10x) and radial section (right) of natural hornbeam wood (Richter and Dallwitz, 2019).

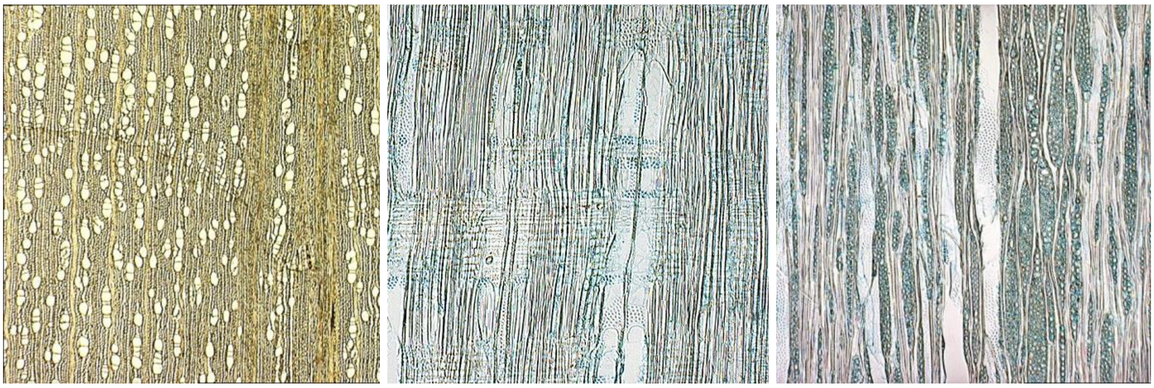

Figure 8. From left to right: transverse, radial and tangential section of natural hornbeam wood (Richter and Dallwitz, 2019).

Hornbeam wood is diffuse porous. Its vessels are arranged in no specific pattern, in multiples, commonly in short (2–3 vessels) radial rows (Figure 8). The vessel diameter continuously decreases from earlywood to latewood. The average tangential vessel diameter is 52–68–88 μm. The average number of vessels per mm² is 20–50. The vessel proportion is 10 %. It has simple perforation plates. Intervessel pits are alternate, having an average diameter (vertical) of 9–11 μm. Vessel-ray pits, with reduced borders or apparently simple, rounded or angular, are located throughout the ray, or restricted to marginal rows. Helical thickenings are present, but only in narrow vessel elements (in latewood), throughout the body of vessel elements. Thin-walled tyloses are occasionally present (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

The libriform fibers of hornbeam have a medium wall thickness. The average fiber length is 880–1800 μm. They make up a high proportion of the xylem (66%) which provides excellent hardness and strength to the wood. Fiber pits are common in both radial and tangential walls, and are simple to minutely bordered. Hornbeam has scattered (apotracheal) axial parenchyma with a ratio of only 2%. Axial parenchyma appears as strands, having an average number of 4–8 cells per strand (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

Hornbeam wood has about 14–18 rays per tangential mm. They are multiseriate, 1–2 cells wide, or within aggregates, some are 3–4 seriate rays. Aggregate rays present. The height of large rays is up to 500 μm, or commonly over 1000 μm (in case of only aggregate rays). Rays constitute 22% of the cross-sectional surface. They are composed of two or more cell types (i.e. heterogeneous or heterocellular rays) (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

Heterocellular rays with square and upright cells are restricted to marginal rows, and there is mostly only 1 marginal row of upright or square cells. In ray cells, prismatic crystals are present. Crystal-containing ray cells are procumbent and enlarged (idioblasts). Silica is not observed (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

The cellulose, hemicellulose and lignin content of hornbeam is 43%, 32.0-34.5%, and 19.3-22.5%, respectively. The heartwood of hornbeam wood, its water extract, and its ethanol extract are not fluorescent. The color of its water extract is yellow, the color of ethanol extract is colorless to brown. Hornbeam splinter burns to full ash, which is white to gray, making up about 0.5%. Hornbeam contains low amount (2.4%) of extractives, like resins, lipids, waxes, etc. Its pH value is about 5.2 (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

The physical and mechanical properties of hornbeam wood are listed in Table A27. It has the highest density among all industrial wood species in Hungary. The ratio of tangential and radial shrinkage is 1.69, which indicates a tendency to moderate warping. Moisture uptake is moderately fast. Dimensional stability is satisfactory. Its fiber saturation point is very high. Based on its physical and mechanical properties, hornbeam is a very dense, hard, wear-resistant, and strong wood (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

Hornbeam trunks frequently have cancerous wounds (excessive growth), caused by the parasitic *Nectria galligena* fungus. It is recommended to properly store and process its wood, as freshly felled trees are susceptible to asphyxiation in the spring and early summer period. The natural durability of hornbeam is Durability Class 5 (not durable). It lasts 2-3 years outdoor in soil, 35 years outdoors without soil contact, approximately 500 years under water, and approximately 800 years indoors. It turns gray when exposed to sunlight. It is highly resistant against acids and alkalis. Built-in wood may be attacked by several fungi (*Serpula, Coniophora*, *Trametes*) and insect species (*Xyleborus*, *Scolytus*, *Anobium* etc.) (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

It is easy to glue. Though rather hard, it is rated satisfactory for sawing, planing, routing, and turning. It finishes smoothly, but pick-up, and grain tear may result from its irregular grain. Nails and screws require pre-boring. The wood generally dries generally well and fairly readily, however with a marked tendency to distort and split along the grain. As a precaution, end-grain surfaces should be treated with a sealant during air seasoning. Technical drying requires a mild drying schedule to avoid excessive splitting and deformation (due to high shrinkage and growth stresses), schedule E is recommended (Boone et al., 1988). Seasoning takes 5-6 months, kiln drying takes 3-6 weeks depending on its dimensions and the target moisture content. There is no problem with surface coating. Finishing is commonly done with transparent varnishes or waxes as the perishable wood is used only for interior applications. On stained surfaces, ray flecks may appear even more prominent due to a lesser uptake of pigment. Its wood is permeable. Iron does not corrode on contact. It can be bent after hydrothermal treatment. Fine sawdust may cause skin irritation (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

Assortments of hornbeam are 50-60% firewood and charcoal, and the rest is fiber and chip raw material (15-20%), pulp (15-20%), and some sawlogs (<8%). The yield of logs unfortunately does not exceed 61%. It is very important for the firewood industry (for export too) thanks to its high calorific value, and for the pulp and paper industry for its chemical inactivity and long fibers (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

Hornbeam wood is suitable for interior applications, for non-structural purposes. It is particularly suitable for: flooring (parquet, floorboards, etc.), staircases (especially industrial floors requiring high resistance to wear), musical instruments (especially in piano actions and drumsticks) (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

Other uses are picture frames, decorative, carved components and ornaments, tabletops, chess pieces and other wooden toys, plates, bowls, shoe lasts, buttons, and for small technical parts such as cutting blocks, pulleys, dead-eyes, mallets, skittles, shuttles, chucks, spindles, brush and tool handles, casting molds, planes, clamps, yardsticks, pegs, workbench components, machine parts, etc. It is also used in furfurol production. By staining, other desired wood species can be imitated (Molnár and Bariska, 2002; Richter and Dallwitz, 2019).

There are possible actions which could help propagate the use of hornbeam, and extending its life cycle, thereby supporting a sustainable economy:

- creating a questionnaire for professionals in forestry, in wood industry and in research regarding the cultivation and utilization of hornbeam, then summarizing and categorizing the results, and collecting solution options;
- making a survey on the forest occupation in countries with high availability of hornbeam, analysis of international forestry practice and experience, comparison with Hungary;
- assessment of user needs, looking for properties which hornbeam partially or fully meet, defining product groups for high-quality (e.g. parquet) and low-quality (e.g. unique design furniture) logs.

It is hard to find supplier of hornbeam logs and boards in Hungary. In the spring of 2022, 4-sides clear boards of hornbeam were about 400-600 EUR/m^3 in Hungary in case of a few sawmills (Table A26). The dimensions ranged between 25-50 mm thickness and 1-3 meters in length. High-quality boards for hobby purposes were available for 2,200 EUR/m^3. For research, it is a more obvious choice to acquire the log(s) from a forestry and hire a sawmill for further manufacturing and drying.

1.7. Improving the properties of hornbeam wood

There are important advantages and disadvantages of hornbeam wood which need to be taken into account when choosing it for industrial production. Hornbeam rots away on soil contact in 2-3 years, if it is exposed sunlight, it will turn gray in 3-5 months. It has a high equilibrium moisture content (EMC), fiber saturation point, volumetric swelling which makes it dimensionally unstable in frequently changing climate. Its high density, compression strength (CS), bending strength (BS) or modulus of rupture (MOR), Brinell hardness and modulus of elasticity (MOE) are perfect for applications where hardness and wear-resistance are key factors. The utilization of hornbeam is problematic as the wood defects make it difficult to manufacture, and the low dimensional stability and durability narrow the possible fields of use to indoors (Molnár and Bariska, 2002).

Hornbeam tends to have irregular growth rings due to its fluted tree growth, which increases the inhomogeneity of its properties, and the yield of sawing. Majid Kiaei carried out several tests regarding the difference in hornbeam wood properties from different regions of Iran. He found that the site and elevation has significant effect on the density and volumetric shrinkage of hornbeam wood in Iran. With increasing elevation, wood density and volumetric shrinkage increased (Kiaei, 2012). When analyzing the difference between dominant and suppressed trees in Iran, there was no significant difference between densities and shrinkage values. On the other hand, its MOE and MOR were higher in suppressed trees than in dominant trees. The average values of compression strength parallel to the grain and perpendicular to the grain, and hardness were higher in the dominant trees than in the suppressed stands. The quality of wood was fair in terms of mechanical properties of hornbeam wood in suppressed and dominant trees (Kiaei and Abadian, 2018). Hornbeam from intermediate (800m) and high altitudes (1200m) had smoother surface roughness than that from low altitudes (400m) (Kiaei and Paloj, 2018). The density and shrinkage results were lower for hornbeam from Iran than from Hungary or Turkey (Ashrafi et al., 2022)

Wood modification could improve the disadvantages of hornbeam wood which hinder its utilization. The thermal modification of hornbeam was the subject of several research projects in Turkey (Gunduz et al., 2009; Gunduz and Aydemir, 2009), Iran (Ghalehno and Nazerian, 2011), Ukraine (Pinchevska et al., 2019), and Croatia (Župčić et al., 2009; Sinković et al., 2011; Sedlar et al., 2019), where the physical and mechanical properties were evaluated according to different temperatures (130-220°C) and treatment times (1-20 hours). All the papers identified a reduction of physical and mechanical properties, increasing mass loss, and darkening color from increasing the treatment temperature and duration. These results were proven by chemical analysis (Tumen et al., 2010).

Hungarian researchers also reported improved physical properties as the EMC decreased from 11.40% to 4.5-8.5%, the shrinking rate decreased from 18.54% to 7.5-17.77% and the maximum swelling decreased from 114% to 87% which all indicate better dimensional stability. The color darkened and the grain texture became more dominant ($L^*<60$, $a>8$, $b^*>25$). On the other hand, due to photodegradation it turned gray the same way as untreated wood after 6 months of outdoor exposure. Thus, surface treatment is needed after heat treatment. The material became harder but also more rigid and brittle which is explained by the 7.66% lower density, the increase in CS and BS, reduction of MOE, 37-49% higher Krippel-Pallay hardness, slightly higher wear resistance but 3-5 times lower resistance to waterjet abrasion. The durability increased as proven by fungi culture laboratory tests, where heat-treated hornbeam had 86% lower mass loss, and soil contact tests where it was classified as Class 0-1 according to EN 252 after 6 months of outdoor exposure. All of these properties depend a lot on the temperature (140-180°C) and treatment time (2-6 hours) (Puskás, 2006; Molnár et al., 2010; Bak et al., 2012; Aranyos, 2014; Németh et al., 2014; Csizmadia, 2015).

If high-quality raw material is selected and proper processing parameters are chosen during the modification treatment, hornbeam can have a bigger share of the wood market. Therefore, it could be a perfect feedstock for manufacturing parquet flooring, wood sidings, garden furniture, gardening utensils, playground elements, gates, fencing, decking, cladding, paneling, railroad crossties, heavy construction, pulley wheel, and even durable wood-based panels made from it can be used as engineered wood products.

1.8. Research background

The material tested in this dissertation was prepared during my master thesis. In order to better understand the results discussed in the following chapters, some important information is shared here from previous work (Pozsgayné Fodor, 2015), and evaluated further, including statistical analysis. Twenty pieces of edged and air-dry hornbeam boards from the southwest part of Hungary were ordered from a Hungarian sawmill (BOPAÁR Ltd.). The boards' dimensions were 28 × 160 × 2500 mm^3 (t × w × l), the average moisture content was 15.2 ± 0.6 % and the average density was 789 ± 64 kg/m^3. Half of the boards remained untreated, and the other half was acetylated under industrial conditions at Accsys Technologies. The WPG ranged between 13.6% and 16.5%, having an average of 15.3%. The WPG level indicated that the wood was successfully impregnated. The average acetyl content was 21.9 ± 0.7 %. The average moisture content decreased to 3.3 ± 0.1 % and the average density decreased to 784 ± 58 kg/m^3.

Statistical analysis was performed using the Dell Statistica software (version 13, Dell Inc., Round Rock, TX, USA). Correlation tests, t-tests and factorial analyses of variances (ANOVA) combined with the Fisher's LSD test were conducted, and the differences were considered significant at $p < 0.05$.

Before acetylation, the moisture content and density had a correlation coefficient of 0.5614, but this decreased to 0.1726 after acetylation. This can be explained by the fact that the moisture content significantly decreased after acetylation, while the density did not. After acetylation, a significant correlation was found between the moisture content and acetyl content of acetylated hornbeam wood, having a correlation coefficient of 0.7473.

The lower moisture absorption and greater dimensional stability after acetylation was confirmed by our results seen in Table A28. Anti-swelling efficiency was measured from the saturated to dried state, and from the conditioned (20°C, 65% RH) to the dried state, which resulted in 81% and 88% ASE, respectively (Fodor 2015).

Due to acetylation, the color of hornbeam darkened, became less homogenous and developed a wavy figure. According to the color measurement, lightness (L*) decreased to 50, redness (a*) increased to 7, yellowness (b*) remained 20, the hue angle (h*) slightly increased to 22 and the chroma (C*) slightly increased to 22. Thus, the color turned more reddish, grayish brown like walnut and similarly colored tropical species, like sucupira, cedrinho, mutenye, itaúba, tamaquaré or cumaru (Melo et al., 2019). This color was achieved after planing about 4 mm off the surface, as the outer layer was darker and unevenly colored because of sticker marks.

High resistance against fungal decay was achieved for acetylated hornbeam, which in its natural state is a non-durable wood species (Class 5 according to EN 350). After being exposed to fungi for 16 weeks, the treated samples' weight loss was below 1%, which makes it a very durable material (Class 1 according to EN 350). The presence of the acetylated material also had an impact on the reference samples, as these were less decayed by fungi than the virulence specimens (Table A29).

Every mechanical property of hornbeam wood increased after acetylation which is very promising although there were many instances of high variation in the results. Acetylated hornbeam showed even higher strength and hardness properties than acetylated beech and Radiata pine (Table A30). According to ANOVA tests, acetylation significantly increased the compression strength, impact bending strength, dry and wet MOR, MOE, Brinell hardness and Janka hardness of hornbeam wood. For acetylated hornbeam, the higher the density was, the higher the compression strength (0.7778), impact bending strength (0.6826), dry bending strength (0.6233), wet bending strength (0.5326), dry MOE (0.5570) and wet MOE were (0.2543). Here, the correlation was higher in dry state than wet state. In both untreated and acetylated hornbeam, there is a significant decrease between dry and wet values of MOR, MOE, Brinell and Janka hardness tests.

Hornbeam in its natural form is a non-durable wood species with a strong, hard, dense, tough, and wear-resistant structure. Its sensitivity to moisture and low durability hindered its use outdoors but after acetylation it became a denser, less moisture-sensitive, more dimensionally stable and a more durable material. Next to acetylated beech and Radiata pine it could become the raw material for many indoor and outdoor products which are exposed to varying humidity, fungi and heat load like decking, marine decking, fencing, outdoor stairs and furniture, handrails, etc.

This investigation of improving the properties of hornbeam wood by acetylation has been a unique form of research since 2014. To my knowledge, there have not been other reports about this research field. In a similar research, Bari et al. (2019) published an article about acetylating hornbeam wood on a laboratory scale, using acetic acid (100%) and liquid formalin (35% v/v) at 120°C for 60 minutes. The highest WPG (9.9%) was achieved with 5% formalin and 10% acetic acid. Water absorption after 170 hours also decreased significantly from 82.7% to 53.6-59.0%. The most effective treatment for fungal resistance was acetylating using 10% formalin and 5% acetic acid, having mass losses of 12.9% against *Trametes versicolor*, 11.8% against *Coniophora puteana*, and 8.1% against *Chaetomium globosum*.

1.9. Aim of this research

The aim of this dissertation was to continue the investigation of improving the properties of hornbeam from Hungary by (semi)industrial means of acetylation. The goals were to:

- investigate the chemical transformations in the wood structure after acetylation using chemical analytical methods and FTIR;
- explore differences in the cell structure after acetylation;
- carry out tests regarding product-specific applications in order to verify the conformity to utilization:
    - examine durability on soil-contact;
    - test photostability when exposed to weathering and UV irradiation
    - carry out bonding strength tests;
    - and assess compatibility with surface finishes regarding photostability;
- characterize it as a product:
    - analyze its position in the market;
    - propose possible product groups, use classes;
    - define its advantages and disadvantages, make a SWOT analysis.

Chapter 2. Chemical composition

2.1. Introduction

Cellulose, which makes up about half of the wood structure (46-48% in broadleaves), is less reactive with acetic anhydride and is thermally stable. During acetylation, it reacts only above 20% WPG, and the degree of crystallinity changes above 25% WPG (Zhao et al., 1987).

Hemicelluloses (26-35% in hardwoods) have proportionally higher amount of free OH groups, so they are more reactive, and less thermally stable. They are the most hygroscopic cell wall polymers (Rowell and Bongers, 2015). The degradation of hemicelluloses (e.g. during thermal modification) makes the wood more rigid and brittle, and it also results in the increase of dissoluble sugar and furfural contents of the wood (Esteves et al., 2011). The hemicellulose fraction of broadleaved species, such as hornbeam, is mainly composed of xylans, which have a high natural degree of acetylation (Németh, 1997).

Lignin (15-28% in hardwoods) also has high reactivity with acetic anhydride (Hill, 2006) but it has less OH groups available for acetylation and its proportion is lower compared to hemicelluloses. It reacts overall not as readily with acetic anhydride as hemicelluloses (Rowell and Bongers, 2015). The degradation of lignin during wood modification reactions is reflected in the reduced stiffness properties (Hill, 2006) as well as in the increase of cleavage products, mostly simple phenols. Hardwood species have higher syringyl lignin content (20-60%) than coniferous species (Fengel and Wegener, 1989).

The amount of extractives influences the wood’s color, durability, odor, gluability, surface treatability and technological properties (Molnár, 2004). During wood modification the extractives are usually leached out from the wood into the modification medium (Hill, 2006). However, with acetylation modification the extractive content generally increases, because extractives can react with the excess, non-reacted, non-bonded anhydride and/or liberated acetic acid, moreover these acetylated extractives can also be bulked in the cell wall (Ajuong and Birkinshaw, 2004; Németh et al., 2010).

The small proportion of ash content (0.2-0.6% in broadleaves) is made of minerals, which affect the durability and machinability of the material (Molnár, 2004) but the amount of ash is not affected by wood modification, only the proportion can change.

The chemical composition of acetylated hornbeam has not been examined in literature before. In a study of heat-treated hornbeam (Tumen et al., 2010), the changes in the chemical structure was eamined after heat-treatment at three temperatures (170, 190, and 210 °C) and three durations (4, 8, and 12 hours). After heat treatment, the extractive content increased from 1.89% to 2.43-5.14%, holocellulose content decreased from 86.91% to 65.29-83.71%, α-cellulose content decreased from 47.23% to 24.73-43.77%, and lignin content increased from 17.57% to 18.65-32.71%. Generally, the trend has intensified with increasing temperature and duration. Heat-treating at 210°C for 12 hours resulted in the maximum decrease of holocellulose and α-cellulose, and the maximum increase of lignin content. Acetylation takes place at lower temperatures (~130°C), thus smaller changes are expected in the chemical components. The increased durability of acetylated wood can be evaluated by chemical analysis. At higher WPG levels, acetylated wood shows lower reduction of cell wall components compared to untreated wood attacked by microorganisms (Mohebby, 2003).

In this chapter, the aim was the assessment of the effect of acetylation on the chemical properties of hornbeam wood and how these are related to the change in physical and mechanical properties.

Main chemical constituents (cellulose, hemicellulose, and lignin) as well as extractive content and ash content were measured and compared in untreated and acetylated wood. As percentage changes show only the relative increase or decrease of compounds compared to each other, the special markers (formic acid, acetic acid, levulinic acid, furfural) and parameters (total soluble carbohydrate content, total phenolic content, pH, buffering capacity), indicating the breakdown or cleavage of structural polymers were also measured to track the transformation reactions taking place during acetylation. FTIR spectra of the wood and of the lignin prepared with Klason-method were also evaluated. Changes in the chemical composition were discussed and were related to the alterations in the mechanical and physical properties.

2.2. Materials and methods

2.2.1. Preparation

The samples were taken from the same material used previously (Paragraph 1.8). For the tests the samples were made from untreated and acetylated hornbeam as well. First small pieces were cut from the boards then knife milled with 2 mm screen then fractioned with Fritsch Analysette 3 Pro vibratory sieve shaker. The distribution of wood flour, particles above 0.2 mm and particles above 0.63 mm were 9%, 35% and 56% for untreated hornbeam and 17%, 37% and 46% for acetylated hornbeam, respectively. For the chemical analysis particles with the size of 0.2 - 0.63 mm were used. The acetylated wood’s brittleness and the possibility of degradation can be anticipated observing the higher distribution of wood flour.

2.2.2. Measurement of wood polymers, total extractive and ash content

The cellulose content was determined with the Kürschner-Hoffer method (Kürschner and Hoffer, 1929) by digesting 1 g of wood sample. The lignin content was measured with the Klason method (Ritter et al., 1932) using 1 g of wood sample. Wood extractive content was determined with Soxhlet extractions using 1:1 cyclohexane:ethanol solution and 3 g of wood sample. Ash content was measured according to EN 15403:2011, using Nabertherm B180 burn-off furnace. All determinations were run in triplicates. The hemicellulose content was given by subtracting the chemical components (cellulose, lignin, extractive, ash content) from 100%.

2.2.3. Measurement of organic extractives

In order to monitor the possible breakdown products of the structural carbohydrates and lignin, the total soluble carbohydrate content as well as the total phenolic content were measured from the wood samples. Extract solutions were prepared as follows: 0.2 g wood particles were extracted with 20 ml 4:1 methanol:water solution by sonication (20 min) in an ultrasonic bath (Elma Transsonic T570, Elma Schmidbauer GmbH, Singen, Germany).

The total soluble carbohydrate content was measured by the Dubois method (Dubois et al., 1956) using glucose as standard at 490 nm. Results were given in mg glucose/g dry weight unit. Total phenolic content was determined by the Folin-Ciocâlteu method (Singleton and Rossi, 1965) at 760 nm using quercetin as standard. Results were evaluated in mg quercetin/g dry weight unit. Both assays were run in triplicates using a Hitachi U-1500 Spectrophotometer.

In order to measure the concentration of volatile compounds as well as of the pH and buffering capacity, extraction was carried out as follows: 2.5 g wood was extracted with 50 ml water for 24 h in a closed beaker. The solutions were filtered and the particles were washed with water into a conical flask to a final volume of 100 ml. Out of this extract solution precisely 1.5 ml was taken for the HPLC determination of furfural, acetic acid, formic acid and levulinic acid.

The HPLC analysis was run by a Shimadzu LC-20 equipment (Shimadzu Corporation, Kyoto, Japan) operating a Bio-Rad Aminex HPX-87H column (Bio-Rad Laboratories Inc., Hercules, USA) at 60 °C, with 0.6 ml/min flow of 0.005 M H_2SO_4 mobile phase, and UV detection at 210–240 nm. Concentrations were given in mg/100 g dry wood. The measurements were taken in duplicate.

From the remaining part of the aqueous extract solution the pH was determined by a Hanna HI 2550 pH meter which corresponded to the pH of the wood. The buffering capacity of the solution was measured by titration using 0.02M NaOH to pH=7. Measurements were run in triplicates.

The analysis of extractives was done using HPLC-PDA-ESI-MS/MS (high-performance liquid chromatography-photodiode array detection-tandem electrospray mass spectrometry). Ground and sieved wood samples were extracted as follows: 0.2 g wood was mixed with 20 mL methanol:water 80:20 v/v solution and extracted for 20 min. in an ultrasonic bath (Elma Transsonic T570 ultrasonic bath, Elma Schmidbauer GmbH, Singen, Germany). Prepared extracts were filtered using 0.45 µm cellulose-acetate syringe filters. For the separation and identification of the polyphenolic compounds a Shimadzu LC-20 type liquid chromatograph coupled with a Shimadzu SPD-M20A type diode array detector (PDA) (Shimadzu Corporation, Kyoto, Japan) and an AB Sciex 3200 QTrap triple quadrupole/linear ion trap LC/MS/MS detector (AB Sciex, Framingham, USA) was used. A Phenomenex Synergy Fusion-RP 80A, 250 mm x 4.6 mm, 5µm column was applied for the separation with a Phenomenex SecurityGuard ULTRA LC type guard column (Phenomenex Inc., Torrance, USA) at 40°C. The injection volume was 30 µL. A gradient of the mobile phases A (H_2O + 0.1% HCOOH) and B (CH_3CN + 0.1% HCOOH) was run with 1.2 mL/min flow-rate as follows: 3% B (0-4 min), 5% B (15 min), 100% B (55 min), 100% B (55-65 min), 3% B (66-71 min). Basic separation was monitored using a PDA detector at (250-380 nm). Because of the relatively high flow rate of the mobile phase, flow-splitting was applied using a split valve, which allowed 0.6 mL/min flow to enter the MS ion source. Electrospray ionization was used for the MS detector in negative mode. Ion source parameters were as follows: ion spray voltage: -4500 V, curtain gas (N_2) pressure: 40 psi, spray gas (N_2) pressure: 30 psi, drying gas (N_2) pressure: 30 psi, ion source temperature: 500°C. Mass spectrometric fragmentation data was acquired using the Information Dependent Analysis (IDA) scanning function of the mass spectrometer by performing automatic on-line MS/MS experiments: survey (Q1) scans were performed between 150-1300 m/z (mass/charge ratio). After the selection of a particular m/z ion and Q2 fragmentation, the dependent (Q3) product ion scans were performed between 80-1300 m/z. The recorded MS/MS spectra were evaluated using scientific data found in the literature. Data were acquired and evaluated using the Analyst 1.6.1 software.

2.2.4. Moisture content

Ohaus MB 23 moisture analyzer was used to determine the moisture content. of the samples.

2.2.5. FTIR analysis

Samples of 5 × 10 × 30 mm^3 (t × w × l) were analyzed with diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy using JASCO FT/IR-6300 spectrophotometer and Spectra Manager program.

The same was done on lignin samples in order to compare the FTIR spectra of wood and isolated lignin. First, the background spectrum was obtained against an aluminum plate in order to see the contribution of the instrument and environment to the spectrum.

These effects were removed from the samples' spectrum by ratioing the sample single beam spectrum to the background spectrum. Secondly, the spectrometer did 50 scans of each sample. There were 4 untreated hornbeam, 4 acetylated hornbeam samples, and two lignin samples of untreated hornbeam, and two lignin samples of acetylated hornbeam. After measurement, the spectra were smoothed with 15 convolution width. A two-point base line correction was made by setting the lowest point between 3800 cm^{-1} and 1900 cm^{-1} to a zero absorbance. The intensity of the infrared peaks was converted to Kubelka-Munk (K-M) units for quantitative analysis. The chemical changes in wood were evaluated observing the difference spectra, which are the spectra of untreated samples subtracted from the spectra of acetylated samples. Here, the absorption increase was represented by positive band while absorption decrease was represented by negative band. The band assignments were made using the difference spectra.

2.3. Results and discussion

The results are discussed according to the chemical analysis (Table 2, Table 3) and the FTIR spectrum (Table 4). The peaks are referred as numbers in brackets (1-13) (Figure 9, Figure 11). The moisture content decreased significantly from 6.50% to 2.50% as a result of the bulking of the cell wall OH groups (Rowell, 2005). This means the hydroxyl groups in the cell wall polymers were substituted by acetyl groups which resulted in a WPG of 15% (Paragraph 1.8). The number of OH groups changed and rearranged in the system which explains the positive and negative peaks in the spectrum (1). The increase of methine (CH), methylene (CH_2) and methyl (CH_3) groups (2) is due to the exchange of OH groups into acetyl groups. The degree of moisture sorption decreased which led to lower moisture content values. This affected the anti-swelling efficiency, linear and volumetric swelling and shrinkage values and the mechanical properties in wet state (Paragraph 1.8).

Table 2. Chemical composition of untreated and acetylated hornbeam. Average values are presented with standard deviation in brackets.

Chemical composition	Unit	Untreated	Acetylated	Difference (pp)	Percent change (%)
Cellulose content	%	51.57 (1.16)	43.02 (0.35)	- 8.55	- 17
Hemicellulose content	%	27.40	38.49	+ 11.10	+ 41
Lignin content	%	19.09 (0.89)	16.23 (1.04)	- 2.86	- 15
Extractive content	%	1.51 (0.13)	1.91 (0.15)	+ 0.40	+ 27
Ash content	%	0.44 (0.05)	0.34 (0.06)	- 0.09	- 22
Moisture content	%	6.50	2.50	- 4.00	- 62

This is important in case of outdoor wood-based products where they can be exposed to frequent climatic changes, humid air, rain or even very dry conditions. The active sites in the wood polymers were blocked which means they were not accessible for wood-decaying organisms (Rowell et al., 2009; Mohebby and Militz, 2010). This was confirmed by fungi culture tests too (Paragraph 1.8). Although, there were improved mechanical properties of hornbeam after acetylation, many researchers experienced reduction instead of improvement in these parameters. This can be also explained by the fact that different wood species can react diversely on acetylation process (Dreher et al., 1964; Bongers and Beckers, 2003; Papadopoulos and Tountziarakis, 2011).

Table 3. Organic extractives of untreated and acetylated hornbeam. Average values are presented with standard deviation in brackets.

Organic extractives	**Unit**	**Untreated**	**Acetylated**	**Difference (pp)**	**Percent change (%)**
pH	-	5.11 (0.02)	4.73 (0.02)	-	-
Buffering capacity	mg/g	1.11 (0.09)	2.15 (0.07)	+ 1.04	+ 94%
Soluble carbohydrate content	mg/g	14.63 (3.18)	3.49 (0.85)	- 11.14	- 76%
Total phenolic content	mg/g	2.65 (0.31)	1.39 (0.12)	- 1.26	- 48%
Furfural content	mg/100g	0.291 (0.014)	0.729 (0.031)	+ 0.44	+ 151%
Levulinic acid content	mg/100g	n.a	< 40	-	-
Formic acid content	mg/100g	2.55 (1.32)	6.98 (0.62)	+ 4.43	+ 174%
Acetic acid content	mg/100g	131.3 (10.2)	439.4 (14.1)	+ 308.10	+ 235%

Table 4. Wavenumber characterization of the infrared spectra of untreated and acetylated hornbeam, according to Tolvaj (2013). (Band number): numbers assigned to the bands in Figure 9 and Figure 11.

Band number	Wavenumber (cm^{-1})	Functional group	Assignment
1	3600-3100	OH stretch	
2	2970	CH stretch	Methine (CH), methylene (CH$_2$), methyl (CH$_3$) groups
3	1800-1700 1769 (max. wood) 1739 (max. lignin)	Unconjugated acetyl C=O (carbonyl) stretch	Xylan
4	1597	Conjugated C=O (carbonyl) stretch	Xylan
		Aromatic skeletal vibration	Syringyl lignin
5	1505	Aromatic skeletal vibration	Guaiacyl lignin
6	1464 1432	Asymmetric C-H deformation	Lignin, carbohydrates
7	1382	Symmetric C-H deformation	Cellulose and hemicellulose
8	1361	C-H deformation vibration in CH$_3$	Cellulose
		C-O vibration	Syringyl derivates
9	1270	Syringyl ring and C-O stretch	Lignin and xylan
10	1174	Asymmetric C-O-C stretching	Cellulose and hemicellulose
11	1136	Symmetric C-O-C stretching	Cellulose and hemicellulose
		Aromatic C-H skeletal vibration	Lignin
12	1094	C-O vibration	Cellulose and hemicellulose
13	899	C-H deformation	Cellulose

Cellulose is composed of the aggregation of rigid linear polymer chains of β-D-glucose; wood cellulose is highly crystalline with a degree of crystallinity of 50-90%. Content and structure of cellulose is directly related to wood strength properties (Winandy and Rowell, 1984). The cleavage of cellulose was not confirmed either by a significant elevation of the soluble carbohydrate content or by the increase of the levulinic acid concentration. If there was a significant degradation of cellulose it would have resulted in the elevation of concentration of the breakdown products of cellulose, that is of soluble sugars as well as of levulinic acid, which is a degradation product of hexose sugars.

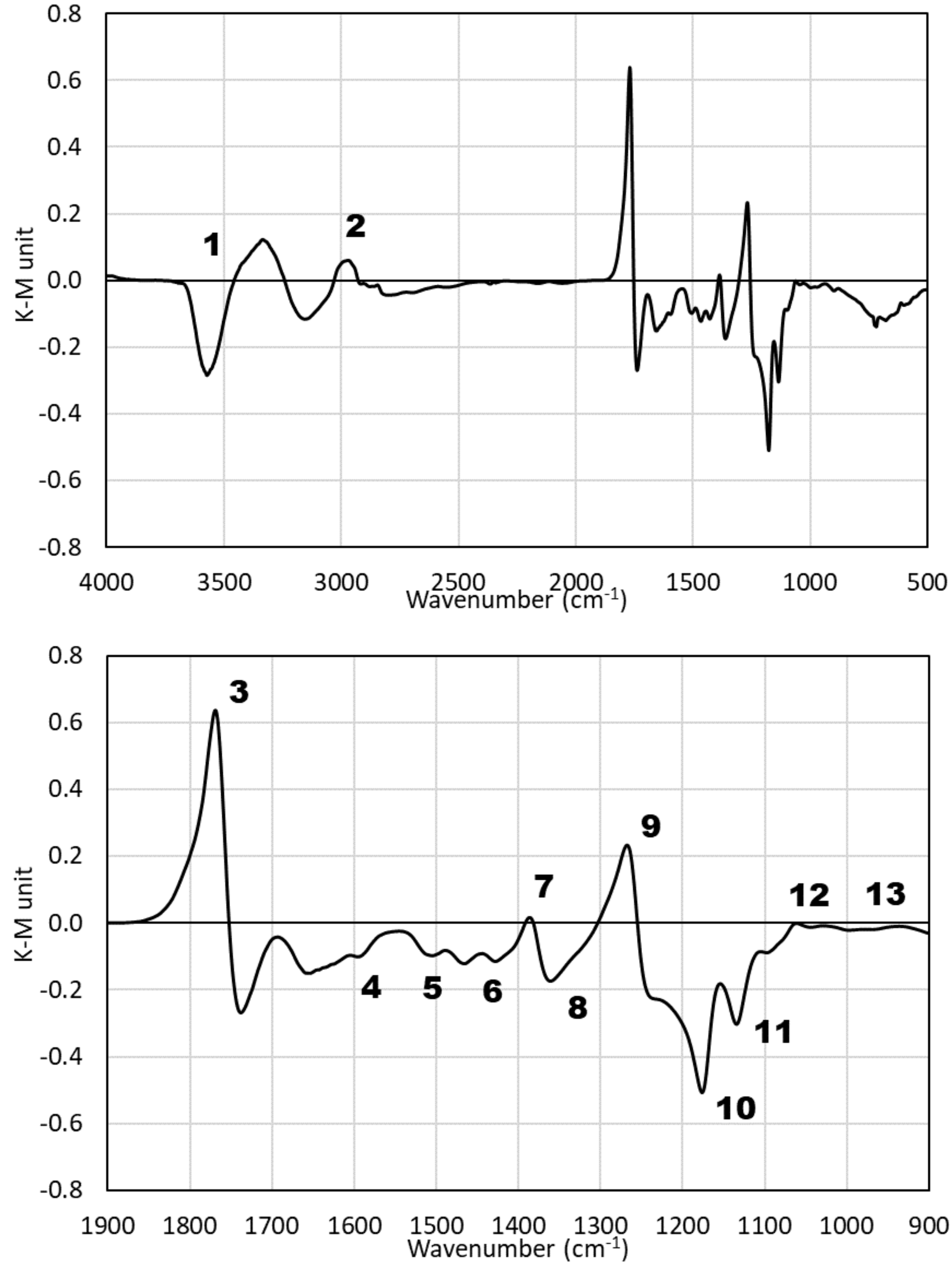

Figure 9. FTIR difference spectrum of acetylated and untreated hornbeam wood. Description and assignments of band numbers 1-13 are listed in Table 4.

The evaluation of the FTIR spectra did not prove the unequivocal alterations of the cellulose fraction, too: although there was a significant decrease of the peaks of C-H deformation (8) and asymmetric C-O-C stretching (10) in cellulose, in some cases this change is not significant or close to zero (symmetrical C-H deformation (7), C-O stretching (12), and C-H deformation (13) in cellulose). It is suggested from the results that cellulose may undergo only slight transformations, which is mainly of structural character (e.g. decrease of crystallinity), yet mass loss or degradation was not evidenced. Results were also proved by mechanical properties, as the strength properties of acetylated hornbeam were equal or higher than those of untreated hornbeam (Paragraph 1.8).

Hemicelluloses have shorter polymer chain length as compared to cellulose, not crystalline and are composed of both hexose and pentose sugars. They are very reactive and they have proportionally the most hydroxyl groups (Winandy and Rowell, 1984). This means when the OH groups were substituted by acetyl groups, the hemicellulose was mostly acetylated which increased the weight of the polymer. This was proved by the increase of its proportion from 27.40% to 38.49%. The FTIR spectra also indicated a significant acetylation of the hemicellulose fraction by the higher absorption of the C=O (carbonyl) groups (3) and of the C-O stretching (9) in xylan. Similar results were obtained for acetylated beech, Scots pine and acacia wood (Militz, 1991; Mohebby, 2003; Khalil et al., 2011).

However, the absorption of the conjugated carbonyl groups decreased slightly in the acetylated wood, probably due to minor degradation of xylans in acidic medium (4). This was also confirmed by the slight increase of furfural concentrations: as furfural is the primary degradation product of pentose sugars deriving from the hemicelluloses (predominantly xylans) fraction, the somewhat higher furfural concentration in acetylated wood was explained by a mild hydrolysis of the hemicelluloses due to acidic media and heat.

Figure 10. Isolated Klason lignin samples of untreated (left) and acetylated (right) hornbeam particles, before (above) and after (below) drying.

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). The amount of lignin is reduced after acetylation from 19.09% to 16.23%. In fact, in acidic medium some parts of lignin can dissolve (Rowell, 2005) and lignin degradation could also be tracked by FTIR measurements, which indicated the decrease of the aromatic skeletal vibration in syringyl (4) and guaiacyl lignin (5), of the asymmetric C-H deformation in lignin (6), and of the aromatic C-H skeletal vibration (11) bands.

However, the total phenolic content of the acetylated wood did not increase markedly, which contradicts the fact of a significant lignin cleavage. If there was a lignin breakdown, significant amount of cleavage products (mainly simple dissoluble phenolic compounds) would have formed, just as with thermal modification of wood (Hill, 2006; Tumen et al., 2010) and this would have caused increased total phenolic concentrations. Instead, total phenolic content decreased during treatment, which can possibly be explained by an extraction effect of the native phenolic compounds of hornbeam into the treatment media during acetylation process. In this way the real decrease of the lignin content is only minor, and changes in the FTIR spectra only indicate internal structural changes of the lignin matrix.

The changes in the lignin structure were also apparent in the isolated Klason lignin samples, which had a more "porous" structure with smaller particle size compared to the lignin isolated from untreated wood (Figure 10). Klason lignin samples were also subjected to FTIR analysis. In the investigation of the FTIR difference spectra of the lignin samples of the acetylated and untreated wood (Figure 11) the reduction of the absorption of the methine (CH), methylene (CH_2), methyl (CH_3) groups (3), as well as the heavy decrease of the absorption of the vibration or deformation of some specific functional groups in lignin was also observed (4, 5, 6, 8, 9, 11). Results hint at a structural transformation of lignin, yet without a less pronounced loss of its mass which was proved by total phenolic levels.

Alterations of the lignin structure can also account for the slightly darker, walnut-like color of acetylated hornbeam (Paragraph 1.8). 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) which results in not only structural changes of lignin, but also alterations in the color of wood. The change of lignin did not affect negatively the mechanical properties of acetylated hornbeam.

In related literature, an increase in acetyl groups was observed at wavenumber 1745 and 1240 cm^{-1} with increasing WPG (Stefke et al., 2008; Schwanninger et al., 2011), similar to acetylated hornbeam (3, 9). On the other hand, peak 1374 cm^{-1} showed also increment, but it was a reduction in acetylated hornbeam (8) due to alterations in cellulose structure and decrease of crystallinity.

In a study where hornbeam wood was acetylated with acetic acid (0-10%) and formalin (5-10%), similar results were obtained (Bari et al., 2019). The increase of acetyl groups was indicated by higher absorption of CH stretch in methine, methylene and methyl groups (2790cm^{-1}). Carbonyl stretching in hemicelluloses (1730 cm^{-1}) were unaffected, but C=O stretching (1750cm^{-1}) increased due to increase of formalin and formaldehyde. Acetic acid and wood interactions were observed at peaks 1165cm^{-1} and 1110cm^{-1}.

The slight increase of the extractive content from 1.51% to 1.91% can also contribute to the darkening of the wood color. The higher proportion indicate that some part of the extractives acted like scavengers of acetic acid or acetic anhydride, and became bulked in the cell wall (Ajuong and Birkinshaw, 2004). However, these extractives are not of the polyphenolic type as the total phenolic content decreased from 2.65 mg/g to 1.39 mg/g. The reduction of the total phenolic content could have occurred due to the transformation of polyphenols or a leaching during the acetylation process. The structure of extractives needs further structural evaluation to elucidate their role in determining the color changes in acetylated hornbeam wood.

The ash content seemingly decreased from 0.44% to 0.34% but the lower value is just due to the higher weight (WPG) of the acetylated sample before incineration. Consequently, the ash content was not affected by acetylation and has little importance.

The reduction of pH from 5.11 to 4.73 is not the result of the acetyl groups, rather the residual acid content in the wood after acetylation. Acetic acid content increased indeed from 131.3 mg/100g to 439.4 mg/100g, while formic acid levels also increased significantly. This also resulted an increase in buffering capacity from 1.11 mg/g to 2.15 mg/g. This could be a problem because of the corrosion of the metal joints (Zelinka, 2014). The pH and buffering capacity play an important role in the bonding, surface treatment and joining of the wood material (Németh, 1997). The higher buffering capacity indicates higher need of added base in order to adjust the pH to achieve the best bonding strength.

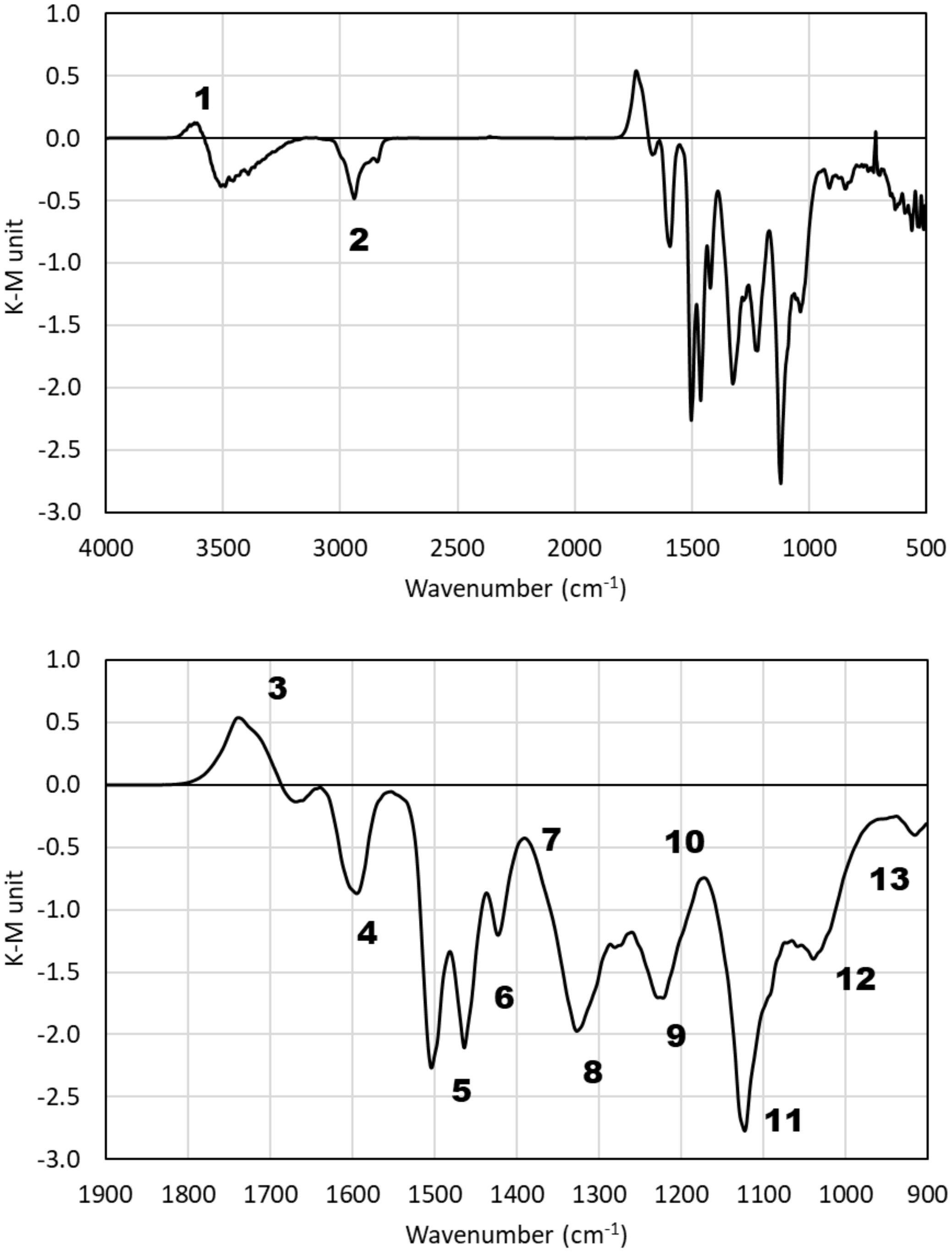

Figure 11. FTIR difference spectrum of the lignin fraction of acetylated and untreated hornbeam wood. Description and assignments of band numbers 1-13 are listed in Table 4.

In the results of HPLC-PDA-ESI-MS/MS, the difference in extractives was evaluated according to the chromatogram (Figure A68). The question was that what kind of extractives appear in case of acetylated hornbeam that does not in case of untreated hornbeam. For example degradation products, color-dependent extractives can have higher peaks (concentrations).

In case of the peaks at 29.39 min. and 29.65 min. retention time, the peaks were identified as isomers of sinapaldehyde. Identification was carried out by using literature data and mass differences in the mass spectrum (Figure A69). Comparing untreated and acetylated sample it was apparent that sinapaldehyde levels (peak heights) were higher in the acetylated samples, which was explained by the degradation of lignin in highly acidic media. The slight lignin degradation was also confirmed by the previous measurements as well as by the FTIR analysis (Figure 11).

The peak at 34.87 min. was corresponded to a derivative of syringic acid, which was confirmed by the simultaneous presence of the *m/z* 197, 182, 153, 138 fragment ions, typical to syringic acid (Figure A70). At the peaks of 37.73 and 37.85 min retention times, the concentration of certain extractives increased in the acetylated sample extract. Analyzing the mass spectra (Figure A71, Figure A72) the periodic loss of acetic acid (neutral loss of 60 Da) as well as of acyl groups (neutral loss of 42 Da) was evidenced which confirmed that these extractives are esterified with multiple acetyl groups. However, the precise structure of these compounds has not been elucidated from the present data and requires further research.

To determine the degree of acetylation the peak at 1739 cm^{-1} (C=O stretch) was correlated to highest peak at 1505 cm^{-1} (C=C stretch), taking into account that the benzene ring vibration in lignin does not change during acetylation. The difference between untreated and acetylated hornbeam was 0.269 at peak 1739cm^{-1}, and 0.098 at peak 1505cm^{-1}, which means the ratio was about 2.735. If this data is compared to the correlation between FTIR and HPLC acetyl content of acetylated beech (Beckers et al., 2003) (Figure A73), then an HPLC acetyl content of 19+% can be read which is higher than the WPG calculated from weight (15.3%).

2.4. Conclusions

In this work, the chemical analysis of untreated and acetylated hornbeam was carried out in order to find connection between the change of physical and mechanical properties and change of chemical structure in wood after acetylation.

According to the results, the proportional increase of the hemicellulose content (+11.10%) was compensated by the decrease of cellulose (-8.55%) and of lignin (-2.86%) contents. By FTIR spectra and monitoring main indicators of cleavage and breakdown products it was concluded that during the acetylation of hornbeam wood it is the hemicellulose fraction that gets acetylated and which is primarily responsible for the WPG, while a slight degradation also occurs to it. The structure of lignin is altered as an effect of heat and acidic medium and is also possibly acetylated to a small extent. The alterations in the structure of lignin (oxidation, reaction with furfural) as well as the increase of the extractive content can both account for the slightly darker, walnut-like color of acetylated hornbeam wood.

Chemical analysis and FTIR analysis confirmed that previous results regarding lower moisture sorption and improved physical and mechanical properties were due to bulking of the cell wall with acetyl groups.

Chapter 3. Microscopic characterization

3.1. Introduction

The rate of cell-wall degradation, and the reduction of mechanical strength caused by wood modification is not always clear, as the macroscopic wood structure can seem to be intact and sound, while the microstructure may be damaged (e.g. the cells collapse), which can lead to a failure in meeting the product requirements in use. The physical and mechanical properties of wood, which is a cellular, three-dimensional structure, are determined by its microstructure (Kollmann and Côté, 1968). The cell walls of wood can be divided into two layers: primary (P), which mainly consists of hemicelluloses, pectin, lignin, and it contains low amount of cellulose; and secondary (S). The secondary layer is further divided into S_1, S_2, and S_3 layers, which mainly contain cellulose, hemicelluloses, and it contains low amount of lignin and extractives. The middle lamella, found between the cell walls, is composed primarily of pectin and lignin. These chemical components have great importance during wood modification as each reacts in a different way.

Thermal stability is greatest of lignin, followed by cellulose; the lowest thermal stability is of hemicelluloses. Hemicelluloses and lignin influence the elastic properties of wood, which means their degradation results in a more rigid and brittle material. If the process parameters are well established for a species, the degradation of the microstructure can be avoided.

In a study regarding heat-treated hornbeam, there were no significant defects or cracks observed after heat-treatment in open system at 200°C, nor in closed system at 145-175°C, 90% relative humidity (Horváth et al., 2016). Oil-heat-treated hornbeam was investigated with scanning electron microscopy (SEM) after oil-heat-treatment at 200°C for six hours (Bak and Németh, 2015). The SEM imaging technique showed that the cracks – some of which were even visible to the naked eye – only appeared in the radial direction, mostly located in the cumulative rays between single cells, along the middle lamellae. No damage was observed in the vessels. It was found that the higher the initial moisture content, the bigger the cracks and the more frequently the cracks appeared.

During acetylation, the acetic anhydride molecule, whose diameter is 0.7 nm (assuming it is spherical) penetrates the cell wall under release of acetic acid as a swelling agent. In swollen state, the cell-wall micropores are about 2-4 nm across (Hill et al., 2004). If the wood is dried to 0% moisture content, the micropores shrink, which means the reagent will not be able to access the lumen. Wood does not swell in acetic anhydride (Rowell, 1983).

When dry wood is acetylated, acetic acid produced during the reaction causes cell-wall swelling, which increases the rate of reaction. The reaction can also be promoted by pyridine, which functions as a swelling agent and catalyst (Tarkow et al., 1946). Moisture also increases cell-wall accessibility because the cell wall is swollen. However, the reaction of water with acetic anhydride results in a loss of the reagent as acetic acid is formed. The degree of acetylation (often expressed as Weight Percent Gain – WPG) decreases with increasing moisture content (Hill, 2006).

The maximum WPG can be reached if the cell wall is fully swollen, since the reaction of acetic anhydride with hydroxyl groups attached to cellulose, hemicelluloses, and lignin occurs within the cell wall. In this case, the WPG is about 25%, which means the acetyl content is around 28% (Hill, 2006). The acetylation reaction depends on the diffusion probability. This means it is not the reactivity of $-OH^-$ groups that influences the reaction, but the availability of reaction sites for the reagent – for example, how much time is available for the reagent to reach the cell wall. The reaction time is significantly shorter than the time taken for the reagent to reach the reaction site (Hill and Hillier, 1999).

Examining acetylated wood with SEM using Energy Dispersive X-Ray Analysis (EDXA), it was found that the remaining anhydride was mainly in the S_2 layer but, with increasing reaction time there were greater concentrations in the middle lamella (Rowell et al., 1982). Cellular ultraviolet (UV) spectroscopy tests showed that, after acetylation, the UV absorption of lignin decreased in the middle lamella, but was unaffected in the S_2 layer. This was associated with the leaching of lignin breakdown products in the reaction medium during the acetylation process (Sander and Koch, 2001). Cellulose is less reactive with acetic anhydride. During acetylation, it reacts only above 20% WPG, and the degree of crystallinity changes above 25% WPG (Zhao et al., 1987). During acetylation, the acetic anhydride reacts mainly with the hemicelluloses, which are the most hygroscopic cell-wall polymers, followed by lignin (Rowell and Bongers, 2015).

Studying the distribution of reacted chemicals, it was found that both lignin and holocellulose were substituted in acetylated southern pine (Rowell, 1982). Reacting wood at 120°C with acetic anhydride and no catalyst, at an acetyl weight gain of 16 to 19%, theoretically approximately 90% of the lignin, and 25% of the holocellulose is esterified. Another study reported that at a WPG of 13.5%, about 86.4% of OH groups in lignin, 21.6% in hemicelluloses and 9.3% in cellulose were substituted (Kumar and Agarwal, 1983).

Lignin reacted at a faster rate with acetic anhydride than hemicelluloses and holocellulose after isolation (Rowell et al., 1994). At high WPG (~18%), all lignin hydroxyl groups were substituted, while only about 20% of holocellulose hydroxyl groups were substituted.

Using microautoradiography, an environmental scanning electron microscope (ESEM) and a backscatter emission detector (BSED), it can be identified where exactly are acetyl groups in the acetylated wood cell wall (Rosenqvist, 2001). During full impregnation of Scots pine, the acetic anhydride was evenly distributed, and the penetration into the cell wall was uniform. Complete acetylation took place when the specimens were heated.

Fluorescence microscopy could show differences of fluorescence intensity in lignin of acetylated wood even at low degrees of acetylation (Beckers et al., 2003). On the other hand, further investigation showed that this method was not suitable for acetylation level determination as the measured change of autofluorescence of acetylated wood compared to untreated wood was mainly caused by a reduction of moisture content, and not the change in lignin. Although time of flight secondary ion mass spectroscopy (Tof-SIMS) requires thorough sample preparation and cleanliness to achieve the best results, high correlation can be achieved between WPG and Tof-SIMS intensity.

Using hyperspectral near-infrared image regression, significant differences were found in the acetylation of earlywood and latewood, which means different duration of acetylation is needed for the complete acetylation of earlywood and latewood cells (Mäkelä et al., 2021). Earlywood regions had significantly higher WPG values than latewood regions of the wood surface. This difference was less pronounced in heavily acetylated samples. Cluster analysis of Raman microspectroscopy images was also carried out to see these differences at the wood-cell level.

The effect of acetylation was analyzed with SEM and transmission electron microscopy (TEM) on beech, pine, and spruce acetylated to 20.0%, 17.8%, and 15.6% WPG respectively, where it was found that the cell wall was extremely swollen and permanently bulked (Sander et al., 2003). There was no fracture in the microstructure (pits, ray parenchyma, epithelia cells) even at the highest WPG. Resin canals often lacked resin as this was dissolved by the reagent during the process. No significant cell-wall degradation or alteration was observed by SEM in acetylated poplar (Németh et al., 2010) or acetylated maple (Moghaddam et al., 2017).

In a study on untreated and acetylated beech (WPG 3.41-17.15%) and Scots pine (WPG 2.71-19.95%), they were exposed to white and brown rot fungi for 12 weeks to compare the durability at different WPG levels (Mohebby, 2003). Fungal hyphae could easily colonize cell lumina and ray cells in non-acetylated and acetylated wood of both species at low WPGs as there were enough nutrients for hyphal growth. In moderately and highly acetylated wood, these nutrients were probably removed during acetylation and no or insufficient nutrients remained for fungal growth in ray cells. Similar results were reported on acetylated pine (Rowell and Bongers, 2015). The control sample was almost completely covered with fungal hyphae which destroyed the cell wall, while the acetylated sample only had a few hyphae growing on the inner cell wall. This means that although no weight loss was detected in acetylated wood, acetylation itself was not toxic to the fungus.

In a seven-year-long soil block test, bacteria, soft rot and white rot fungi attacked untreated beech and Scots pine samples, while they were at an initial stage or developing stage in acetylated wood at the end of the test (Mohebby and Militz, 2010). The results showed that, although the fungal hyphae were able to colonize the cell lumina, they did not decay the wood significantly, as they failed to attack the acetylated cell walls. At higher WPGs the acetylated wood could withstand the exposure of weather, moisture, and fungal decay for a long period of time. Of course, the rate of fungal decay is very dependent on the moisture level, oxygen level and pH of the soil. In a 12-month-long weathering test of *Acacia mangium* and *Acacia* hybrid wood, the results showed that the cell walls swelled after acetylation and that the rate of weathering degradation was lower in acetylated samples; the middle lamella, cell walls, and cell lumina were less distorted (Bhat et al., 2010).

The physical, mechanical and durability testing of untreated and acetylated hornbeam is covered in Paragraph 1.8. Improved mechanical properties and dimensional stability suggests that the cell wall became swollen but there were no cracks or cell-wall collapses that could weaken the microstructure. The aim of this work was to carry out microscopy tests to determine the effect of acetylation on the microscopic structure of hornbeam wood, furthermore analyze the differences between decayed samples at microscopical level. For the tests, two suitable methods were chosen. Bright-field microscopy is good for rapid and simple usage. The main advantage is staining, which could highlight the differences in chemical composition or fungal degradation; however, resolution and depth of focus is limited. Scanning electron microscopy is good for the identification of structural differences or crack formation on the surface with much higher resolution and magnification, and larger depth of field; however, the chemical differences cannot be observed. Several methods of sample preparation and staining were tested and compared.

3.2. Materials and methods

3.2.1. Preparation

Wood samples for this research were prepared in the same way as in Paragraph 1.8: sound, dry specimens of untreated and industrially acetylated hornbeam (average WPG 15.3%) were used, as well as decayed specimens of untreated and industrially acetylated hornbeam. The decayed samples were exposed to fungi in a previous durability test (Paragraph 1.8), with various results of mass loss. The mass loss of the untreated hornbeam samples was 47.6%, 21.7%, and 35.6% for *Coniophora puteana, Rhodonia (Poria) placenta*, and *Trametes (Coriolus) versicolor*, respectively. On the other hand, only minor mass loss was observed in acetylated hornbeam samples: specifically, 1.1%, 0.5%, and 1.0% of mass loss in the presence of *Coniophora puteana, Rhodonia (Poria) placenta,* and *Trametes (Coriolus) versicolor*, respectively. The preparation and examination were carried out at Mendel University in Brno.

3.2.2. Bright-field microscopy

Sections were cut with a Leica SM2000R (Leica Biosystems Nussloch GmbH, Germany) sledge microtome after softening (Figure A74). Softening of untreated hornbeam was done with water and of acetylated hornbeam with acetone. The sections were stained with safranin and astra blue or potassium permanganate (1% solution) for two minutes and embedded in Euparal. Bright-field microscopy images of the sections were prepared with a Leica DM 2000 (Leica Microsystems CMS GmbH, Germany) optical microscope equipped with a Leica DFC295 digital camera.

3.2.3. Scanning electron microscopy

Small samples of 8 × 8 × 8 mm^3 (t × w × l) were split to the width of 3 mm. The cross section was given a smooth surface by hand cutting with a razor blade after softening the samples in water (untreated wood) or acetone (acetylated wood). Samples dried at room conditions were sputter coated with gold using a LUXOR™ gold coater (APTCO Group, Germany). The layer thickness was 15 nm. The cross section was observed with a Tescan Vega 4 scanning electron microscope (TESCAN ORSAY HOLDING, a. s., Czech Republic). The scans were prepared in Resolution scanning mode in a high vacuum using a detector of secondary electrons (SE detector). The images were obtained with these settings: landing energy 7 keV, beam current 30 pA, scan speed 5 (10µs/pixel) and image resolution of 2,048 × 1,536 pixels. The magnification of the microscope was set to 6,000×.

The microscope setting was based on a basic setting recommended by the microscope producer; however, the optimal parameters had to be found to reach the best image quality at that magnification.

Cell-wall thickness was measured in many different SEM micrographs of both acetylated and untreated hornbeam using an ImageJ Fiji open-source software. Two big adjacent fiber cells were selected for each measurement, which included thickness of two cell walls of both adjacent cells and the middle lamella between them. Data set for each material contained 50 measurements. Statistical analysis was performed using the Dell Statistica software (version 13, Dell Inc., Round Rock, TX, USA). A t-test was conducted, and the differences were considered significant at $p < 0.05$.

3.3. Results and discussion

3.3.1. The effect of softening and staining

Cutting of smooth, undamaged sections of acetylated hornbeam was only possible after swelling and softening in acetone (Obataya and Shibutani, 2005; Inoue et al., 2008) (Figure 12). It swells and softens less in water, which makes it much more difficult to cut without cracking or damaging.

After producing sections, they were stained to allow chemical changes and fungal degradation to be seen. Safranin was used to indicate lignin, and astra blue to indicate polysaccharides. Safranin stained untreated hornbeam, but not acetylated hornbeam (Figure 13), which indicates successful acetylation, as reported in previous work (Paragraph 1.8).

During the durability test, brown rot fungus degraded polysaccharides to a great extent, leaving lignin behind, which was stained by safranin. Although the mass loss of acetylated hornbeam was very low, microscopic images show that fungi were able to colonize the cell wall, which also means that acetylated wood is durable and not toxic to fungi. After staining, polysaccharide degradation and lignin were observed in acetylated sections (Figure 13).

Similar results were reported and the same staining method was used in literature (Mohebby, 2003). Safranin also slightly stained new brown deposits in acetylated wood; however, the staining did not reveal any deposits in untreated wood (Figure 13).

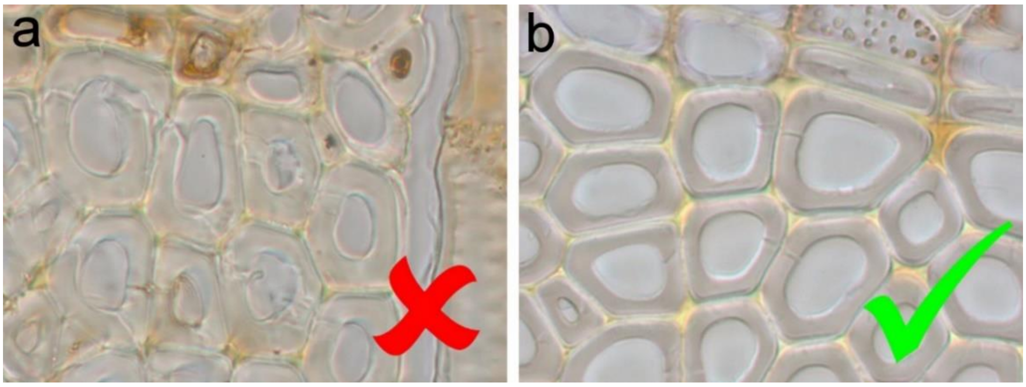

Figure 12. Acetylated hornbeam softened in water (a) and acetone (b). Acetylated hornbeam swells and softens less in water, which makes it much more difficult to cut without cracking or damaging. With acetone, it was possible to cut smooth, undamaged sections.

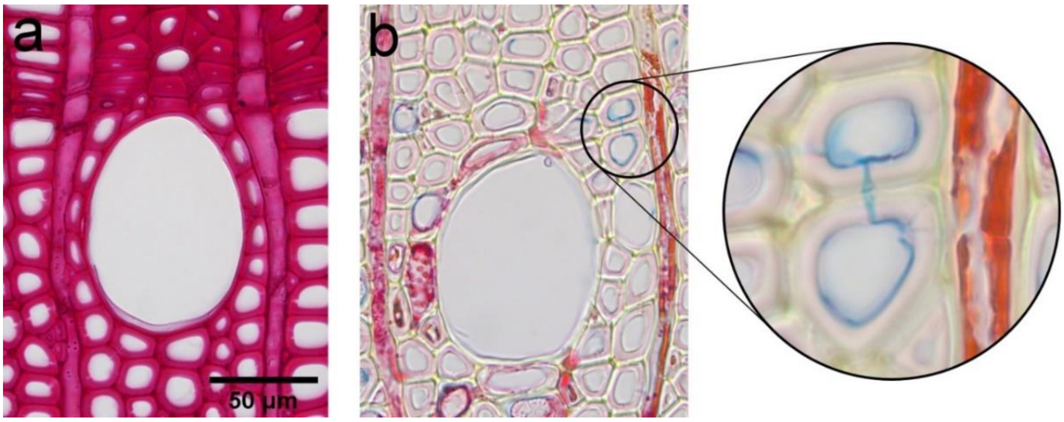

Figure 13. Bright-field microscopy of a cross section of untreated hornbeam (a) and acetylated (b) hornbeam after the durability test. Brown deposits in cell lumina are stained red with safranin; hyphae of brown rot Coniophora puteana are stained with astra blue.

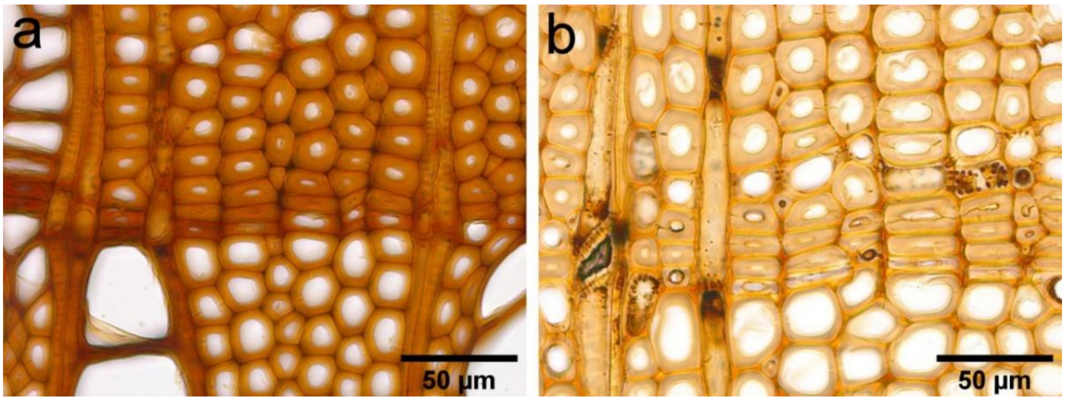

Figure 14. Untreated (a) and acetylated (b) hornbeam stained brown with potassium permanganate. The middle lamella and the deposits are highlighted.

The brown staining of acetylated wood with potassium permanganate was limited, and much lighter than untreated wood. However, the middle lamella was highlighted in both cases, becoming darker (Figure 14).

3.3.2. Bright-field microscopy

After acetylation, the cell walls did not swell significantly and there were no cracks nor fractures observed due to the process (Figure 14, Figure 15). This was also reported by other researchers (Sander et al., 2003; Moghaddam et al., 2017), although the swelling in acetylated hornbeam wood was not large enough to close the cell lumina (Sander et al., 2003). Acetylated hornbeam became denser (Paragraph 1.8) and its chemical structure changed compared to untreated hornbeam (Chapter 2). It was reported that there were no significant changes in cellulose, as it is the least reactive chemical component. On the other hand, structural changes took place in lignin, and there was major degradation in hemicelluloses during the acetylation process (Chapter 2).

Bright-field microscopy revealed significant new deposits in acetylated hornbeam, which were not apparent in untreated wood. These were located mainly in the parenchyma cells in rays, and also in axial parenchyma. The cells were not completely full, but contained a layer of brown substance in the lumen. The substance was mainly deposited in the narrow ends of the cells, in the pits and at the connections between adjacent parenchyma cells (Figure 15).

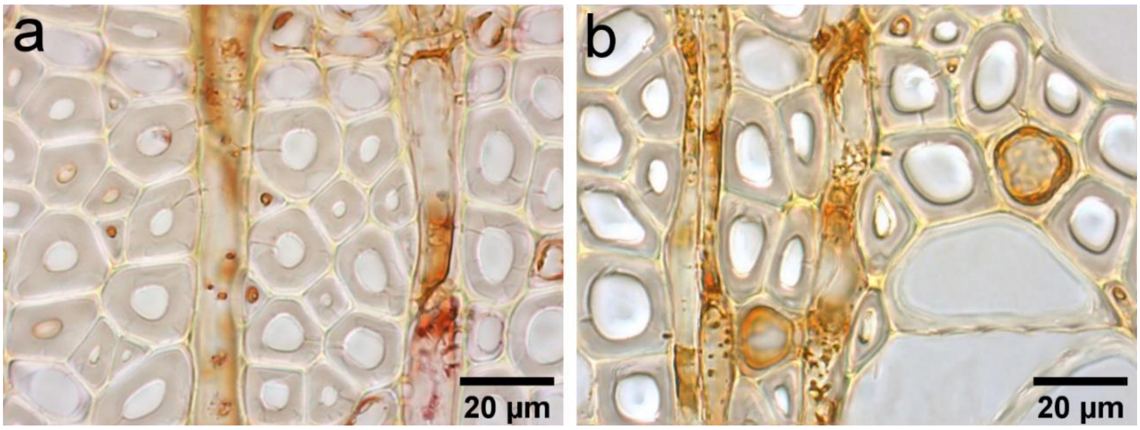

Figure 15. Detail of brown deposits in acetylated hornbeam stained red with safranin and astra blue (a) and stained brown with potassium permanganate (b). The staining had very little effect on the wood or the brown deposits.

Such deposits in acetylated wood have not been reported by other researchers.

One hypothesis was that the deposits in hornbeam could be contamination by resin from Radiata pine wood that were in the same batch in the industrial acetylation process at Accsys Technologies. Resin canals of acetylated spruce and pine often lacked resin, which could have been a result of being dissolved in acetic anhydride (Sander et al., 2003). To test this hypothesis, a simple solubility test was carried out. The brown substance did not dissolve in water, ethanol, acetone, dichloromethane, hexane, or acetic anhydride at normal temperature. It can be assumed that the substance is not resin contamination from softwood.

The deposits were present only in parenchyma cells and the amount in each cell was small. This could lead to a hypothesis that it was a natural component of the living cells, which was made insoluble by the acetylation process. It possibly contains phenolic compounds, which was confirmed by staining (Figure 13b, Figure 14b).

The deposits can be presumed to be or contain lignans, which are similar to lignin, but are deposited in parenchyma cells and cell walls as extractives. Lignans are small, low molecular weight polyphenols, which are soluble in water. This could be the reason it is stained by safranin, and it is washed out during preparation. Lignans can be isolated from hornbeam bark, leaf and catkin (Felegyi-Tóth et al., 2022). If they are acetylated, their water solubility decrease, which explains their appearance in acetylated sections.

Another possible explanation for the deposits is that they are the result of a Maillard reaction which could be proven by verifying the increase of nitrogen content of hornbeam after acetylation with e.g. the Kjeldahl method.

Although acetylated hornbeam had no sign of fungal decay and had less than 1% mass loss (Paragraph 1.8), some hyphae were observed in the microscopic sections. The hyphae, which were stained blue, grew through lumina and pits. They were observed in the cross section (Figure 13, Figure 16, Figure 17) and also in the radial section (Figure 18). The hyphae were usually attached to the cell wall, and looked like blue spots in the cross section (Figure 17). In acetylated hornbeam, few hyphae and no signs of decay were found in samples treated with any of the three fungi *Coniophora puteana, Rhodonia (Poria) placenta*, or *Trametes (Coriolus) versicolor*.

Untreated samples were highly degraded by fungi, which resulted in brittle sections with cracks and cell-wall damage. The blue parts of the cell walls are those delignified by white rot fungal activity (Figure 16, Figure 17). Free hyphae in vessels were probably lost during the staining process.

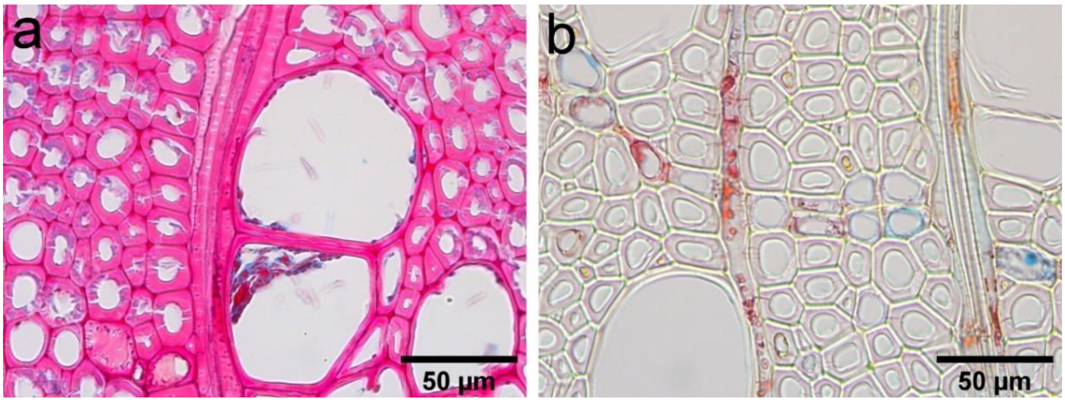

Figure 16. Bright-field micrographs of untreated hornbeam (a) and acetylated hornbeam (b), both after the durability test with brown rot Rhodonia (Poria) placenta. The cross sections were stained with safranin and astra blue.

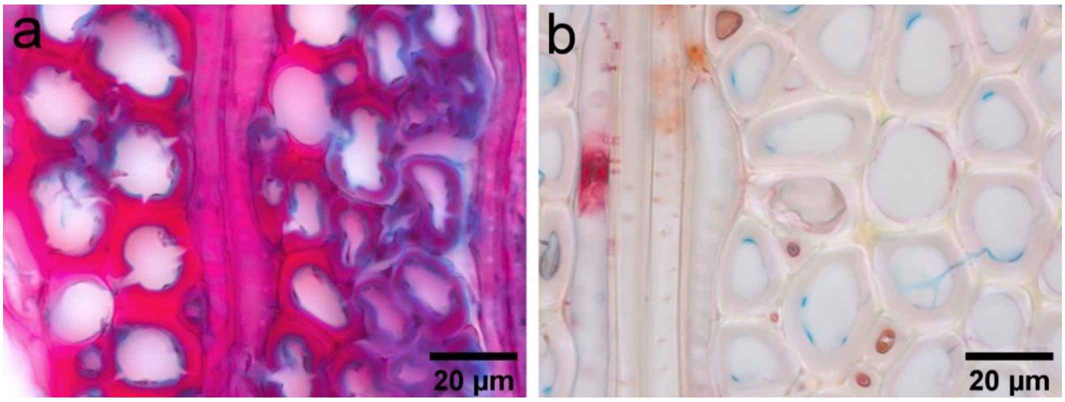

Figure 17. Bright-field micrographs of untreated hornbeam (a) and acetylated hornbeam (b), both after the durability test with white rot Trametes (Coriolus) versicolor. The cross sections were stained with safranin and astra blue.

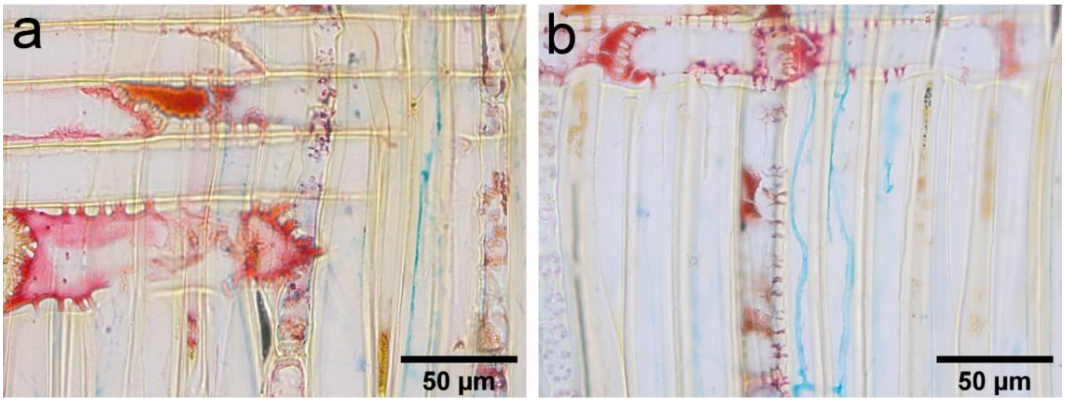

Figure 18. Bright-field micrographs of acetylated hornbeam after the durability test with brown rot Coniophora puteana (a) and white rot Trametes (Coriolus) versicolor (b). Deposits in the radial sections were stained red with safranin and the blue coloration of hyphae is due to staining with astra blue.

Radial sections (Figure 18) show how the deposits were distributed in the ray parenchyma cells. Although there was still some empty space in the cells, the substance blocked all the pits. That could be the reason hyphae were not observed in them.

In other reports, hyphae were usually found in parenchyma cells with no deposits (Kumar, 1994; Mohebby and Militz, 2010). The advantage of bright-field microscopy is staining which can highlight structures with different chemical properties. However, this method is less suitable for observing single cells, because the contrast is lower due to light scattering in cell walls. Sharper images with more detail were obtained by scanning electron microscopy, which was focused on the cross sections.

3.3.3. Scanning electron microscopy

No visible change in cell-wall thickness after acetylation was found by examining with SEM, probably because of the larger lumina : cell-wall thickness ratio and a high variability of cell-wall thickness. However, an analysis of cell-wall thickness proved, that acetylation increased the thickness by 7.0% and the difference was statistically significant. The average thickness (and standard deviation) of two cell walls of two big adjacent fiber cells and the middle lamella between them was 6.28 ± 0.95 µm in untreated hornbeam and 6.72 ± 0.98 µm in acetylated hornbeam. As a result of cell-wall swelling, the pits of acetylated hornbeam were much narrower than in the reference sample (Figure 19). This is the evidence of tangential cell-wall swelling, which could increase cell diameter and thus the volume of the wood. However, the cell diameter was not measured in this study.

The presence of deposits in the parenchyma cells was also observed by SEM (Figure 19, Figure 20, Figure 21). It is very likely that this substance in untreated hornbeam is water-soluble (leached during sample preparation), thus less visible in microscopic images (Figure 14, Figure 15, Figure 21), but after it reacts with acetic anhydride, some kind of phenolic substance is produced which is not soluble in water and is clearly visible in microscopic images.

The most apparent staining of deposits is in the micrographs of decayed acetylated hornbeam (Figure 21b). Here, the staining effect is greater than in non-decayed acetylated samples (Figure 15), which leads to the conclusion that fungi found nutrients in the deposits, leaving lignin behind which was stained by safranin. When these deposits are not decayed, safranin does not stain them.

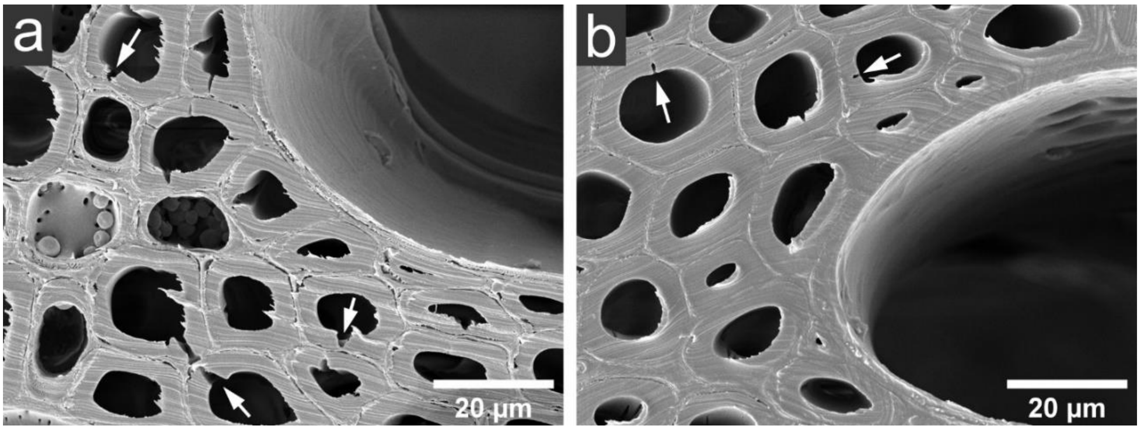

Figure 19. Scanning electron micrographs of cross sections of untreated hornbeam (a) and acetylated hornbeam (b). White arrows show wide pits in untreated hornbeam and narrow pits in acetylated hornbeam.

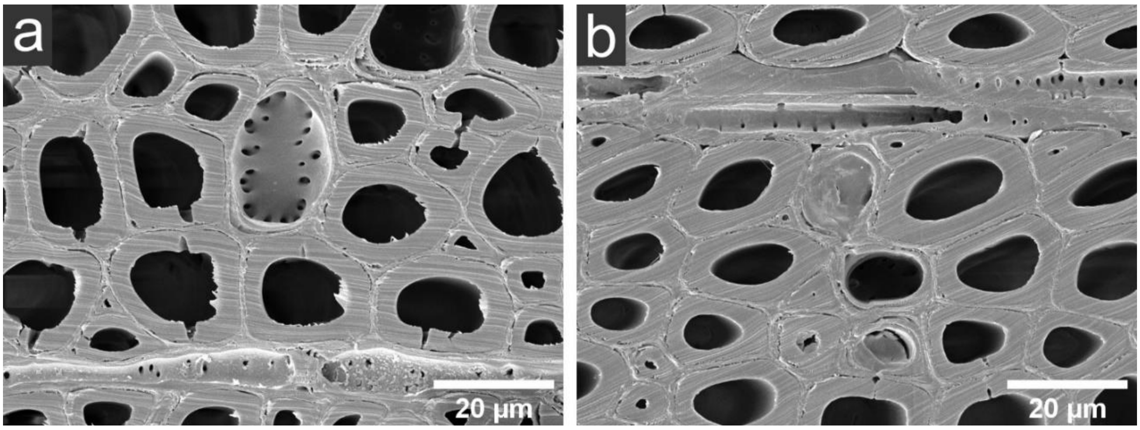

Figure 20. Scanning electron micrographs of cross sections of untreated hornbeam (a) and acetylated hornbeam (b). Axial parenchyma cells are empty in hornbeam (a) and full of deposits in acetylated hornbeam (b).

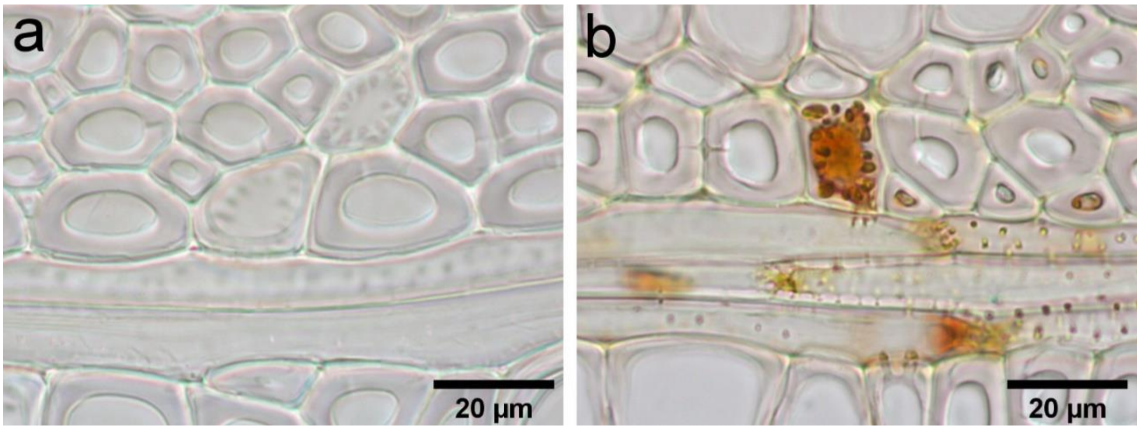

Figure 21. Bright-field micrographs of cross sections of untreated reference hornbeam (a) and acetylated hornbeam (b). Axial parenchyma cells are empty in reference hornbeam (a) and full of brown deposits in acetylated hornbeam (b). The reference is without staining and acetylated wood is stained with safranin and astra blue, but with almost no staining effect.

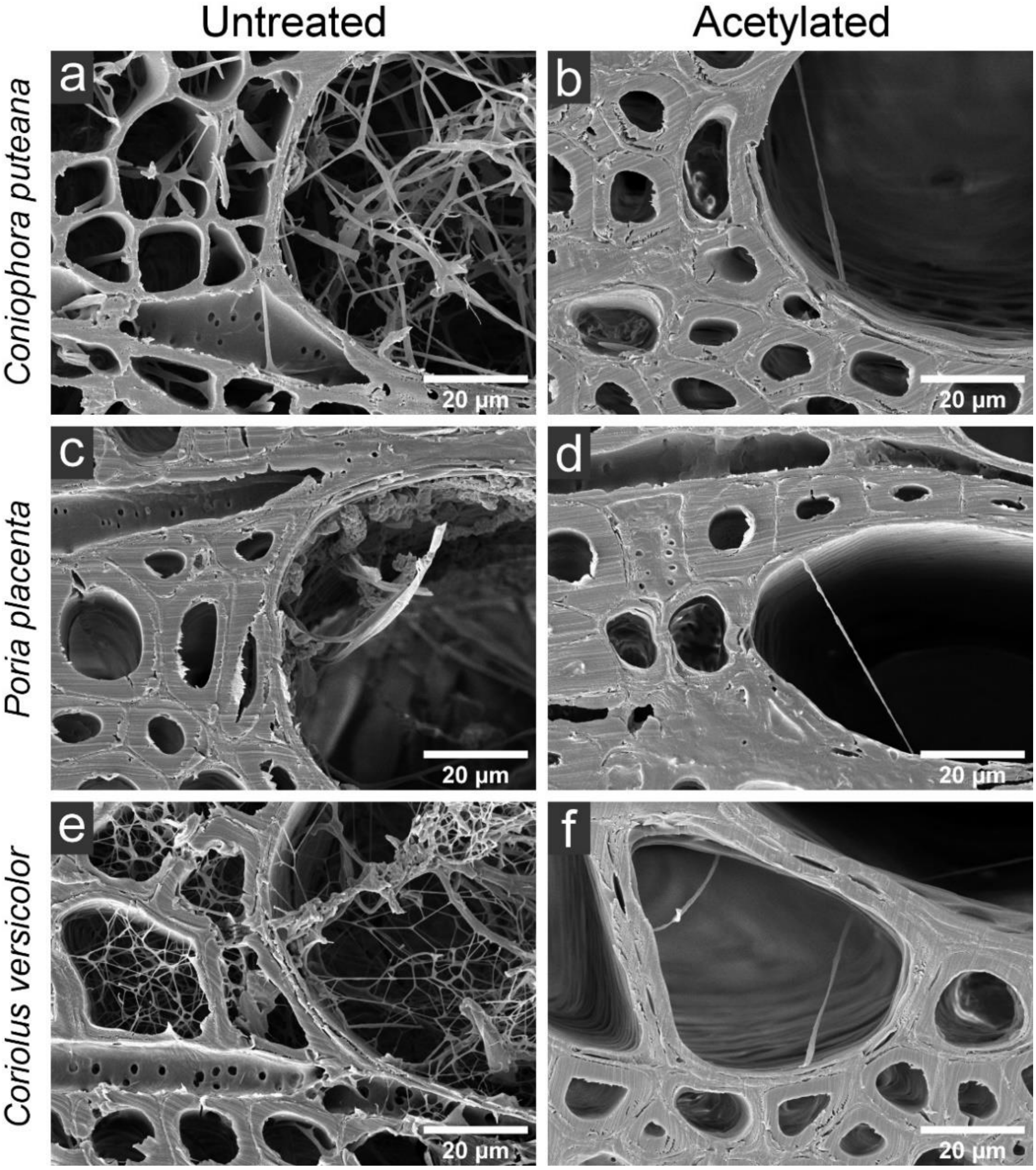

Figure 22. Scanning electron micrographs of untreated reference hornbeam (a, c, e) and acetylated hornbeam (b, d, f), both after the durability test. The reference hornbeam is extensively colonized by fungi, but hyphae in acetylated hornbeam are very rare.

Scanning electron microscopy revealed fine details of hyphae in decayed hornbeam (Figure 22/a, c, e). Significant fungal growth and wood decay was observed in untreated hornbeam. Hyphae were found very rarely in acetylated wood (Figure 22/b, d, f). No decay of the wood structure was observed; on the other hand, hyphae were able to colonize the cell lumina and penetrate pits without decaying the wood. This phenomenon was also observed by other researchers (Mohebby, 2003; Mohebby and Militz, 2010; Rowell and Bongers, 2015).

White rot *Trametes (Coriolus) versicolor* caused extensive local degradation of the cell walls, and the middle lamellae were dissolved. The structure became fibrous as the integrity of the cell walls was lost. The pits in hornbeam were also eroded, opening pathways for hyphae to penetrate deeper into the wood. In a study on acetylated beech, it was found that the fungal hyphae penetrate the fiber lumina and pit chambers after 15 days of exposure at a WPG of 17.15%, but no erosion of walls, opening of pits or hyphae in cell walls occur in fibers or rays during the incubation period of 12 weeks (Mohebby, 2003).

Brown rot *Coniophora puteana* decomposed the cell wall evenly so that only middle lamella remained there. Degradation by brown rot *Rhodonia (Poria) placenta* was less visible by electron microscopy (Figure 22/c), but the delignification process was already shown earlier by bright-field microscopy (Figure 16). The rate of decay can be seen on the broken and collapsed cell walls which is due to dissolved middle lamellae.

During delignification, ray cells separate from each other, hyphae bore holes grow on cell walls to penetrate into neighboring cells, and the wood becomes porous. In acetylated hornbeam, pale bluish color indicates the initial removal of lignin as a result of brown rot (Figure 16, Figure 22). In a study on acetylated beech, it was found that fungal hyphae penetrate into the fiber lumina and pit chambers after 11 days of exposure at a WPG of 17.15%, bore holes in cell walls become visible after 23 days, bore holes in pits after 46 days, and cell walls start eroding after 58 days during the incubation period of 12 weeks (Mohebby, 2003).

If the tested fungi are compared, it seems that white rot fungi degrade hornbeam and acetylated hornbeam more readily than brown rot fungi. Similar results were obtained by other authors (Green and Highley, 1997; Suttie et al., 1998; Schwarze et al., 2000), who found that white rot fungi prefer hardwoods and acetylated hardwoods to softwoods, and brown rot fungi more likely attack untreated softwoods and acetylated softwoods than hardwoods.

The scarce and apparently random presence of fungal hyphae can be explained if the cell walls in wood are not uniformly acetylated during the acetylation process, and there are regions in the cell walls where the acetyl content is low enough for the fungi to colonize. If the WPG is higher, the distribution of acetyl groups in cell walls is more uniform (Rosenqvist, 2001). Hyphae may search for such regions of low levels of acetylation, attack them and produce bore holes (Mohebby, 2003). However, staining with safranin showed uniform acetylation (Figure 17b) and no bore holes were observed (Figure 22/b, d, f). The scarcity of fungal hyphae could be explained by lack of nutrients, while other conditions were sufficient for fungal growth.

3.4. Conclusions

In this work, bright-field microscopy and scanning electron microscopy tests were carried out to find the effect of acetylation on the microscopic structure of hornbeam wood. Several methods of sample preparation and staining were tested and compared, as the modification process altered the wettability and chemical structure of native hornbeam, which influenced the sample preparation for microscopy.

Native hornbeam wood was sufficiently acetylated, which was proven by the minimal staining effect of safranin. Acetylation did not damage the wood microstructure and increased the cell-wall thickness by 7.0%. Despite the increase was statistically significant, it was too small to be visible in the micrographs. However, some changes were observed.

The pits of acetylated hornbeam were much narrower, probably due to permanent cell-wall swelling. New brown deposits were found in parenchyma cells of acetylated hornbeam. Each cell contained a small amount of an insoluble substance, which led to the hypothesis that a natural component of the living cells became insoluble during acetylation. Further investigation is needed to determine what this substance was (probably phenolic, e.g. lignan) that was created during acetylation.

In the case of samples which were tested for fungi resistance against *Coniophora puteana, Rhodonia placenta*, and *Trametes versicolor*, microscopic studies showed that fungi were able to colonize acetylated cell lumina without visible degradation and mass loss.

Chapter 4. Long-term durability in soil

4.1. Introduction

The durability of untreated and treated wood can be examined by laboratory tests (EN 113: 1996) and field tests (EN 330: 1993, ENV 807: 2001, CEN/TS 12037: 2003, AWPA E 18: 2004, EN 252: 2012), which allows it to be classified in durability classes (CEN/TS 15083: 2005, EN 350: 2016) and the suitability to use classes (ISO 21887: 2007, EN 335: 2013).

In this research, a field test, specifically an in-ground test was used, where the wood was partly in contact with the soil, and the impact of atmospheric and biological factors was direct. Non-destructive methods such as visual assessment, macroscopic evaluation, density and mass loss, sound (sonic tomography), optical methods (X-ray tomography), microscopy, radiography, or destructive methods such as the pick/splinter test or strength tests can all assess wood degradation (Råberg et al., 2005; Pánek and Trgala, 2016).

Visual assessment includes the determination of discolorations, cracks, mycelium, and insect damage. Microscopic detection is also possible if the mass loss is at least 5–10%. The signs of decay by soft rot, brown rot, white rot and tunneling bacteria can be well distinguished by their characteristic decay patterns (Råberg et al., 2005; Schwarze, 2007).

Density is closely correlated with strength properties; thus, it can be a rough decay indicator during decay testing. However, the density loss caused by white and brown rot is not comparable because white rot causes a small change in volume while brown rot causes substantial volume reduction. Determining mass loss is also a common method, but it cannot detect the early stages of decay. For this, measuring the strength toughness and impact bending strength are the most sensitive methods (Råberg et al., 2005).

During a pick-test, a pointed knife is poked into the specimens and withdrawn. The fracture characteristics of the splinter and the depth and appearance are assessed visually. Decay types are identified and evaluated according to EN 252: 2015. Failed specimens are analyzed microscopically to identify the type of decay (Jones and Brischke, 2017).

The degradation rate caused by microorganisms depends on many factors, such as wood structure, natural or artificial toxicity of the wood, tolerance to temperature, moisture content, pH, and oxygen range. Although fungi and bacteria can degrade the wood, *Basidiomycetes* are usually more aggressive but less tolerant of extreme conditions than the bacteria or soft rot fungi. When colonizing wood, bacteria, molds, blue stain, and soft rot fungi decay initially, and then *Basidiomycetous* fungi take over (Råberg et al., 2005).

Several authors have reported that acetylation of lignocellulosic materials increases their resistance to biological degradation. Laboratory tests and field tests have shown considerably improved protection against attack by white rot, brown rot, soft rot fungi, tunneling bacteria, and marine borers in various species such as southern yellow pine, beech, Scots pine, and poplar (Goldstein et al., 1961; Peterson and Thomas, 1978; Takahashi et al., 1989; Militz, 1991; Ohkoshi et al., 1999; Larsson-Brelid et al., 2000; Mohebby, 2003; Mohebby and Militz, 2010). For example, beech, which has similar structure to that of hornbeam, showed no signs of decay at WPG 17% (Mohebby, 2003).

The acetylation rate can be expressed as the weight percentage gain (WPG) or the acetyl content, which is usually determined by HPLC or NIR analytical methods. The former is used in laboratory tests, while the latter is used on an industrial level. The higher the WPG, the higher the durability (Takahashi, 1996; Mohebby, 2003).

Studies have reported that the resistance of acetylated wood (with a WPG of ca. 20%) to fungal decay was equivalent to chromated copper arsenate (CCA)-treated wood at a high retention level (e.g., 103 kg/m^3) after 18 years in soil contact (Larsson-Brelid et al., 2000; Larsson-Brelid and Westin, 2010). To provide sufficient durability, a WPG of at least ~10% needs to be reached for soft rot and white rot, and a WPG of at least ~20% for brown rot and tunneling bacteria (Larsson-Brelid et al., 2000; Mohebby, 2003; Mohebby and Militz, 2010).

Fungal colonization requires moisture for oxalate production. Moisture is also necessary for movement in the cell wall, in Fenton chemistry to degrade cell wall polysaccharides, for gene expression and enzyme activity, for glycoside hydrolysis, and for the movement of soluble nutrients. Wood-rotting fungi and insects have their specific enzyme systems, which degrade wood polymers into digestible units. Hydroxyl groups are biological enzymatic reaction sites; if these are chemically changed, the fungal enzymatic action cannot take place (Takahashi, 1996; Suttie et al., 1998; Hill, 2006).

Among the cell-wall chemical constituents, hemicellulose polymers have the highest moisture content (38%) compared to lignin (16%) and cellulose (12%) at 90% relative humidity and room temperature. It seems that fungi access the moisture first in hemicelluloses, which may be the first to be degraded. The hemicellulose polymers are interconnected throughout the cell wall and can act as a hemicellulose moisture pipeline (Mohebby, 2003; Ringman et al., 2019; Rowell, 2020).

Since 2008, Accsys Technologies (in Arnhem, the Netherlands) has been commercially acetylating radiata pine and selling it on the market as Accoya® wood. The biological durability of Accoya® wood is DC 1, the highest class according to EN 350: 2016. It exhibits considerably increased biological resistance against brown rot, white rot, and soft rot fungi (Larsson-Brelid et al., 2000; Papadopoulos and Hill, 2002; Mohebby, 2003; Mohebby and Militz, 2010; Rowell, 2016). In a ten-year-long ground stake test in Greece (southern Mediterranean zone), Accoya® wood exhibited very good performance with no visual signs of decay (Mantanis et al., 2020). Its structural integrity was maintained to some extent, but the MOE and MOR properties decreased considerably, by 33% and 30%, respectively. It was concluded that although there are no visible signs of decay, there could be a significant loss of mechanical properties in acetylated wood.

By improving the durability of hornbeam with acetylation, it could be used to expand the range of durable species for outdoor applications in Hungary such as oak, black locust, Scots pine, and larch (Molnár and Bariska, 2002). Only a few research papers have focused on the durability of acetylated hornbeam wood using laboratory tests. According to EN 113: 1996 and EN 350: 2016, industrially-acetylated hornbeam had DC 1 against *Rhodonia (Poria) placenta*, *Coniophora puteana*, and *Trametes (Coriolus) versicolor* (Paragraph 1.8), and DC 2-3 against *Trametes versicolor*, *Coniophora puteana*, and *Chaetomium globosum* when acetylated with 10% liquid formalin and 5% acetic acid (Bari et al., 2019). In spite of this, microscopic studies revealed a scarce appearance of hyphae, so fungi were able to colonize in lumina of acetylated hornbeam (Chapter 3).

This research aimed to see if acetylated hornbeam could be utilized as an outdoor product in real-field conditions, with many different microorganisms that can attack the wood separately or cooperatively. The test was conducted according to EN 252, and it also considered soil and weather characteristics of the field, as well. The difference in the rate of degradation was determined visually, by microscopy, and by calculating density and mass loss. The test is ongoing since April 2016, the results are presented here for the past 7 years.

4.2. Materials and methods

4.2.1. Sample preparation

The long-term field test was performed according to EN 252:2015 with some slight modifications: the sample dimensions were changed from 25 × 50 × 500 mm^3 to 20 × 50 × 300 mm^3 (t × w × l) because the dimensions of raw material were limited. There were 12 stakes of each type: untreated hornbeam and industrially acetylated hornbeam, supplemented with beech and Scots pine sapwood according to standard. Acetylation is described in Paragraph 1.8. The stakes were cut from these boards, having WPG levels ranging from 13.55 to 16.15%. The average WPG was 15.10 ± 1.03%. The beech and pine stakes indicated the intensity of the decaying mechanism of the soil. Table 5 shows the important characteristics and parameters of the stakes. The stakes were conditioned at 20 ± 2 °C and 65 ± 5% relative humidity before measuring their parameters and weight.

Table 5. Information about the stakes. Average values are presented with standard deviation in brackets.

Average	Acetylated hornbeam	Hornbeam	Beech	Scots pine sapwood
No. of annual rings	5 on 10 mm surface 10 on 2 cm surface	4 on 10 mm surface 8 on 2 cm surface	4 on 10 mm surface 8 on 2 cm surface	5 on 10 mm surface 9 on 2 cm surface
Air-dry density (kg/m^3)	794 (49)	745 (45)	719 (7)	525 (19)
Mean density (kg/m^3)	804 (50)	822 (55)	799 (10)	614 (23)
Moisture content (%)	3.35 (0.06)	14.16 (0.96)	13.50 (0.16)	13.34 (0.50)

The stakes were buried in the outdoor exposure testing field at the University of Sopron (47°40′41.4″ N 16°34′32.6″ E) in April 2016 (Figure 23). The stakes were buried half of their length, one by one from each type (Figure A75). The distance between stakes was 30 cm. The vegetation on the field was cut regularly, and no chemicals or herbicides were used during the test. The presence of wood-decaying fungi and insects was also observed during the evaluation.

Figure 23. Stakes placed in soil in April 2016 in the outdoor exposure testing field. Twelve pieces of acetylated hornbeam, untreated hornbeam, beech and Scots pine stakes were buried half of their length.

4.2.2. Soil of testing field

In October 2021, five samples were taken from the soil of the testing field in order to examine the soil properties that influence the intensity of degradation. The samples were taken from four corners and the middle of the field.

Skeletal grain content was determined by their dry weight relative to the dry weight of the soil. These particles had low water-holding capacity compared to fine-sized fractions.

The measurement of soil pH was performed electrometrically at a soil/liquid ratio of 1/2.5 according to MSZ-08-0206-2: 1978. Then, 10 g of soil samples were soaked in distilled water and one molar solution of KCl, respectively. Soils with pH above 6 provide an ideal chemical environment for plant and fungal growth.

The calcium carbonate ($CaCO_3$) content of the soil was determined with a Scheibler calcimeter according to MSZ-08-0206-2: 1978.

Humus or organic matter content was measured by the wet incineration process using potassium dichromate for the oxidation of organic matter. Water and phosphorus iron were added. It was then back-titrated with 0.2 M Mohr's salt in the presence of ferric ion and diphenylamine sulfonic acid indicator. The organic carbon content of the soil was calculated based on the amount of Mohr's salt used in the titration. Microbial activity in soil is related to carbon stabilization and storage, water holding capacity, and aeration (Gómez-Guerrero and Doane, 2018).

Particle content or fine-earth fraction was determined by the pipetting method according to MSZ-08-0205: 1978. Particles of fine earth fraction have a larger surface area and charge characteristics that promote soil aggregation, structural development, and the regulation of soil water movement (Hatten and Liles, 2019).

4.2.3. Weather and climate

The weather parameters of the testing field were received from the Department of Ecology and Bioclimatology of the University of Sopron. These included average and maximum monthly temperature, monthly precipitation, number of days with precipitation above 0.25 mm, sunshine duration per month, solar irradiance per month, and monthly relative humidity.

The Scheffer climate index (SCI) was also calculated, which was proposed in 1971 to estimate decay hazard by geographic location within the conterminous United States for wood exposed above ground to exterior conditions (Scheffer, 1971). The index is calculated from local weather data using the mean monthly temperature and mean number of days with at least 0.25 mm of precipitation over the exposure period. An index of less than 35 represents the least favorable conditions for decay; 30 to 65, intermediately favorable conditions; and greater than 65, conditions most conducive to decay. As a metric by which relative hazard can be compared between geographic locations, the Scheffer index is not intended to predict the decay propagation rate or time to failure in specific constructions (Carll, 2009). The rate of decay also depends on application, design, material resistance, soil water holding capacity, etc. This particularity is not necessarily a limitation of the approach, but it has been debated. However, the SCI is still, beyond doubt, the most frequently used index of its kind for estimating the relative climate-induced decay hazard of geographical locations (Brischke and Selter, 2020).

4.2.4. Rate of degradation

Every six months, the level of degradation of each stake was determined from 0 to 4 according to EN 252:2015. Stakes with no sign of decay were rated 0, and stakes with slight, moderate, or severe attack were rated 1, 2, or 3, respectively. If the stake failed, broke during the test, it was rated 4. Photos were taken before, during, and after exposure to observe the changes perceivable to the eye. Photos were taken monthly in the first years. After the failure of a stake, the broken pieces were dried at 103 °C in a drying kiln until a constant mass was reached, and the dry weight and parameters were determined to calculate the dry mass loss and dry density loss caused by degradation.

4.2.5. Microscopic evaluation

Cubes with $10 \times 10 \times 10$ mm^3 (t × w × l) dimensions were cut from the lower part of the failed stakes and dried at 103 °C in a drying kiln to constant weight. Then, they were placed into a desiccator. As the cubes were cut with a circular saw, which resulted in rough surfaces, the surfaces were smoothed with a razor blade/scalpel before examination with a Hitachi S-3400N PC-Based Variable Pressure Scanning Electron Microscope (Hitachi, Tokyo, Japan) and its software (Figure A76). Cross and longitudinal sections were examined as well. Microscopic analysis was performed at a 60 Pa vacuum and a 10 kV accelerating voltage using a BSE detector. The working distance was 10 mm. The surfaces were not coated with a sputter coater before imaging.

4.2.6. FTIR analysis

Acetylated hornbeam stake number 7 showed local signs of decay (see Results and discussion), which was examined with FTIR. The measurement was performed using a Specac Golden Gate ATR (attenuated total reflection) with zinc selenide (ZnSe) crystal. Sound (control) and decayed parts of the stake were ground separately into smaller pieces (0,25 μm) using mortar and pestle to improve the contact area of the sample with the crystal on the ATR FTIR.

The FTIR spectra were measured in transmittance mode (%T). A three-point baseline correction was applied to 850, 1180 and 1800 cm^{-1} to maximum transmittance (100%). The peak intensity was determined at peaks 1740 cm^{-1} and 1230 cm^{-1}.

Then, it was translated to absorbance mode (%A), using the following formula (1):

$$A = 2 - \log(\%T) \qquad (1)$$

where A denotes absorbance unit, %T denotes percent transmittance (%).

Normalization was performed at peak 1030 cm^{-1} having 1% absorbance. Then, the peak height ratios (PHR) were calculated using the following formulas for peaks 1740 cm^{-1} (2) and 1230 cm^{-1} (3) in order to draw conclusions on difference in acetyl levels:

$$PHR_{1740} = \frac{\mathrm{A}_{1740}}{\mathrm{A}_{1030}} \qquad (2)$$

$$PHR_{1230} = \frac{\mathrm{A}_{1230}}{\mathrm{A}_{1030}} \qquad (3)$$

where PHR denotes peak height ratio, which means the peak height relative to the peak height at 1030 cm^{-1}, A denotes absorbance unit at given wavenumber.

Both measurements for the sound part and decayed part were performed in triplicates. The rest of the stakes remained in the testing field for further studies.

4.3. Results and discussion

4.3.1. Soil of testing field

Table 6 presents the summary of results regarding the testing field soil properties.

Table 6. Soil characteristics of testing field. Average values of 5 samples are presented with standard deviation in brackets.

Skeletal Grain Content > 2 mm (%)	pH		Calcium Carbonate ($CaCO_3$) Content (%)	Particle Content ≤ 2 mm				Organic Matter Content (Humus) (%)
	Water (H_2O)	Potassium chloride (KCl)		Clay (%)	Silt (%)	Fine Sand (%)	Coarse Sand (%)	
7	7.2	6,8	3	19	18	43	20	4.0
(3)	(0.1)	(0.1)	(0)	(1)	(4)	(1)	(4)	(0.8)

The skeletal grain content ranged from 4 to 11%, having an average of 7 ± 3%. This does not significantly influence the water and nutrient holding capacity of the soil.

In the case of pH_{H2O} or current acidity, there was no significant difference between the samples, as the values ranged from 7.1 to 7.3. This is neutral (< 7.2) and slightly alkalic (> 7.2). As expected, pH_{KCl} was lower than pH_{H2O}, and it ranged from 6.7 to 6.9. There was no significant difference between pH_{KCl} and pH_{H2O}, which means there was no latent (hidden) acidity rate. From an agricultural point of view, the pH of this soil is sufficient for most plant species, as most nutrients are best absorbed by plants and are most mobile in this pH range.

The calcium carbonate ($CaCO_3$) content ranged from 2 to 3%, which corresponded to the expected values based on soil pH. This amount of $CaCO_3$ is favorable because it improves the soil structure. It is also advantageous in that there was no expected calcium deficiency.

Based on the tests, the amount of sludge (clay and silt fraction) ranged from 31 to 43%, with an average of 37%, which indicates a sandy loam type. This type has favorable water management properties because it allows water to enter well, retains it well, and makes it available for plants.

Humus or organic matter content was between 2.7 and 4.9%, having an average of 4-0 ± 0.8%, which is classified as a good/medium supply. This result also corresponded to the other soil properties.

According to these results, the soil in which the wooden specimens were tested was rich in nutrients and had good aeration and drainage properties. These characteristics were favorable for not just plant growth but also fungal growth, such as soft, white and brown rot fungi.

Basidiomycetes live in conditions with high oxygen content (soil with good aeration), moist wood with moisture content between 40 and 80%, and their optimal temperature range is from 24 °C to 32 °C. White rot fungi require higher moisture content and higher pH than brown rot fungi. They can decay wood during a short period when the temperature and the moisture are at optimal levels, e.g., summer, end of spring, and early autumn seasons. Soft rot fungi activate in a wide range of moisture contents, from relatively dry wood to saturated conditions, and a wide range of temperatures from 0 °C to 60 °C. They are active at a pH close to neutral and have better adaptability properties than other fungi during the whole year when soil moisture and temperature change periodically (Råberg et al., 2005; Mohebby and Militz, 2010).

4.3.2. Weather and climate

According to its solar-climatic classification, Hungary is situated about halfway between the Equator and the North Pole, in the temperate climatic zone. Hungary has a continental climate, with hot summers with low overall humidity levels but frequent showers and frigid to cold snowy winters. Sopron is in the moderately cool–moderately dry climatic region (Péczely, 1998).

Table A31 and Table A32 list the weather parameters of the study site. The area of the study site has a warm and wet summer season (May–September) with mean temperatures between 13–23 °C, with a maximum of 37 °C, and monthly average precipitation between 61–82 mm. It has a drier winter season (October–April) with 26–48 mm of average precipitation per month, mean temperatures between −4–16 °C, with a maximum of 31 °C. The average annual rainfall during the test period was approximately 592 mm; the average annual temperature was 12 °C; the maximum temperature was 37.2 °C. The relative humidity ranged from 45 to 91%.

According to the ombrothermic diagram (Figure A77), there was no dry season during the year, which would be the area below the temperature line and above the precipitation line. On the other hand, the wet season—the area below the precipitation line and above the temperature line—was typical for the whole year.

The wet and warm periods at the exposure site were quite long, which enabled fungal growth. For *Basidiomycetes*, the summer period was favorable, while for soft rot, the conditions for growth were good throughout the whole year when temperatures did not drop below zero. The moisture content of the soil and that of the wood specimens are related to each other, and the change in their moisture content is related to the oxygen level of the soil. The oxygen level and aeration properties of the soil enable the growth of microorganisms in the wood.

The Scheffer climate index of this site is 47.0, which indicates intermediately favorable conditions for decay. This index is similar to other reports regarding the SCI of different countries, including Hungary. The SCI of Hungary ranged from 35 to 50 in other investigations (Brischke et al., 2011; Niklewski et al., 2021; Niekerk et al., 2022). Compared to European countries, it is in about the middle range. Those territories that have the highest decay potential (so-called hot spots) are on the west coast of Norway, Ireland, the UK, and France, reaching a maximum SCI of 81 (Brischke et al., 2011; Niklewski et al., 2021). These territories will expand in the future, as the activity of wood degrading organisms (e.g., termites) is expected to increase in Europe as a result of warmer climate (Niekerk et al., 2022).

The decay rate of this testing field can also be perceived by the results of other field tests in the past. In a six-month-long test (Csizmadia, 2015), Turkey oak, hornbeam, Pannonia poplar, and Scots pine stakes with dimensions of 20 × 20 × 300 mm^3 (t × w × l) were tested. These stakes were heat-treated for 5 hours at 200 °C. After 6 months of exposure, the decay rating decreased after heat treatment from 1.6 to 0.9 for Scots pine, 1.4 to 0.3 for Turkey oak, 4.0 to 3.0 for poplar, and 2.3 to 1.4 for hornbeam.

In a nine-month-long test (Nagy, 2016), oak and black locust samples of 20 × 20 × 300 mm^3 (t × w × l) and teak samples of 10 × 10 × 150 mm^3 (t × w × l) were tested to detect changes in physical properties. After 9 months, the density was reduced to 83%, 75%, and 97% for black locust, oak, and teak, respectively. Mass was 91%, 82%, and 99% of the initial mass of black locust, oak, and teak, respectively.

In a two-year-long test (Salamon, 2021), five stakes of beeswax-impregnated beech and Scots pine with dimensions of 25 × 50 × 500 mm were tested. After 1 year of exposure, the decay rating due to beeswax impregnation decreased from 3.6 to 1.6 for beech and from 3.2 to 0.6 for Scots pine. After 2 years of exposure, it was from 4.0 to 2.2 for beech and 3.2 to 1.4 for Scots pine. These findings indicate the soil which is the subject of investigation was biologically active, ideal for durability testing.

4.3.3. Rate of degradation

Mold started growing and cracks appeared on untreated stakes already after 1 month. There was no sign of decay on the acetylated hornbeam after 1 year. Wasp stripping was observed on untreated hornbeam and beech after 8 months (Figure A78, Figure A79). Moss appeared on Scots pine stakes after 10 months. Signs of fungal decay were visible on untreated stakes already after 5 months (Figure A78). After 1 year, three untreated hornbeam and one untreated beech stake broke during evaluation. Signs of soft rot, white rot, and insect damage were observed (Figure A80). Whitish discoloration, long-fibered splinter and fibered structure indicated white rot attack. Mushrooms of *Coprinellus micaceus* were identified on untreated hornbeam stakes (Figure A78). Soft rot decay attacks hardwoods more than softwoods because the lignin is more methoxylated in hardwoods (Råberg et al., 2005; Mohebby and Militz, 2010).

After 15 months, mushrooms of *Bjerkandera adusta* and *Coprinellus micaceus* formed on beech stakes. Moss was found later on acetylated hornbeam stakes after 17 months (Figure A81). One of the acetylated hornbeam stakes showed signs of brown rot decay after 18 months (Figure A82). The rate of white rot and soft rot decay, as well as insect damage in untreated stakes, worsened after another year.

After 2 years of exposure, three hornbeam and seven beech stakes failed the test. Fungal degradation and mushrooms frequently appeared on them (Figure A83). Scots pine stakes were heavily degraded by soft rot and brown rot. All untreated hornbeam stakes failed after 3.5 years, while all beech stakes failed already after 2.5 years. Scots pine stakes started to fail after 3.5 years, and all of them broke after 6 years of exposure. Small cubic breaks, softened surface, dark discoloration, insect damage, and moss were observed on them (Figure A84). The soil was probably less optimal for the growth of brown rot fungi, which can explain the slower decaying mechanism compared to soft rot and white rot. This corresponds to the results of other research carried out at this site (Csizmadia, 2015). After 5.5 years, acetylated hornbeam stake Number 7 was taken out from the test to examine its properties as the only locally decayed stake (Figure 24).

Figure 24. Acetylated hornbeam stake no. 7 which was taken from the test in order to examine its damage after 5.5 years.

The local decayed part of the sample may have been a "wet pocket" in the untreated wood, which was acetylated at a lower degree due to the higher moisture content. When wood is acetylated with higher moisture content, it results in a loss of the reagent as acetic acid is formed, and the WPG decreases with increasing moisture content (Hill, 2006). At a lower WPG, it is more prone to be attacked by fungi. White rot has the same preference in case of acetylated wood as untreated: it degrades acetylated hardwoods faster than acetylated softwoods (Mohebby, 2003). On the other hand, acetylated wood is less susceptible to white rot than brown rot, as the decaying mechanism of white rot depends on the presence of hydroxyl groups in the cell walls, which help initialize the attack by hydrolyzing enzymes. The higher the WPG, the more hydroxyl groups in lignin are exchanged by acetyl groups during acetylation, and the less likelihood that white rot fungi can diffuse into the cell walls and attack. Brown rot was observed on acetylated wood, as it can attack it even at this WPG (15%) or higher due to its non-enzymatic system (Mohebby, 2003; Rowell, 2020).

The test was valid according to EN 252:2016 because at least 75% of the untreated stakes were rated 4, and the acetylated stakes were rated not less than 2. In addition, local signs of decay existed on at least one acetylated stake. Figure 25 summarizes the rating and lifetime of each stake. The average lifetime of untreated hornbeam, beech and Scots pine was 2.0 ± 1.0, 1.8 ± 0.6, and 5.1 ± 1.0 years, respectively, and all of the stakes broke. Acetylated hornbeam stake number 7 had mild local brown rot decay, while the others showed no signs. The photo series of appearance change in one year can be observed on Figure A85.

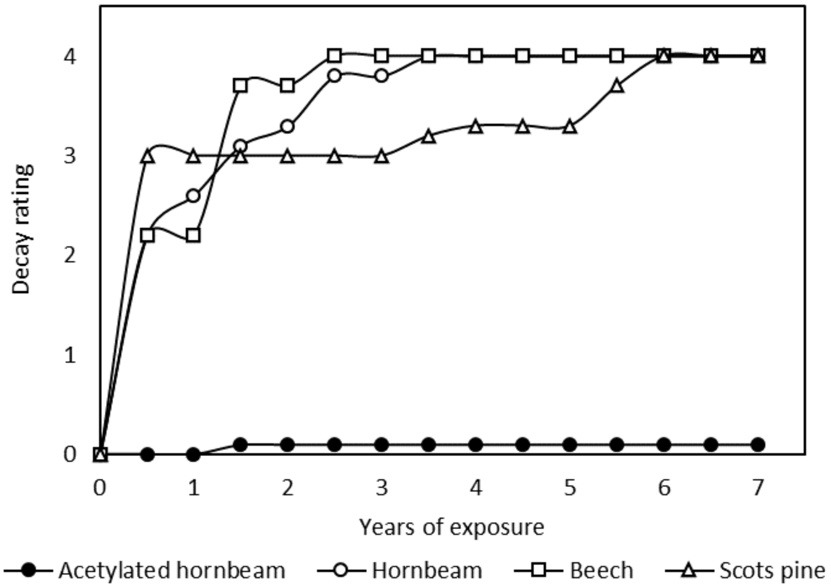

Figure 25. Average rating of in-ground stakes during exposure period (2016–2023). Decay rating or durability class is given according to EN 252 (2015): 0—sound, 1—slight attack, 2—moderate attack, 3—severe attack, 4—failure.

On average, one-third of mass and one-third of density were lost during the exposure in the case of untreated stakes (Table A33). The local brown rot-decayed acetylated hornbeam sample lost 6% of its mass and density after 5.5 years of field test. Depth of degradation was calculated by halving the thickness loss of samples, which was 0.02, 0.18 ± 0.34, 0.34 ± 0.11, and 1.98 ± 0.82 mm for acetylated hornbeam, beech, hornbeam, and Scots pine sapwood, respectively. In Scots pine, there was a great difference between the degradation of earlywood and latewood because earlywood was more susceptible to fungal attack. There were no correlations found between density, annual ring density, and lifetime.

4.3.4. Microscopic evaluation

After visual inspection, we inspected acetylated hornbeam stake Number 7 with a microscope to investigate the biological damage. The results show that some parts were not damaged or only the presence of hyphae was observed without cell wall damage. This corresponds to other reports in the literature (Mohebby, 2003; Mohebby and Militz, 2010; Ringman et al., 2019; Rowell, 2020) (Chapter 3). Hyphae can colonize cell lumina and ray cells of acetylated wood because they penetrate the wood across open ways like vessel lumina and rays, then into fiber cell lumina through inter-fiber pits and cross-fields between rays and fibers (Mohebby, 2003; Mohebby and Militz, 2010).

In the case of decayed parts in acetylated hornbeam, typical signs of soft and brown rot decay have been found, such as hyphae and cavity formation in cell walls, amorphous cell walls, erosion, and the thinning of cell walls with intact middle lamella (Figure 26) (Råberg et al., 2005; Schwarze, 2007).

In untreated stakes, the microscopic investigation revealed the rate of damage by soft rot and white rot. Fungal decay caused massive damage with cell wall thinning, the gradual disappearance of rays and bordered pits, erosion, fibrous tissue, and disappeared middle lamella (Figure A86, Figure A87, Figure A88). Large boreholes, large round holes in the cell wall, and hyphae with clamp connections could also be found in the microscopic sections (Råberg et al., 2005; Schwarze, 2007).

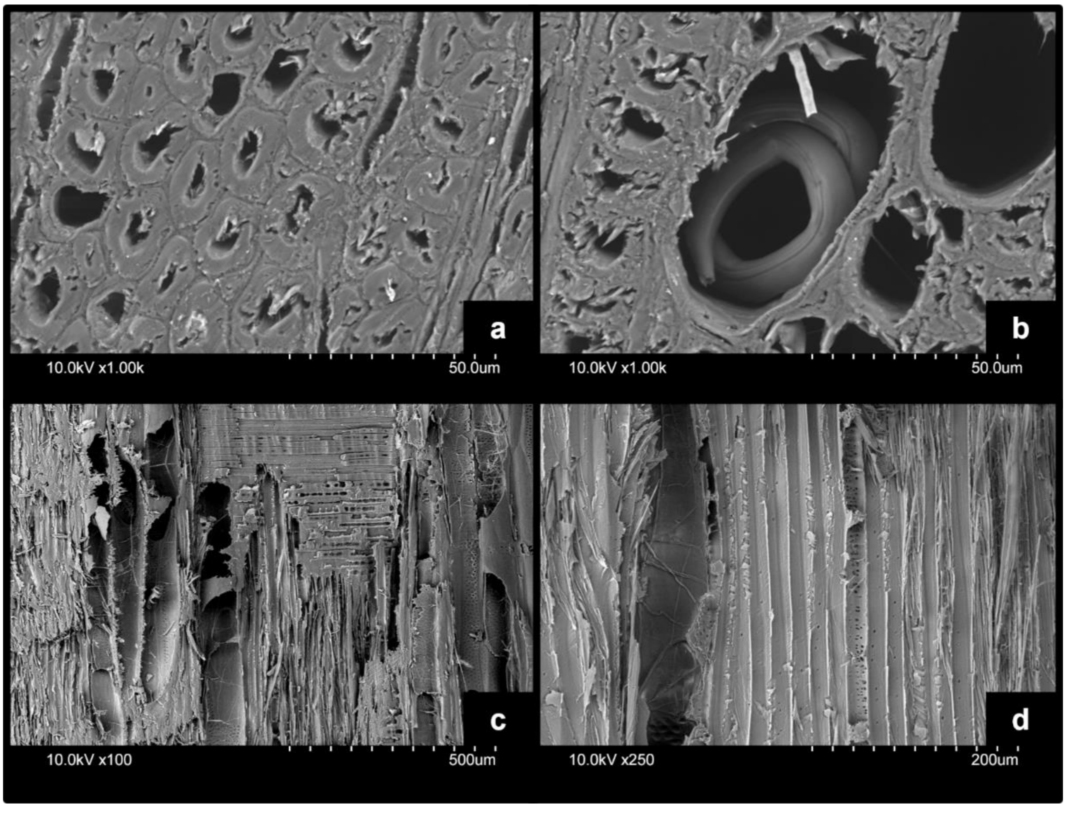

Figure 26. SEM pictures of cross section (above) and longitudinal section (below) of partly decayed acetylated hornbeam stake: (a) non-decayed parts with thick cell walls, (b) worm in cell lumen, (c) disappeared bordered pits, fibrous tissue, (d) hyphae in lumen, gradual thinning of cell walls, typical signs of soft rot decay.

4.3.5. FTIR analysis

The wood that originated from the “initial decay” area was relatively brittle, which made working with the mortar and pestle relatively easy. The piece of wood that originated from the intact part of the board was much less brittle and required more force than could be applied through the mortar and pestle.

Figure 27 displays the difference spectrum of decayed and sound acetylated hornbeam wood, where two important peaks related to acetyl content have been identified in Table 7. The largest peak with maximum intensity and absorbance was caused by C-O vibration in hemicellulose (1034 cm^{-1} for decayed, and 1032 cm^{-1} for sound part) (see also Chapter 2). This peak was considered constant (absorbance equals 1) in order to compare the 1736 cm^{-1} and 1221 cm^{-1} peaks between both spectra. Thus, the PHR between examined peak and 1030 cm^{-1} equaled the absorbance of the examined peak.

Table 7. Wavenumber characterization of the infrared spectra of sound and decayed acetylated hornbeam, according to Tolvaj (2013). (Band number): numbers assigned to the bands in Figure 27.

Band nr.	Wave-number (cm^{-1})	Absorbance change after acetylation (a.u.)	PHR change to 1030cm^{-1}	Functional group	Assignment
1	1736	− 0.118	− 0.115	Unconjugated acetyl C=O (carbonyl) stretch	Hemicellulose
2	1221	− 0.116	− 0.103	C-O stretch	Xylan and mannosan

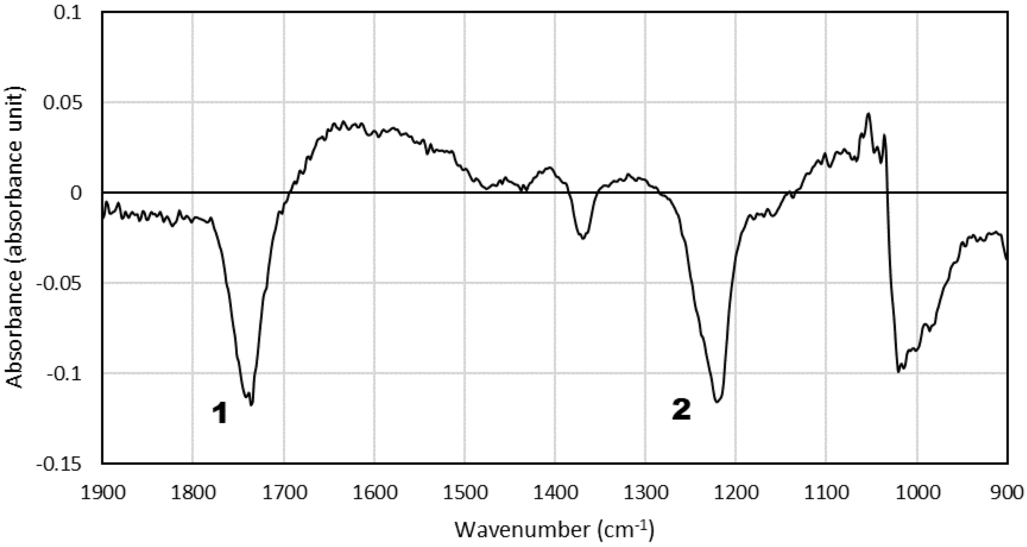

Figure 27. FTIR difference spectrum of sound and decayed acetylated hornbeam wood. Description and assignments of band numbers 1 and 2 are listed in Table 7. The spectra shows lower acetyl content in decayed wood compared to non-decayed.

The intensity at peak (1) was relatively smaller for the decayed part compared to the non-decayed part. This peak was caused by unconjugated C=O (carbonyl) bond stretching in acetyl in hemicelluloses (Takahashi et al., 1989) (Chapter 2). The PHR decreased from 0.306 to 0.191 due to decay.

There was also a lower absorption at peak (2), which was caused by C-O stretching in the acetyl groups in hemicellulose xylan and mannosan (Chapter 2). The amount of acetyl-groups present in the decayed part of the wood was lower than in the rest of the wood, having PHR of 0.258 compared to 0.360 for sound part.

This means that the “affected part” had a much lower acetyl content. It was likely a wet pocket or a place with lower acetylation. This stake had the least number of annual rings on cross section (7 per 2 cm) and the lowest WPG (13.55%) among other acetylated boards from which the stakes were taken.

In a research study concerning acetylated Radiata pine exposed to brown rot fungi (Beck et al., 2018; Thygesen et al., 2021), fungal deterioration was enabled by a de-acetylation mechanism during an initial lag phase. It was concluded that the bonds between chemical groups and biopolymers can be attacked and broken by fungi in optimal conditions for decay. This could also explain partially the lower acetyl content of the acetylated hornbeam stake, although it was of a different wood species. This also means that the acetyl content may not have been as low initially, as it was measured by FTIR.

4.4. Conclusions

To date, long-term field tests have shown that acetylated hornbeam exhibits greater resistance against fungal decay, mold, insects, and moisture than untreated hornbeam, beech, and Scots pine sapwood do. These tests were evaluated every 6 months.

The testing field had a sandy loam type of soil, being pH neutral, rich in nutrients, calcium carbonate, humus, and having water management properties favorable for fungi. The wet period was typical for the whole year, and warm periods were more than half a year long, which also enabled fungal growth.

After 7 years of exposure, there was no sign of decay on almost all acetylated hornbeam stakes, which became dry shortly after being taken from the soil. Acetylated hornbeam stake number 7 had local signs of superficial brown rot decay after 1.5 years, which slowly worsened over the years.

FTIR analysis indicated the affected area of this stake had a much lower acetyl content compared to sound areas of the stake. The local lower acetyl content could have been caused by a wet pocket in the untreated hornbeam.

On the untreated hornbeam stakes, insect damage, soft rot decay, white rot decay, wasp stripping, and cracks were observed during the test. There was one stake that already broke after a half-year of exposure, but all hornbeam stakes eventually broke after 3.5 years. On average, the lifetime of hornbeam stakes was 2 years, which means that acetylation lengthened its lifetime by at least three times (in soil and climate of testing field).

Beech had the same types of decay and damage as hornbeam did. There was one stake that broke after only a half year of exposure, but all beech stakes broke eventually after 2.5 years. On average, the lifetime of beech stakes was 1.8 years.

Stakes made from Scots pine sapwood had insect damage, soft rot decay, white rot decay, brown rot decay, moss, and cracks. Although the signs of decay were severe, there were only two stakes that broke after 3.5 years, and the last stakes lasted in the soil for 6 years. On average, the lifetime of Scots pine stakes was 5.1 years. The soil and the climate were probably more favorable for soft rot and white rot decay, which attack pine less rapidly than hardwoods such as beech and hornbeam.

In future work, acetylated hornbeam stakes having different WPG levels should be tested to evaluate the threshold value of maximum durability.

Chapter 5. Bonding properties

5.1. Introduction

There are many fields of application for acetylated wood and wood-based panels where the bonding quality is of the utmost importance. In order to justify long-lasting bonding performance, it can be tested similarly to the shear strength of solid wood. Here, the aim is to have an adequately high bonding strength depending on the conditions of application and an increased percentage of wood failure (Clauss et al., 2011). Bonding strength is more intense in earlywood than in latewood (Smith and Côté, 1971).

The present study chose polyvinyl acetate (PVAc) and polyurethane (PUR) adhesives to examine the bonding properties of acetylated hornbeam wood. The wood industry uses both adhesives widely because they form flexible bonds that adapt to dimensional changes under different climatic conditions and provide high bonding strength. On the other hand, PUR can be used for structural purposes, while PVAc cannot. PVAc hardens through polymerization (loss of water), leading to a flexible linear chain. It also has a flexible aliphatic backbone. Some formulations have limited cross-linking, enabling interfacial strain due to dimensional changes in the wood that are readily distributed through the adhesive. One-component polyurethanes consist of flexible (soft) polyether or polyester segments joined together by a reaction with diisocyanates, which react with the hydroxyl (OH) groups of the adherent surfaces via CO_2 disposal (Frihart, 2009). These polyurethanes retain their strength even in wet conditions, which is optimal for acetylated wood.

The hygroscopicity and hydrophilicity of wood strongly influence its bonding performance. The better the adhesive wets the wood surface, the more it penetrates the material, and the more links develop between the resin and the wood surface, ensuring a higher bonding strength (Chandler et al., 2005). Adhesive penetration is defined as the movement of fluid glue from the surface into the voids and porous structure of wood tissue, and it can be classified as “gross penetration” (mainly filling cell lumens and large voids) or “cell wall penetration” (into the tiny voids and microstructure of wood cell walls). There are several mechanisms involved in adhesion, such as mechanical interlocking, covalent bonding, and secondary interactions (e.g., hydrogen bonds), which adhesive penetration can influence. Factors related to the fluid properties of the resin, anatomical characteristics, wood permeability, and processing conditions influence the degree of adhesive penetration into wood tissue (Marra, 1992). If the adhesive is manually applied to the wood material, it has deeper penetration on the bottom side where it is first applied, which allows more time for adhesive penetration (Sernek et al., 1999).

Several methods can monitor adhesive penetration (Kamke and Lee, 2007): light microscopy of cross sections, scanning thermal microscopy, scanning electron microscopy (SEM), fluorescence microscopy, porosimetry, neutron radiography, or neutron activation analysis, etc. Penetration behavior can be described by maximum penetration depth, but this is more precise in softwood species (Suchsland, 1958; Hass et al., 2012). Here the adhesive-filled tracheids are visible as a more or less interconnected zone. Hardwood species tend to have vessels filled with adhesive isolated from the bondline. Thus, the penetration can also be described by the saturation of the accessible pore space (Mendoza et al., 2010; Hass et al., 2012), defined as the ratio of the adhesive amount and sample porosity without the adhesive. Hardwoods are more difficult to bind than softwoods because they have fibers with narrow lumens and thicker cell walls that hinder adhesive flow (Siau, 1984).

When the properties of wood are modified, improved durability against decaying organisms and higher dimensional stability can be achieved. On the other hand, new issues can arise, e.g., difficulties with adhesion.

A recent study discovered that furfurylation decreased the effective penetration of PUR and PVAc in Scots pine (Bastani et al., 2016). On the other hand, heat treatment at 195 °C and 210 °C increased the effective penetration of PUR in beech and Scots pine. With PVAc, the effective penetration increased in heat-treated beech and Scots pine at 195 °C but was lower at 210 °C compared to untreated wood.

Due to acetylation, the wood surface becomes more hydrophobic and less polar, which leads to a higher water contact angle compared to untreated wood (Hill, 2007; Bryne, 2008; Bryne and Wålinder, 2010; Wålinder et al., 2013; Moghaddam et al., 2016, 2017). As the acetylated wood surface has a lower water uptake, it absorbs less water-based or moisture-curing adhesives, which can lead to lower penetration and bonding strength. On the other hand, its bonding strength is less affected by dimensional changes or tension caused by moisture. Acetylated wood bonding was reported to be enhanced by a primer (Treu et al., 2020) and sanding (Lütkemeier et al., 2018).

The change in mechanical properties after acetylation is not unequivocal. The lower moisture uptake and higher density can increase the mechanical properties of acetylated wood (Larsson-Brelid and Tillman, 1989; Bongers and Beckers, 2003; Rowell, 2006). On the other hand, permanent cell wall swelling takes place, which reduces the fiber proportion of the cross-section, and thermo-chemical degradation also takes place, which all can reduce the mechanical properties of acetylated wood (Dreher et al., 1964; Tjeerdsma et al., 1998). In related literature, acetylated wood usually had a higher bonding strength and a higher rate of wood failure in dry conditions. In wet conditions, it had lower bonding strength but a higher rate of wood failure compared to untreated wood (Larsson-Brelid et al., 1992; Vick et al., 1993).

Initially, it was generally concluded that the acetyl groups hinder wetting and hydrogen bond formation, which cause bond failure (Rowell et al., 1987; Youngquist et al., 1988). Later, it was found that various factors control the performance of acetylated wood bonds (Vick and Rowell, 1990; Vick et al., 1993).

Various studies followed up on the bonding of acetylated wood with different adhesive types, and they all concluded that PUR (Bongers et al., 2016; Lütkemeier et al., 2018), resorcinol-formaldehyde, phenol resorcinol-formaldehyde, and epoxy (Brandon et al., 2005; Bongers et al., 2016; Frihart et al., 2017; Treu et al., 2020; Frihart et al., 2021) give satisfactory results for acetylated wood bonding. On the other hand, using emulsion polymer isocyanate, melamine-formaldehyde, and polyvinyl acetate had lower bonding strengths after acetylation (Brandon et al., 2005; Frihart et al., 2017, 2021).

Some researchers found no notable difference between adhesive penetration in untreated and acetylated wood (Bongers et al., 2016), while others reported poorer adhesive penetration after acetylation (Treu et al., 2009; Bastani et al., 2015).

The bonding strength of natural hornbeam is 11.06 ± 0.14, 10.15 ± 0.17, and 9.93 ± 0.10 MPa when using polyurethane (PUR), polyvinyl acetate (PVAc-D4), and melamine formaldehyde (MF), respectively (Uzun et al., 2016). A recent study stated that higher-density species like hornbeam tend to have higher tensile strength and higher variability in strength values (Konnerth et al., 2016). Hornbeam showed considerable bonding strength loss of lap-joint samples in wet conditions and achieved low performances during delamination tests. Among tested adhesives, phenol-resorcinol-formaldehyde exhibited the highest bonding strength values (Konnerth et al., 2016).

After acetylation, hornbeam pH decreased from 5.11 to 4.73, and the buffering capacity increased from 1.11 mg/g to 2.15 mg/g (see Chapter 2), which can influence the reaction and curing time of acid-curing adhesives (Bongers et al., 2016).

The present research examined bonding property changes in industrially acetylated hornbeam wood. Investigating the compatibility of adhesives and modified wood is crucial to determining how the change in wood chemistry affects bonding characteristics. Several tests were performed to draw reliable conclusions regarding this complex property. These included testing surface wettability, assessing the shear strength of solid wood samples, determining the bonding strength of samples bonded with different adhesives, and conducting microscopical studies of bonded samples.

5.2. Materials and methods

5.2.1. Material preparation

The specimens were made of untreated hornbeam and industrially acetylated hornbeam (Paragraph 1.8).

5.2.2. Wettability

Untreated and acetylated hornbeam samples were prepared with radial and tangential surfaces. They were conditioned at 20 °C and 65% relative humidity until they reached a constant weight. The weight percentage gain (WPG) of the acetylated hornbeam was 15.42 ± 0.69%. The average densities of the untreated hornbeam and the acetylated hornbeam were 745 ± 6 kg/m^3 and 757 ± 47 kg/m^3, respectively.

The Sessile Drop Technique was used with water (polar) and diiodomethane (DIM) (nonpolar) as test liquids. The surface energies of distilled water (polar and dispersive) and diiodomethane (dispersive) are 72.8 mN/m and 50.8 mN/m, respectively. The polar component of distilled water is 46.4 mN/m (63.74%), and the dispersive component is 26.4 mN/m (36.26%).

Before measuring the contact angle, the surfaces were sanded in the same way as if they were to be bonded with adhesive (EN 205: 2016). A PGX goniometer was used for the test. The volume of the probe liquids was 5 µL, and the contact angles were determined at 0, 0.1, 1, 2, 5, 10, 20, 30, 40, and 50 s. The surface energy was calculated by the Owens–Wendt equation (Owens and Wendt, 1969).

5.2.3. Shear strength

The shear strength was determined according to MSZ 6786-6:1977 in the conditioning sequences (CS) defined by EN 204:2016:

- CS 1: seven days in a standard atmosphere (20 °C and 65% RH);
- CS 3: CS 1, four days in cold water at 20 °C;
- CS 4: CS 3, seven days in a standard atmosphere (20 °C and 65% RH);
- CS 5: CS 1, six hours in boiling water and 2 h in cold water at 20 °C.

The shear strength was tested with an Instron 4208 universal testing machine, and a Memmert WNB 7-45 water bath was used to heat the samples. The testing speed was 1 mm/min. There were at least seven samples of each species for each conditioning sequence.

5.2.4. Bonding strength

Bonding strength was determined according to EN 205:2016, using beech, hornbeam, and acetylated hornbeam standard samples.

The densities of beech, untreated hornbeam, and acetylated hornbeam were 658 ± 41 kg/m^3, 725 ± 45 kg/m^3, and 794 ± 49 kg/m^3, respectively. The adhesives were a PVAc D3 adhesive (‘Ponal Super 3’), a PVAc D4 adhesive (‘Ponal Super 3’ + 5% ‘Ponal D4 Hardener’), and a one-component PUR adhesive (‘Ponal Pur-Leim’), all supplied by Henkel Magyarország Ltd. (Table A34). They were applied on the tangential surface, where 0.5 N/mm^2 pressure was applied for at least 1 h at 20 °C and 65% relative humidity. The bonding strength was tested using a Tinius Olsen H10KT universal testing machine. A Memmert WNB 7-45 water bath was used to heat the lap joint samples. The durability classes were determined according to EN 204:2016. There were 20 samples of each species for each conditioning sequence (CS 1, 3, 4, and 5). The testing speed was 50 mm/min.

5.2.5. Microscopic evaluation

Cubes of 10 × 10 × 10 mm^3 were cut from the sample ends and dried at 103 °C in a drying kiln to achieve a constant weight. Afterward, they were placed in a desiccator. The cubes were cut with a circular saw, which resulted in rough surfaces. Hence, the surfaces were smoothed with a razor blade before examination with a Hitachi S-3400N PC-Based Variable Pressure Scanning Electron Microscope (Hitachi, Tokyo, Japan) and its software (version 1.24, serial number: 340632-01). Cross and longitudinal sections were also examined. Microscopic analysis was performed at a 60 Pa vacuum and a 10 kV accelerating voltage using a BSE detector. The working distance was 10 mm. The surfaces were not coated with a sputter coater before imaging. SEM was used due to its high level of magnification and greater depth.

The microscopic images were examined manually in AutoCAD 2019 software, to measure dimensions and area. The field of view was 1100 × 600 µm (Bastani et al., 2016; Hemmilä et al., 2019). Adhesive penetration was quantified by effective penetration (EP) and maximum penetration (MP) (Sernek et al., 1999). Effective penetration is the total area of adhesive detected in the interphase region of the bondline divided by the width of the bondline. Maximum penetration is the average penetration distance of the five most distant adhesive objects detected within the field of view.

5.2.6. Statistical analysis

Statistical analysis was performed using the Dell Statistica software (version 13, Dell Inc., Round Rock, TX, USA). Factorial analyses of variances (ANOVA) combined with the Fisher’s LSD test was conducted, and the differences were considered significant at $p < 0.05$.

5.3. Results and discussion

5.3.1. Wettability

Table 8 displays the test results, with data measured at 1 second. Acetylated hornbeam had a higher water contact angle and lower surface energy compared to untreated hornbeam, which corresponds to its lower water uptake and higher dimensional stability (Paragraph 1.8). Other researchers also reported a higher water contact angle after acetylation (Hill, 2007; Bryne, 2008; Wålinder et al., 2013; Moghaddam et al., 2016, 2017), e.g., the water contact angles of unmodified and acetylated (WPG 24%) radiata pine were 45° and 98°, respectively (Hill, 2007).

These numbers correspond to our results, where the contact angle of water increased from 43–44° to 61–62° (WPG 15%), which is more than a 40% increase after acetylation. Water penetration time was longer (Figure A89, Figure 28). The polar component of the surface energy is reduced by more than half after acetylation.

Table 8. Contact angle and surface energy of untreated and acetylated hornbeam. Average values are presented with their standard deviations in brackets, measured at 1 s. A significant change after acetylation is marked by an asterisk if $p < 0.05$.

Wood	Contact Angle				Surface Energy					
	Water		Diiodo-Methane		All		Polar Component		Dispersive Component	
	Tan	Rad	Tan	Rad	Tan	Rad	Tan	Rad	Tan	Rad
	°				mJ/m2					
Hornbeam	44.02 (2.58)	43.14 (1.80)	18.26 (1.73)	18.50 (2.75)	63.83 (1.30)	64.23 (1.10)	15.57 (1.37)	16.06 (0.90)	48.26 (0.47)	48.16 (0.74)
Acetylated hornbeam	62.25 * (4.23)	61.12 * (1.76)	20.26 (3.24)	19.70 (5.28)	54.63 * (1.67)	55.32 * (1.45)	6.99 * (1.82)	7.61 * (0.99)	47.64 (0.93)	47.72 (1.54)

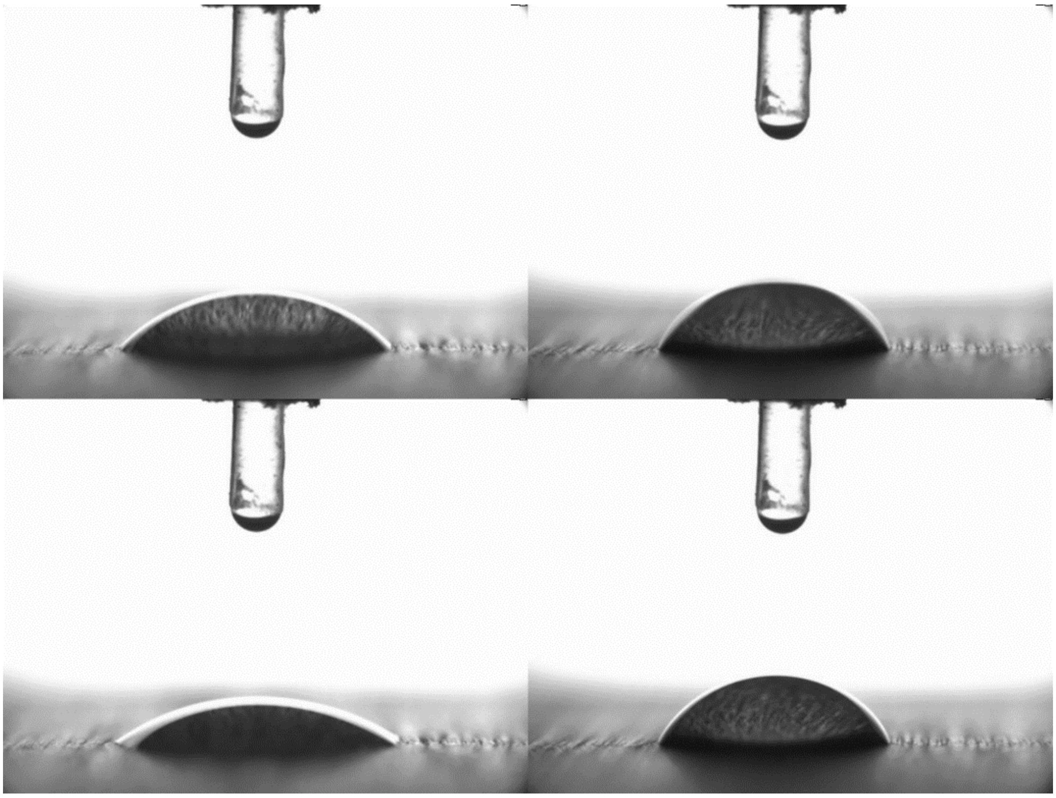

Figure 28. A water drop on untreated (left) and acetylated (right) hornbeam, at 0 second (above) and 50 second (below). The field of view was 7.0 mm wide and 5.2 mm high.

The dispersive component makes up the greater part of the surface energy, which is 75% in hornbeam and 87% in acetylated hornbeam. The large aggregate rays occasionally present in hornbeam do not influence the wetting characteristics, as there was no significant difference between the wettability of the tangential and radial surfaces. The water contact angle significantly changed after acetylation in both anatomical directions. The difference between the water contact angles of the radial and tangential surfaces of acetylated hornbeam was statistically significant. The results for diiodomethane were not significantly different for untreated and acetylated hornbeam (Table 8).

5.3.2. Shear strength

Table 9 contains the shear strength test results, which reveal that CS1 shear strength decreased by 9% after acetylation. This phenomenon can be explained by cell wall degradation caused by the increased temperature and pressure, and the presence of acetic acid during acetylation.

Table 9. Shear strength results of untreated hornbeam and acetylated hornbeam at different moisture states and conditioning sequences (CS) according to EN 204:2016. Average values are presented with their standard deviation in brackets.

Conditioning Sequences (CS)	Moisture Content (%)		Shear Strength (MPa)	
	Hornbeam	Acetylated Hornbeam	Hornbeam	Acetylated Hornbeam
1	12.29 (0.14)	4.68 (0.17)	17.36 (1.26)	15.72 (3.91)
3	52.97 (1.99)	28.39 (1.28)	7.92 (0.50)	16.94 (1.21)
4	16.30 (0.18)	7.45 (0.62)	15.31 (0.87)	17.96 (2.48)
5	79.67 (1.14)	48.32 (2.91)	8.71 (0.23)	15.73 (1.61)

On the other hand, due to its lower moisture uptake, acetylated hornbeam had a higher shear strength compared to untreated hornbeam in moist conditions (CS3, CS4, and CS5). After soaking the samples in cold water for four days (CS3), the shear strength was higher by 114% after acetylation. A similar tendency can be found after another seven days of conditioning (CS4), where the shear strength was higher by 17% after acetylation. After soaking in boiling water for six hours and in cold water for two hours (CS5), the shear strength was greater by 81% after acetylation.

After acetylation, the moisture content and shear strength changed significantly in every CS. It also had a higher deviation than untreated hornbeam. Previous studies encountered similar findings (Paragraph 1.8). Acetylated hornbeam had stiff fractures, while untreated hornbeam had clean breaks (Figure A90), indicating that, due to lower hygroscopicity and chemical alterations in the microstructure (Chapter 2, Chapter 3), hornbeam became more tough and flexible after acetylation.

5.3.3. Bonding strength

Beech species were added to the tests in order to see whether the adhesive met the standard requirements or not. These limit values in the standard are defined for beech only. The bonding strengths of untreated and acetylated hornbeam can be compared to assess the effect of chemical modification on the bonding properties. Table 10 summarizes the results. In cases of beech and hornbeam wood, there were a high number of samples where soaking resulted in sample twisting, influencing the credibility of the test.

The bonding strengths of beech, hornbeam, and acetylated hornbeam bonded with PVAc D3 adhesive met the requirements for D3 durability grading. Beech and hornbeam have a similar, diffuse-porous microstructure, which enables easy bondability. On the other hand, hornbeam had the worst bonding properties, having the greatest bond strength reduction after soaking (CS3, −83%) and after conditioning (CS4, −19%). After acetylation, the bonding strength increased by 65% in wet conditions (CS3), but it had a weaker bonding strength after conditioning (CS1 and CS4). Similar results were found in the literature (Brandon et al., 2005; Frihart et al., 2017, 2021). Untreated and acetylated hornbeam both displayed a high incidence of glue line failure, revealing that the wood was stronger than the bondline.

Beech and hornbeam samples bonded with the PVAc D4 2-C adhesive failed to meet D4 grading according to the standard in wet conditions (CS3 and CS5). In this case, most of the specimens broke in the bondline. These results could be explained, e.g., by the wrong viscosity of the adhesive mix, leading to reduced bonding quality. Hornbeam had the lowest reduction in bonding strength after soaking in cold water (CS3, −62%) but the greatest after soaking in boiling water (CS5, −78%).

Because hornbeam had lower permeability than beech, their bonding strength results could differ (Taghiyari, 2012). Acetylated hornbeam met the D4 standard requirements. Acetylation improved the bonding strength of hornbeam after conditioning (CS1, +39%) and soaking in boiling water (CS5, +153%).

All three species that bonded with the "PUR" adhesive met the standard requirements for D4 grading. Hornbeam had similar (CS1 and CS3) or worse (CS5) bonding strength results compared to beech. It had the largest bonding strength reduction after soaking in cold water (CS3, −66%) and boiling water (CS5, −73%), while acetylated hornbeam had the lowest reduction (CS3, −37% and CS5, −38%, respectively). Acetylation greatly increased the bonding strength of hornbeam when soaked in cold water (CS3, +63%) and boiling water (CS5, +103%).

The PUR adhesive exhibited a higher bonding strength than PVAc in dry conditions, and it also retained its strength better when exposed to water. This corresponds to other studies (Bongers et al., 2016; Uzun et al., 2016; Lütkemeier et al., 2018). Thus, PUR is a suitable choice for exterior products made of acetylated hornbeam.

Table 10. Summary of bonding strength test results for beech (B), hornbeam (H), and acetylated hornbeam (AH) at different conditioning sequences (CS) (EN 204:2016). The average bonding strength of ten lap joint samples are given with their standard deviation in brackets. Wood failure is given as the proportion of samples that presented an apparent cohesive wood failure during the test; conformity is given as the proportion of samples that met the standard limit (compared to the maximum number of samples, 20 pieces). A significant change after acetylation is marked by an asterisk if $p < 0.05$.

Conditioning Sequences (CS)	1			3			4			5		
EN 204:2016	≥10 MPa			≥2 MPa (D3) ≥4 MPa (D4)			≥8 MPa			≥4 MPa		
"PVAc D3"	B	H	AH	B	H	AH	B	H	AH	B	H	AH
Bonding strength (MPa)	12.4 (1.1)	12.1 (1.6)	10.4 (1.6)	2.2 (0.4)	2.0 (0.4)	3.3 * (0.3)	11.3 (1.3)	9.8 (1.5)	9.0 (1.8)	-	-	-
Wood failure (%)	70	35	15	0	0	0	95	60	0	-	-	-
Conformity (%)	70	60	35	35	20	65	90	45	40	-	-	-
"PVAc D4 2-C"	B	H	AH	B	H	AH	B	H	AH	B	H	AH
Bonding strength (MPa)	11.1 (1.1)	7.6 (3.6)	10.6 * (1.4)	3.2 (0.5)	2.9 (0.4)	2.9 (0.2)	-	-	-	3.5 (0.5)	1.7 (0.8)	4.3 * (0.3)
Wood failure (%)	50	10	25	0	0	0	-	-	-	0	0	0
Conformity (%)	50	10	30	0	0	0	-	-	-	15	0	50
"PUR"	B	H	AH	B	H	AH	B	H	AH	B	H	AH
Bonding strength (MPa)	11.6 (0.9)	12.9 (1.2)	11.4 (1.7)	4.6 (0.6)	4.4 (0.3)	7.2 * (0.4)	-	-	-	4.1 (0.3)	3.5 (0.7)	7.1 * (0.5)
Wood failure (%)	65	35	70	0	0	0	-	-	-	0	0	25
Conformity (%)	60	90	40	55	45	80	-	-	-	30	10	70

In an Accoya® study, PUR-bonded Accoya® had a low delamination percentage and met the standard requirements. The bonding strength in wet conditions decreased by 13–27% and 65% for acetylated and untreated radiata pine, respectively. The wood failure of acetylated radiata pine failed to meet the standard requirements in dry conditions. Acetylated radiata pine laminates bonded with PVAc showed poor performance in the delamination tests compared to those bonded with PUR (Bongers et al., 2016).

A high percentage of wood failure indicates greater adhesive penetration and interfacial bonding between the wood and the adhesive (Neese et al., 2004), which was true for the conditioned samples.

After acetylation, hornbeam dimensional stability (anti-swelling efficiency) increased to 81-88% (Paragraph 1.8), which has a direct influence on reducing stresses on bondlines in delamination tests associated with water immersion and drying cycles. Furthermore, compared to untreated wood, the mechanical properties decreased less in wet conditions, indicating a higher bonding strength in wet conditions as well (Hofferber et al., 2006; Marcroft et al., 2014).

The shear strength of solid wood was significantly higher than the bonding strength of the same species (at the same conditioning sequences), but with a similar trend of change.

Statistically significant differences can be found in the results where acetylation increased the bonding strength of hornbeam wood (Table 10). When comparing the results of different adhesives, PUR exhibited a significantly higher bonding strength than PVAc.

5.3.4. Microscopic evaluation

Penetration is mainly influenced by adhesive characteristics and wood microstructure. Hornbeam is a diffuse-porous species in which the adhesive flows through longitudinal vessels and proceeds along paths of lowest resistance toward the wood tissue (Weigenand et al., 2007). Typical bondline imperfections are bondline starvation for PUR due to the high adhesive mobility and void formation inside the bulk adhesive in PVAc due to excessive shrinkage (Hass et al., 2012). Table 11 lists the results of effective penetration and maximum penetration for untreated and acetylated hornbeam.

Table 11. Effective penetration and maximum penetration results of untreated and acetylated hornbeam bonded with PVAc and PUR adhesives. Average values are presented with the standard deviation in brackets.

Adhesive	Material	No. of sections	Effective Penetration (μm)	Maximum Penetration (μm)
PVAc D3	Untreated	7	106 (8)	114 (40)
	Acetylated	8	67 (14)	178 (19)
PVAc D4	Untreated	5	71 (4)	87 (33)
	Acetylated	7	48 (7)	135 (42)
PUR	Untreated	7	58 (4)	136 (23)
	Acetylated	7	88 (18)	83 (17)

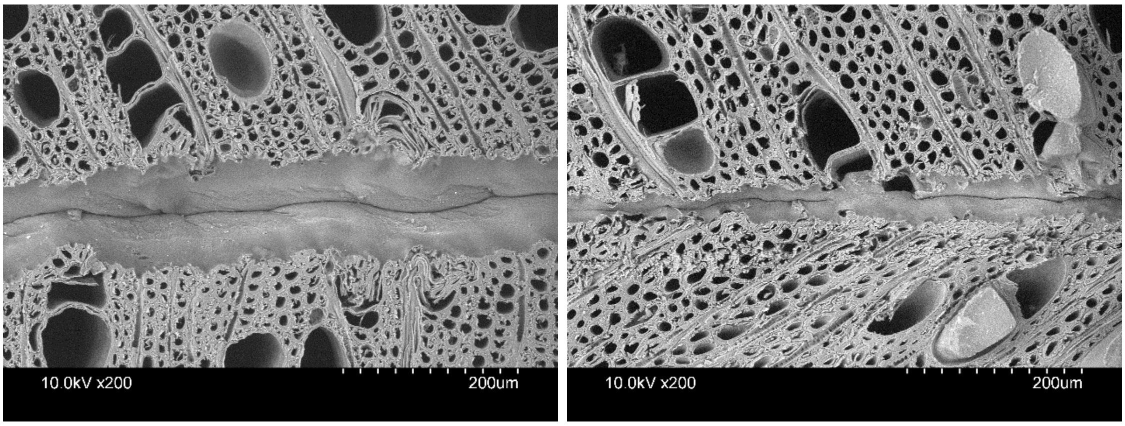

Figure 29. Micrographs of D3 PVAc-bonded untreated (left) and acetylated (right) hornbeam wood. A thinner bondline, greater penetration, and more small voids can be observed in acetylated hornbeam than in untreated hornbeam.

Acetylated hornbeam bonded with PVAc D3 adhesive had a lower effective penetration and a thinner bondline than untreated hornbeam (Figure 29). PVAc is a water-based, water-dispersed adhesive that may reach an adhesion optimum when the water has penetrated the wood substrate (Boehme and Hora, 1996).

PVAc has good flow into cell lumens, but its high molecular weight prevents it from penetrating cell walls; thus, only gross penetration can be observed (Frihart et al., 2004). According to a related study, chemical modification (furfurylation) can decrease PVAc bondline thickness and penetration depth (Bastani et al., 2016). On the micrographs of PVAc D3-bonded wood, the lumens and large vessels were rich in adhesive. These correspond to the fact that the bonding strength of acetylated hornbeam was similar to untreated hornbeam and that it had a low percentage of wood failure, indicating poorer bonding.

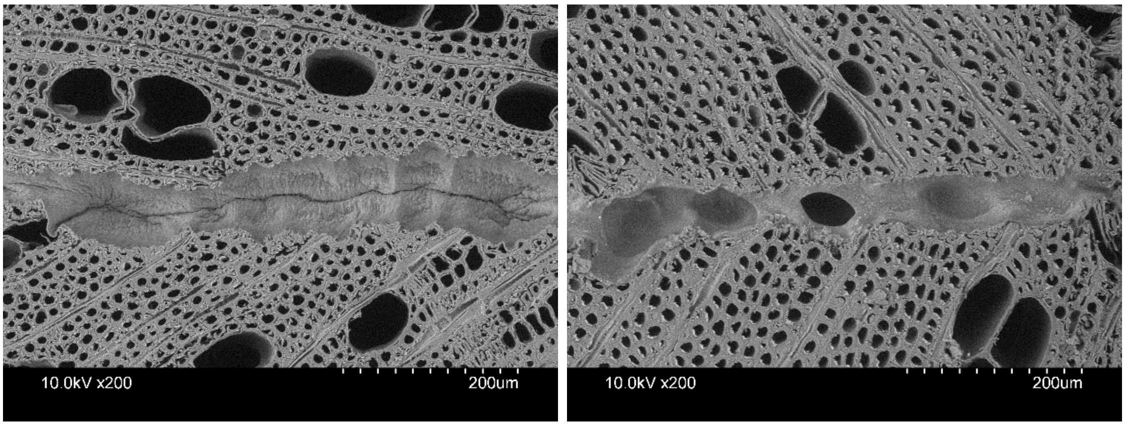

Figure 30. Micrographs of D4 2-C PVAc-bonded untreated (left) and acetylated (right) hornbeam wood. Thin bondlines and low penetration can be observed on both untreated and acetylated hornbeam.

PVAc D4 had a lower effective penetration and a thinner bondline after acetylation, but the adhesive penetrated deeper into the wood than the untreated hornbeam (Figure 30), which may explain its enhanced bonding strength and high incidence of wood failure. The results of PVAc D3 are higher in both effective penetration and maximum penetration compared to PVAc D4.

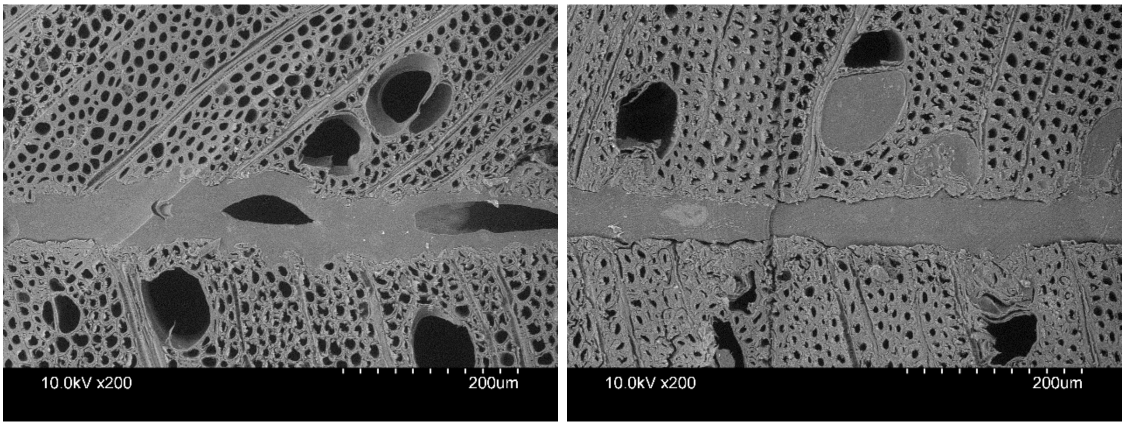

Figure 31. Micrographs of PUR-bonded untreated (left) and acetylated (right) hornbeam wood. Hornbeam shows signs of overpenetration with starved bondlines and voids. This was not observed in acetylated hornbeam.

PUR exhibited the highest bonding strength and greatest effective penetration in acetylated hornbeam, which is attributable to its lower molecular weight compared to PVAc. It can also be explained by the fact that there are fewer available functional hydroxyl groups in acetylated hornbeam, which enabled fewer chemical reactions with the isocyanate ingredient of PUR. There were signs of overpenetration in untreated hornbeam, with starved bondlines and voids in bondlines (Figure 31) (Hass et al., 2012).

Acetylated hornbeam had greater effective penetration, lower penetration depth, and no signs of starved bondline, which corresponded to the literature (Chandler et al., 2005; Bastani et al., 2016). In a similar study, the effective penetration was 76.06 µm in beech and 96.87–99.09 µm in heat-treated beech (Bastani et al., 2016).

PVAc D3 achieved the greatest effective penetration in hornbeam, while PUR achieved the same for acetylated hornbeam. After acetylation, the effective penetration was higher for PUR than PVAc, while the maximum penetration was lower, matching the conclusions of a similar study on modified beech (Bastani et al., 2016). After acetylation, effective penetration changed by −37% in PVAc D3, −32% in PVAc D4, and +52% in PUR adhesives. Maximum penetration changed by +56%, +55%, and -39% in PVAc D3, PVAc D4, and PUR adhesives, respectively. The change in effective penetration and maximum penetration after acetylation and the difference between the effective penetrations of different adhesives were all statistically significant.

5.4. Conclusions

The present study aimed to determine how acetylation affected the bonding properties of European hornbeam wood. The research was supplemented with the investigation of wetting properties, wood shear strength, and microscopical studies of bonded wood, as these all have strong relationships with wood bonding.

Acetylated hornbeam showed a higher water contact angle (+40%) and lower surface energy (−14%, with a −55% reduction of the polar component) than untreated hornbeam. This finding corresponds to the related literature and connects to the lower equilibrium moisture content, water uptake, and better dimensional stability of acetylated hornbeam. Bonding strength limit values given by EN 204:2016 were achieved by PVAc D3 and PUR (D4) adhesives, while PVAc D4 2-c did not meet the requirements for D4 durability grading. Despite its similar diffuse-porous structure, hornbeam had similar (PUR), or lower (PVAc) bonding strengths compared to beech. Acetylation improved the properties of hornbeam wood to have similar (PVAc D3) or higher (PVAc D4; PUR) bonding strengths compared to untreated hornbeam. Microscopical studies proved that PUR-bonded samples obtained better results than PVAc-bonded samples. In the micrographs of lap joint samples bonded with PVAc, thin bondlines and lower effective penetration but greater maximum penetration were observed after acetylation. Using PUR, the lower bonding strength of untreated hornbeam was attributed to bondline starvation and voids in the bondline. Although the adhesion of the acetylated wood surface is lower due to its lower polarity and porosity, the bonding strength of hornbeam was not significantly reduced by acetylation. In most cases, the acetylated samples broke in the bondline, resulting in a lower proportion of wood failure. After acetylation, the wood becomes more dimensionally stable when exposed to moisture, which enables better mechanical properties in wet conditions. Corresponding to the literature, acetylated hornbeam had significantly higher shear strength and bonding strength when soaked in water or boiling water compared to untreated hornbeam. The shear strength of solid wood was significantly higher than the bonding strength of the same species (at the same conditioning sequences), but with a similar trend of change. Acetylated hornbeam has a somewhat weaker shear strength (−9%) and similar bonding strength (between −14% and +39%) in a dry state compared to hornbeam, but it can even double the shear of hornbeam (+17–114%) and bonding strength (+63–153%) in a soaked state.

According to these results, acetylated hornbeam can be bonded well with PVAc and PUR adhesives and can be used both in wet and humid applications. On the other hand, it requires greater caution than beech, and it is advisable to use a longer pressing time for better bonding performance.

Chapter 6. Photostability

6.1. Introduction

Color inhomogeneity is an important wood characteristic. Usually, the color hue varies between dark brown and bright yellow, but it can also be enhanced for a more intensive color appearance (Teischinger et al., 2012). The overall appearance also depends on the grain figure, the contrast between earlywood and latewood, annual growth ring width, pith rays, and ray flecks. Despite being rather inhomogeneous among species and within wood itself, the contrast and deviation between wooden elements provide little stimuli and no fatigue. Hence, human perception tends to consider wood as “warm”, “natural”, “beautiful”, “soft”, and “elegant” (Masuda, 2001).

Hornbeam has grayish-white sapwood and heartwood, which turn yellowish or occasionally dark brown when exposed to air due to oxidation. It has wavy annual rings and grain, pith flecks, and 3-4 cell-wide aggregate rays mixed with libriform fibers, which are well discernible with the unaided eye as darker flecks on the radial section, and as small stripes on the tangential section (Molnár and Bariska, 2002).

One of the most frequently used method for color determination is the CIELAB color system, 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 color change of wooden products can be determined by calculating the change in color components (ΔL, Δa, Δb) and then the total color difference (ΔE^*). Chroma gives the saturation or vividness of the color, the lower it is, the duller the color gets. Hue angle is an attribute of a visual perception according to which an area appears to be similar to the colors: red, green (a*), yellow, and blue (b*). It ranges between 0°and 360°. In case of wood, a* and b* are both positive, meaning the hue angle lies between 0°and 90° (CIE, 2018). The color range of various domestic European hardwood species comprises about 0.6% of the whole CIELAB color space (Teischinger et al., 2012).

Much research has been performed to determine categories of color differences to grade wood. If ΔE^* reaches or exceeds 2, the color difference is perceivable (Terziev and Boutelje, 1998; Jirouš-Rajković and Ljuljka, 1999; Straže and Gorišek, 2008; Buchelt and Wagenführ, 2012). It is common and accepted in case of wood to have color difference of 1 to 2, it can be even desired. It should be noted that the difference between wooden surfaces cannot be noticed just because of the color change but also of the inhomogeneity of wood itself (vessels, tyloses, ray flecks, wood grain/texture, early and latewood transition, increment zones).

The color of objects is determined by the conjugated double bonds in their chemical structure. These bonds are present in lignin and extractives. The color of wood is mainly defined by the quantity and quality of extractives. The changes in the chemical structure can be examined by FTIR spectroscopy. On uncoated wood surfaces, the UV degradation is due to the degradation of lignin in the cell wall. Lignin absorbs more UV energy than holocelluloses and this energy is absorbed by double bonds, phenolic and carbonyl groups, quinones, quinone methides and biphenyls. The energy absorbance is affected by the density and the chemical composition of wood.

During UV exposure, the photo-oxidation mechanism in lignin leads to demethylation and the formation of quinones (Rowell and Bongers, 2015). As the lignin is degraded by UV light and the breakdown products are washed away by rainwater, the surface cracks and the gray cellulose fibers become visible.

In the past decades, many researchers reported in the topic of photodegradation using mercury-vapor lamp (Ohkoshi, 2002; Colom et al., 2003; Tolvaj et al., 2011; Tolvaj, 2013). The degradation of lignin is presented by the reduction in absorption of guaiacyl lignin (1510 cm^{-1}) and syringyl lignin (1600 cm^{-1}). This phenomenon is always accompanied by the formation of quinones and the increase of carbonyl groups absorption (Mohebby, 2008; Popescu et al., 2011).

Rating the discoloration caused by mold and blue stain are done according to scales defined in standards e.g. EN 16492:2014, ISO 4628:2016, EN 15457:2014, BS 3900-G6:1989, EN 152:2011. In EN 927-3:2012, the discoloration is rated from 0 (unchanged, not visible) to 5 (very marked, larger than 5mm), but this and similar non-standardized scales give ordinal data, not continuous, and the quality and accuracy is subjective (dependent on the evaluator). Multisensory techniques and digital image processing have been studied in order to find more objective and precise results (Jones and Brischke, 2017).

This research has been carried out in Sopron, Hungary. Hungary's climate is very erratic because it is situated in between three climatic zones: oceanic climate with less varying temperature and more evenly dispersed precipitation; continental climate with more extreme temperature and relatively moderate precipitation; and a Mediterranean effect with dry weather in summer, and wet weather in winter. These factors make Hungary's weather variable despite its lower altitudes and relatively small extent. Hungary has a continental climate, with hot summers with low overall humidity levels but frequent showers and frigid to cold snowy winters. Sopron is in the moderately cool–moderately dry climatic region (Péczely, 1998). These characteristics suggest that wood is likely to gray, mold, and crack in a short amount of time without proper treatment.

Various physical, chemical, and biological processes occur when wood is exposed to the weather. A variety of factors cause these processes, including moisture (precipitation, moisture in soil), UV radiation (sunlight), frequent temperature and relative humidity changes, thermal impact, wind, sand, and degradation by fungi and insects (Sell and Feist, 1986; Rowell, 2005) (Table A35). Degradation caused by weathering usually affects depths of 0.5–2.5 mm (Feist and Hon, 1984).

Surface erosion strongly depends on water and not light, as it is a highly effective solvent: it leaches out photodegradation and hydrolysis products, and also extractives and coating compounds. Temperature is also an important parameter in the photodegradation process, as the higher it is (air temperature, surface temperature increase caused by light exposure) the higher the degradation will be (Cogulet et al., 2018).

During exposure, L* can have some initial increment, but after some time its value decreases. In addition, a* and b* can have some initial increment during yellowing, but both eventually decrease as the surface starts to gray (Tolvaj and Papp, 1999; Tolvaj and Mitsui, 2005).

Besides the gray cellulose fibers, the gray color of photodegraded wood can also be associated with fungi. Some fungi grow on weathered wood, for example to metabolize photodegradation products. These fungi are in the division *Ascomycota*, and are usually one or more of the following four species: *Aureobasidium pullulans*, *Hormonema dematioides*, *Epicoccum nigrum*, and *Phoma* spp. Other species belonging to the *Clasosporium* and *Scerophoma* can also be found. They are called "black stain fungi" and they give a gray coloration on delignified wood surfaces, and black or brown coloration on lignified wood (Cogulet et al., 2018).

Besides weathering, laboratories can reproduce photodegradation using irradiating lamps (xenon, mercury vapor, fluorescence) to accelerate the degradation rate using shorter wavelengths. The advantages of this form of photodegradation include measurement reproducibility, constant settings, and shorter testing times. Testing time is shortened by wavelengths that are shorter than the UV spectrum hitting the earth's surface (290-400 nm) (Tolvaj and Mitsui, 2005; Kržišnik et al., 2018). Only photodegradation occurs unlike in case of weather exposure, thus the color coordinates mostly increase. Xenon light can simulate the effect of sunlight during weathering, but only at long exposure times, as the yellowing will be about three-times faster and greater in the short term. On the other hand, it was found that mercury-vapor lamp could not simulate sunlight (Tolvaj and Mitsui, 2005). There can be some high correlations with statistical significance between the in-service test (façade and decking cladding elements exposed to weather) and the laboratory test (exposed to blue stain fungi and xenon lamp irradiation), but it would be impossible to precisely predict the level of color change using only laboratory test (Kržišnik et al., 2018).

Photodegradation starts with the absorption of photon, when the molecule is in an excited state. The chemical groups targeted are chromophoric and phenolic groups which lead to the formation of free radicals. During degradation, chromophoric groups excitate from lignin and quinones and free radicals are generated in the end. Wood does not contain free radicals, they are the indication of degradation. The lower the wavelength, the higher the free radical formation will be. Free radicals can migrate through the wood which causes deeper degradation. Photodegradation is mainly a surface phenomenon, the depth of photodegradation depends on wood species (density), depth of exposure, and light source. As the lignin degrades, the surface becomes more hydrophilic. Depolymerization, the degradation of holocellulose occurs later, but the damages are deeper and weight loss is observable. Greater degradation can be found on softwood than hardwood (Cogulet et al., 2018).

If the rate of deterioration is plotted as a function of time, different patterns can be defined (Figure A91) (Shohet et al., 1999):

- a concave pattern associated with abiotic agents (weathering), whose deterioration develops rapidly at an early stage (first few months), but tends to slow down over time;
- a convex pattern associated with the physical, chemical or biological phenomena, which act slowly initially but whose action is felt cumulatively;
- an "S"-shaped pattern associated with a degradation phenomenon whose intensity changes over time;
- a linear pattern associated with degradation agents that act permanently.

Bio-based materials are sustainable and have a wide range of appearances, unique properties, and natural beauty, which is favorable for users, thus it is important to guarantee the due aesthetical performance. However, specific local and cultural circumstances also need to be considered (Sandak and Sandak, 2017).

It is reported that acetylation increases the weather (light and moisture) resistance of wood (Leary, 1968; Feist et al., 1991; Dawson et al., 1992; Plackett et al., 1992; Ota et al., 1996, 1997; Ohkoshi, 2002; Bhat et al., 2010), noting that the photostability increases at higher WPG levels (Dawson et al., 1992). However, acetylated wood only shows initial stability against UV radiation; later, it begins to fade and gray (Kalnins, 1984; Dunningham et al., 1992; Hon, 1995; Torr et al., 1996; Ota et al., 1996, 1997; Ohkoshi, 2002; Mitsui and Tolvaj, 2004, 2005). This is also true for Accoya® Radiata pine (Lahtela and Kärki, 2015).

This makes acetylated wood vulnerable to color change, graying even at high WPG levels (Plackett et al., 1992). It protects hemicelluloses (xylans) to a greater extent than lignin during UV radiation (Feist et al., 1991).

The color change caused by photodegradation is influenced by the structural change of extractives too. The degradation of lignin is hindered due to acetylation and the increased moisture resistance, and dimensional stability restrains the photodegradation mechanism of wood (Guo and Guan, 2010). On the other hand, acetylating the phenolic -OH groups, which retard the formation of quinones, reduces this protective mechanism (Pu and Ragauskas, 2005; Rowell, 2005). Although the changes caused by photochemical degradation take place differently in acetylated wood, acetylation does not prevent the color change of wood – this can be caused by photodegradation as well as mold, blue stain fungi or corrosion of metal fasteners just like in case of natural wood. Blue stain – which is usually black colored - can be observed on grayed acetylated wood surfaces.

Wood-decaying fungi can colonize acetylated wood, as hyphae can be present in its microstructure, but weight loss does not occur or only to a low extent. This means that acetylated wood is not toxic to the fungus, but the nutrients are not sufficient for fungal growth at higher WPG levels (Plackett et al., 1992).

In this part, the photostability of natural and acetylated hornbeam was tested using weather exposure and UV irradiation using mercury-vapor lamp. As an initial test of coating performance, boiled-linseed oil was used for its natural origin, smooth, uniform finish, quick drying time, and easy accessibility.

6.2. Materials and methods

6.2.1. Preparation

Utreated and industrially acetylated hornbeam (average WPG 16.46%) were prepared for the tests with an average density of 837 kg/m^3 and 784 kg/m^3, respectively. Acetylation was carried out the same way as seen in Paragraph 1.8.

Half of the samples were coated with boiled linseed oil (from Kőházy - Tradíció Ltd., Budapest, Hungary). The oil coating was applied two times as it was recommended by the manufacturer. Its density is 0.89-0.93 g/cm^3, it dries in 6-10 hours and reaches full hardness after 2-3 days. Boiled linseed oil is a mixture of linseed oil, stand oil and metallic dryer to accelerate drying. These solvents cause linseed oil to dry more quickly, acting as if it were “boiled”. Regular linseed oil can take weeks or sometimes months to cure depending on the weather conditions. Boiled linseed oil was found to significantly reduce the degradation and staining of wood when exposed to brown rot and blue stain (Treu et al., 2004). It deepens the color of wood, it protects it from UV and moisture. It is easy to handle, but its flammability needs to be considered during usage. It penetrates deeply into the wood, which is why it is mainly used as a sealant before applying other coating. It was chosen for this preliminary work to test the color change and coating properties of acetylated hornbeam.

6.2.2. Weather exposure

The samples were exposed to weathering without soil contact on a metal stand tilted at 45 degrees in the Outdoor Exposure Testing Field (47°40'41.4"N 16°34'32.6"E) in July 2016 (Figure 32). The samples were of 20 × 45 × 200 mm^3 (t × w × l) with planed, smooth, tangential surface (Csizmadia, 2015). There were untreated, acetylated, coated, and coated and acetylated hornbeam samples, 10 pieces of each. Each sample had five measuring points, which equals 50 for each type per test. The color measurement and visual inspection of the samples were done every month, in its current state, without conditioning. Small spacers provided air gap between the samples. The test was carried out for 1.5 years.

Figure 32. Uncoated and coated hornbeam and acetylated hornbeam samples exposed to weather on metal stand in Outdoor Exposure Testing Field. The photos were taken before (left, July 2016) and after weathering test (right, January 2018).

The weather parameters of the testing field were obtained and Scheffer Climate Index was calculated the same way as described in Paragraph 4.2.3.

The color was expressed in CIE L*a*b* color space with X-Rite SP60 Portable Colorimeter and Color iControl program. The colorimeter's sensor head was 8 mm. The color was measured and calculated based on the D65 illuminant and 10° standard observer. The color coordinates were calculated according to ISO 11664:2019. Photos and scans were taken of the samples in their current state to compare visual appearance.

6.2.3. Irradiation with mercury-vapor lamp, FTIR analysis

The UV irradiation test was performed in an artificial ageing chamber (Figure 33). There were two mercury-vapor lamps used (800 Watt, 76 W/m^2). The lamps were 64 cm above the samples and the equipment temperature was set to a maximum of 50 °C.

Figure 33. Uncoated and coated hornbeam and acetylated hornbeam samples placed in the ageing machine with mercury-vapor lamps.

Mercury-vapor lamp results in a stronger color change in a shorter time than xenon lamp or natural sunlight. This is because the mercury-vapor 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 (380-315 nm) region, 24% is UV-B (315-280 nm) region and 25% is UV-C (> 280 nm) region.

The samples were of 20 × 45 × 140 mm^3 (t × w × l) with planed, smooth, tangential surface. There were untreated, acetylated, coated, and coated and acetylated hornbeam samples, 5 pieces of each. Each sample had five measuring points, which equals 25 for each type per test.

Samples of 5 × 10 × 30 mm^3 (t × w × l) were analyzed with diffuse reflectance infrared Fourier-transform spectroscopy (DRIFT) using JASCO FT/IR-6300 spectrophotometer and Spectra Manager program. First, the background spectrum was obtained against an aluminum plate in order to see the contribution of the instrument and environment to the spectrum. These effects were removed from the samples' spectrum by ratioing the sample single beam spectrum to the background spectrum. Secondly, the spectrometer did 45 scans of each sample. After measurement, the spectra were smoothed with 15 convolution width. A two-point base line correction was made by setting the lowest point between 3800 cm^{-1} and 1900 cm^{-1} to a zero absorbance. The intensity of the infrared peaks was converted to Kubelka-Munk (K-M) units for quantitative analysis. The chemical changes in wood were evaluated observing the difference spectra, which are the spectra of irradiated samples subtracted from the spectra of nonirradiated samples. Here, the absorption increase was represented by positive band while absorption decrease was represented by negative band. The band assignments were made using the difference spectra. The color and FTIR measurements were determined after 0-5-10-20-30-60-120-200 hours of irradiation. Photos and scans were taken of the samples in their current state to compare visual appearance.

6.2.1. Statistical analysis

Statistical analysis was performed using the Dell Statistica software (version 13, Dell Inc., Round Rock, TX, USA). Factorial analyses of variances (ANOVA) combined with the Fisher's LSD test was conducted, and the differences were considered significant at $p < 0.05$.

6.3. Results and discussion

6.3.1. Coating

Table 12 and Figure 34 show the results of color change after coating with boiled-linseed oil. Both untreated and acetylated hornbeam exhibited the same trend: the L* decreased, a* and b* decreased, chroma increased, while the hue angle did not change remarkably. The color of hornbeam and acetylated hornbeam wood changed to a deeper, darker, warmer tone after coating. The color change was more prominent after the first layer than from the first layer to second layer. The change of L*, a*, b* and C* was significant after coating. For acetylated hornbeam, the hue angle did not change significantly after coating.

Table 12. Color parameters of untreated and acetylated hornbeam wood, uncoated, and after one and two layers of boiled-linseed oil. Color parameters include lightness (L), redness (a*), yellowness (b*), C* (chroma), and h* (hue angle).*

Coating	Untreated					Acetylated				
	L*	a*	b*	C*	h*	L*	a*	b*	C*	h*
Before	80.63	3.28	20.52	20.78	80.94	46.77	8.52	24.21	25.66	70.61
One layer	73.25	5.99	33.97	34.51	80.04	36.29	11.42	31.37	33.39	69.97
Two layers	72.06	6.12	33.23	33.80	79.58	33.16	12.31	34.21	36.36	70.19

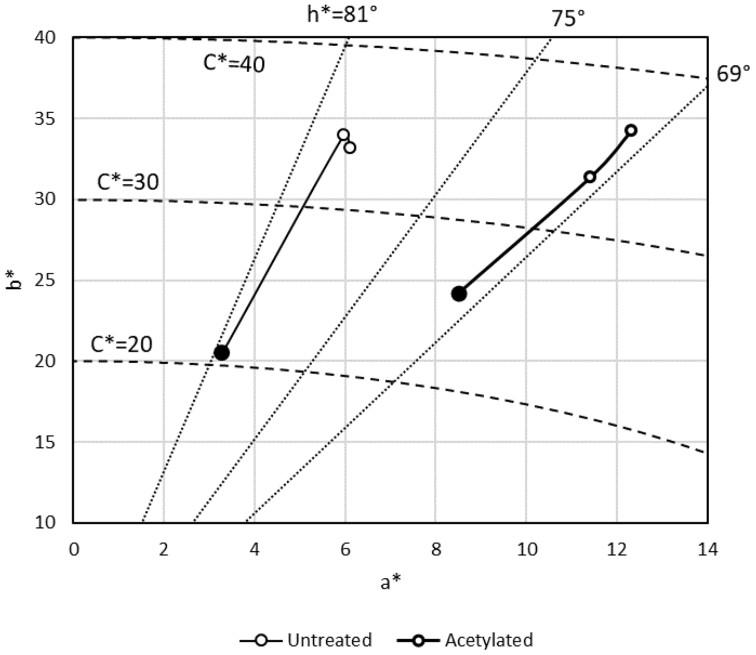

Figure 34. Chromaticity diagram of untreated and acetylated hornbeam during coating. The filled mark is the initial color data point, which is followed by the color of the first layer then the second layer of boiled-linseed oil coating. Redness (a), yellowness (b*) and chroma (C*) increased after coating, while the hue angle (h*) did not change remarkably.*

6.3.2. Irradiation with mercury-vapor lamp

The highest L* change was experienced in the first 5 hours of irradiation, especially for acetylated hornbeam samples. L* of untreated samples decreased, having the highest reduction of 8.06 for uncoated, and 7.48 for coated samples at 200 hours of irradiation. Acetylated samples lightened, having the greatest increment of 15.03 for uncoated and 27.46 for coated samples at 200 hours of irradiation (Figure 35).

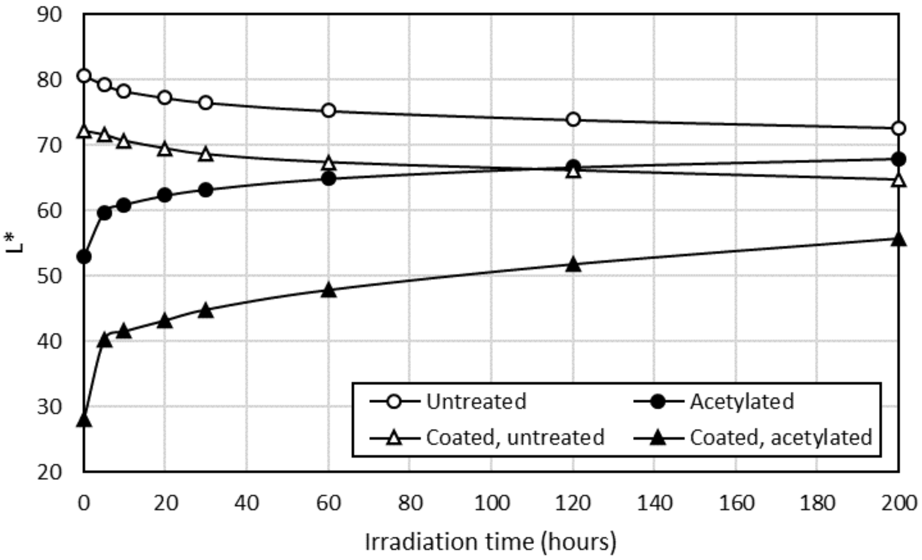

Figure 35. Change of lightness (L) of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 200-hour-long mercury-vapor lamp irradiation.*

Due to photodegradation, the color of untreated hornbeam shifted to a darker yellow, while acetylated hornbeam lightened. The a* change was experienced in the first 5 hours, especially for acetylated hornbeam samples. Coated acetylated samples had the greatest redness reduction of 7.26, while uncoated samples had only 3.22. The redness of untreated hornbeam was not remarkably different between uncoated and coated samples. The increment of a* was 4.84 for uncoated and 4.77 for coated hornbeam (Figure 36).

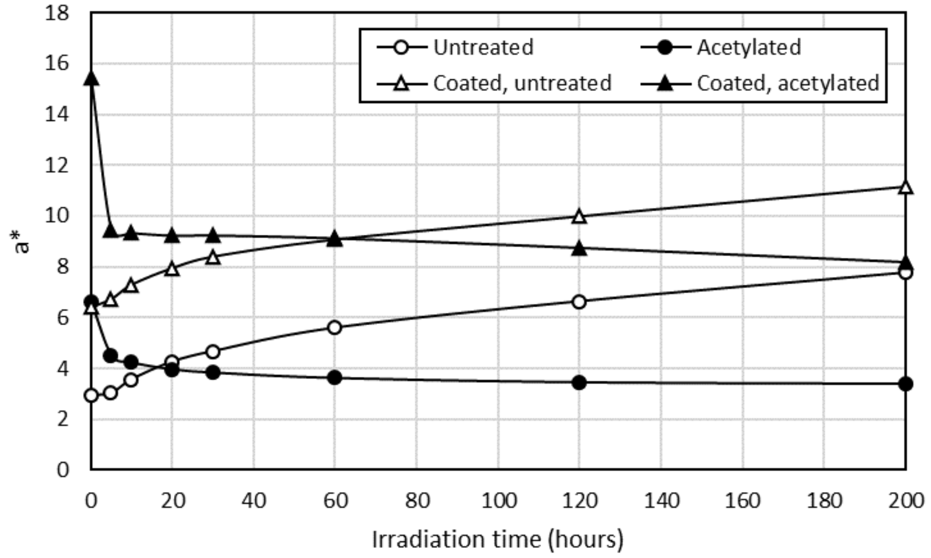

Figure 36. Change of redness (a) of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 200-hour-long mercury-vapor lamp irradiation.*

Except for untreated hornbeam, b* had an initial reduction in the first 5 hours. After 10 hours, b* values gradually increased. The lowest b* change was 2.35, for acetylated hornbeam. The greatest b* increment was 14.18 for untreated hornbeam, while b* increased only by 3.30 for coated hornbeam. The greatest b* change was exhibited by coated acetylated hornbeam, where b* decreased by 14.50 after 200 hours of irradiation (Figure 37).

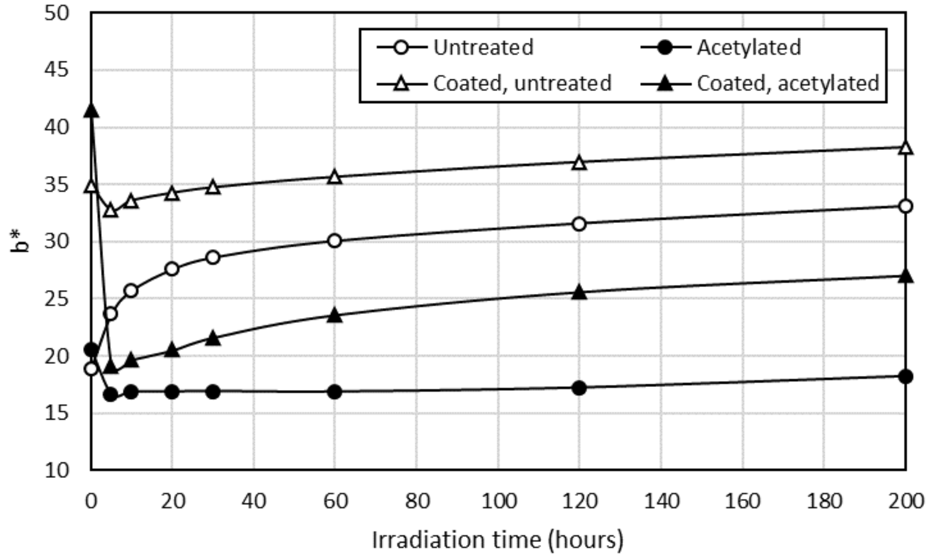

Figure 37. Change of yellowness (b) of untreated and acetylated hornbeam, uncoated or coated with boiled-linseed oil, during 200-hour-long mercury-vapor lamp irradiation.*

Figure 38 shows the color data points of tested wood samples on the a* - b* plane during mercury-vapor lamp irradiation. The filled marks belong to the first, non-irradiated color, followed by the dots of irradiated samples after 5, 10, 30, etc. hours. The diagram shows dotted lines of some relevant hue angles and dashed lines of relevant chroma ranges.

Except for untreated hornbeam, the chroma or saturation of the samples had an initial decrease in the first 5 hours. Then C* increased gradually. During irradiation, the color became more vivid for untreated hornbeam, it increased to 34.00 for uncoated and to 39.84 to coated hornbeam. Their color changed from very pale or pale to light. Acetylated hornbeam also exhibited C* increase, but it remained below the initial C*. The final C* values were 18.55 for uncoated and 28.26 for coated acetylated hornbeam. Their color changed from dark to pale for uncoated, and from deep to dark for coated acetylated hornbeam. After 200 hours of irradiation, the C* of hornbeam was higher by 83% and 41% than acetylated hornbeam, for uncoated and coated samples, respectively. Coating with boiled-linseed oil increased C* of all samples.

The highest hue angles (80-82°) were of uncoated and coated hornbeam wood, which decreased gradually to 74-77° during irradiation as the surface darkened. On the other hand, acetylated hornbeam exhibited hue angle increase from 70-72° to 73-79° due to lightening. The occupied hue interval was 6° for untreated, 6° for coated untreated hornbeam, 7° for acetylated, and 9° for coated, acetylated hornbeam.

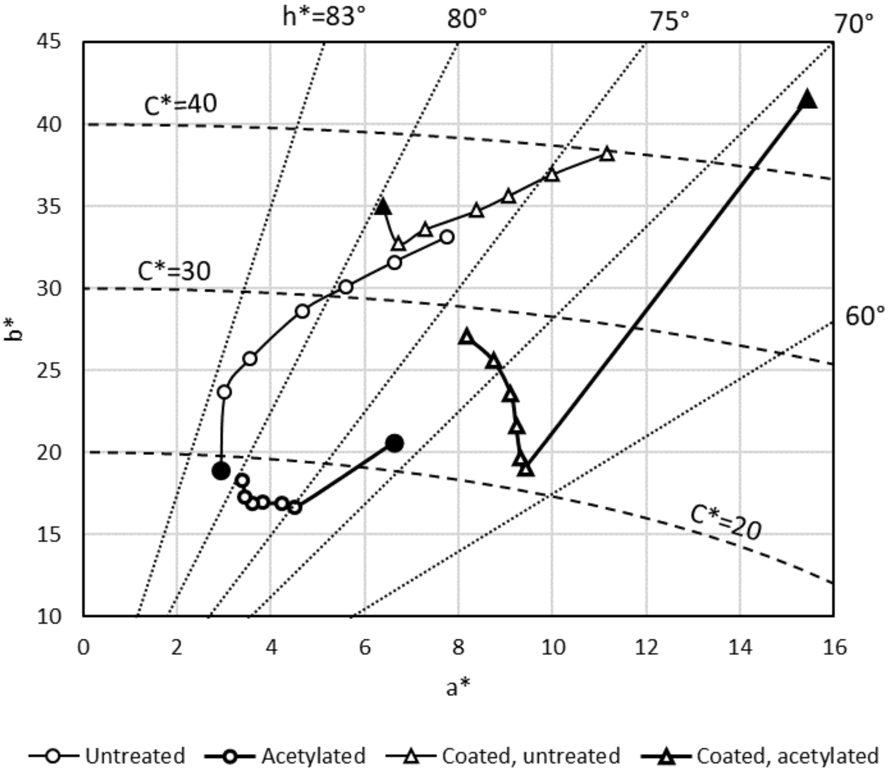

Figure 38. Chromaticity diagram of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 200-hour-long mercury-vapor lamp irradiation. The first, non-irradiated points are full, followed by the colors measured at 5, 10, 30, etc. hours. Redness (a), yellowness (b*), and chroma (C*) changed differently as untreated hornbeam darkened and acetylated hornbeam lightened. The change in hue angle (h*) can be traced by the dotted lines.*

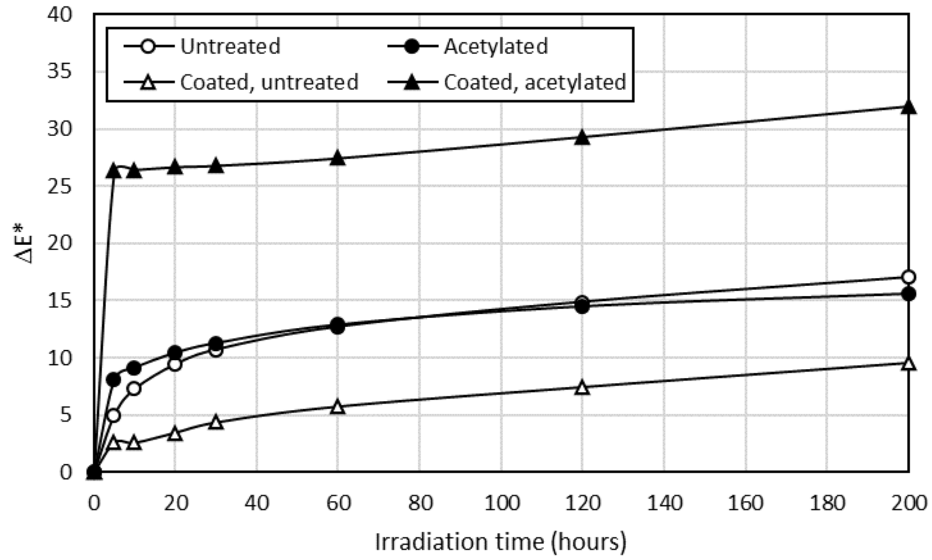

*Figure 39. Change of color difference (ΔE *) of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 200-hour-long mercury-vapor lamp irradiation.*

Table 13. Color coordinates of hornbeam and acetylated hornbeam, uncoated or coated with boiled-linseed oil, after 200 hours of mercury-vapor lamp irradiation. Color parameters include lightness (L), redness (a*), yellowness (b*), C* (chroma), h* (hue angle), and color difference compared to initial color (ΔE*).*

	L*	a*	b*	C*	h*	ΔE*
Untreated	72.64	7.77	33.10	34.0	76.8	17.03
Coated, untreated	64.69	3.40	18.23	18.5	79.4	15.58
Acetylated	67.99	11.17	38.24	39.8	73.7	9.57
Coated, acetylated	55.65	8.18	27.05	28.3	73.2	31.98

The greatest color difference was achieved in the first 5 hours of irradiation, where coated acetylated hornbeam had the lowest photostability (Figure 39). After that, the rate of change was remarkably smaller. In every case, the color difference after 200 h of irradiation was perceivable (ΔE*>2) (Buchelt and Wagenführ, 2012). Among the color coordinates, L* influenced the color difference values the most. The color difference of untreated hornbeam was 17.03 after 200 hours of irradiation, which was improved by coating to 15.58, and by acetylation to 9.57 (Table 13). On the other hand, coating did not enhance the photostability of acetylated hornbeam (31.98). Coated samples had higher deviation in ΔE* (1.12-1.37) compared to uncoated samples (0.79-0.99).

The photodegradation during irradiation had a concave deterioration pattern (Sandak and Sandak, 2017). By comparing the diagrams of L*, a*, b* and E*, it can be concluded the lines of uncoated and coated samples become parallel after 5-10 hours of irradiation, which can indicate a boundary point between the photodegradation of the coating and the wood material. Due to varying acetyl levels across the samples, the oil may have impregnated acetylated hornbeam inhomogenously, which could have resulted in nonuniform color and color change. According to the statistical analysis, there was significant difference between the color of the samples before and after irradiation in every case. Due to acetylation, and also coating, the color of irradiated samples were significantly different (Table 13).

The value of color variation (the color difference calculated compared to the average color) indicated how variable the initial color is. In case of uncoated samples, the color differences were not perceivable, below 2 (Buchelt and Wagenführ, 2012). Acetylated samples had somewhat higher color variation (1.80-3.29) compared to natural hornbeam (1.17-2.40). In every case, the color variation was lower after irradiation than before, 0.83-1.46 for hornbeam and 1.51-2.33 for acetylated hornbeam. Scanned photos of weathered samples are showed in Figure 40. The yellowing and darkening of hornbeam and lightening of acetylated hornbeam is visible to the naked eye.

Figure 40. Scanned photos of hornbeam samples before and after being exposed to 200-hour-long mercury-vapor lamp irradiation. From left to right: untreated hornbeam, acetylated hornbeam, coated hornbeam, and coated and acetylated hornbeam.

6.3.3. FTIR analysis

The FTIR spectra was measured before irradiation and after each phase (5-10-20-30-60-120-200 hours). The changes were determined according to difference spectra, which were calculated by subtracting the initial (non-irradiated) spectra from the irradiated spectra (Figure 41, Figure 42). In each spectrum, the peaks and absorption bands were determined (Table 14) and marked with numbers on each diagram and in the text.

Table 14. Wavenumber characterization of the infrared spectra of untreated and acetylated hornbeam, uncoated or coated with boiled linseed-oil, during 200-hour-long irradiation with mercury-vapor lamp. The wavenumbers were assigned according to the work of Tolvaj (2013).

Band number	Wavenumber (cm^{-1})	Functional group	Assignment
1	3677-3152	Hydroxyl group (OH) stretching	Cellulose, hemicellulose, lignin
2	2983-2844	CH stretching	Methine (CH), methylene (CH_2), methyl (CH_3) groups
3	1804-1773 1745-1698	Unconjugated C=O (carbonyl group) stretching	Xylan
4	1675-1658	Conjugated C=O (carbonyl group) stretching	Xylan
5	1604-1596	Aromatic skeletal vibration	Syringyl lignin
6	1514-1495	Aromatic skeletal vibration	Guaiacyl lignin
7	1476-1411	Asymmetric C-H deformation	Lignin, carbohydrates
8	1397-1383	Symmetric C-H deformation	Cellulose and hemicellulose
9	1372-1309	C-H deformation	Cellulose
		C-OH vibration	Syringyl derivatives
10	1279-1266	Ring vibration	Guaiacyl lignin
11	1219-1215	C-O stretch	Xylan
12	1176-1159	Asymmetric C-O-C stretching	Cellulose and hemicellulose
13	1146-1117	Symmetric C-O-C stretching	Cellulose and hemicellulose
		Aromatic C-H skeletal vibration	Lignin
14	1102-1067	C-O vibration	Cellulose and hemicellulose

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 difference spectrum of acetylated hornbeam than untreated hornbeam.

The absorption of methine (CH), methylene (CH_2) and methane (CH_3) groups (2) decreased in uncoated samples and increased in coated samples after UV-B and UV-C irradiation. 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).

The spectra show reduction in symmetrical C-H deformation (8), asymmetric C-O-C stretching (12), and symmetric C-O-C stretching (13), but increase in C-H deformation (9) and C-O stretching (14). Cellulose is more resistant to photodegradation thus the reduction of these absorption bands were associated with the change in hemicellulose. 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 1800-1760 cm^{-1} and 1740-1700 cm^{-1} (3). In case of acetylated hornbeam, the absorption at 1743 cm^{-1} is higher than at 1793 cm^{-1}. The absorption of hornbeam is smaller at 1698 cm^{-1} than at 1773 cm^{-1}. In every case, the absorption of conjugated carbonyl groups decreased (4). These peaks are less prominent in case of samples coated with boiled linseed oil. 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.

As a result of mercury-vapor lamp irradiation, the aromatic rings of lignin ruptured which was 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 samples coated with boiled linseed oil was lower.

The lightening of acetylated hornbeam during weather exposure and mercury-vapor lamp irradiation was associated with the extractive content, which was transformed during photodegradation. This effect was somewhat eased by coating with boiled linseed oil.

The degradation of boiled-linseed oil can be monitored by the changes at following wavenumbers (Lazzari and Chiantore, 1999; Mallégol et al., 1999):

- reduction of methylene vibrations at 2928, 2856, 727 cm^{-1};
- increment and broadening between 3425-2500 cm^{-1} for OH bands, OH bonded to carboxylic groups, leading to the formation of hydroperoxides;
- broadening of carbonyl absorption between 1772 - 1633 cm^{-1}, forming conjugated and nonconjugated carbonyl groups;
- loss of structural resolution, disappearing peaks between 1400-800 cm^{-1},
- increase of fluoride acid band absorption at 1843 cm^{-1}, showing carboxylic acids accumulate in photooxidation;
- and increment at 1775 cm^{-1}, indicating the formation of γ-lactones and peresters.

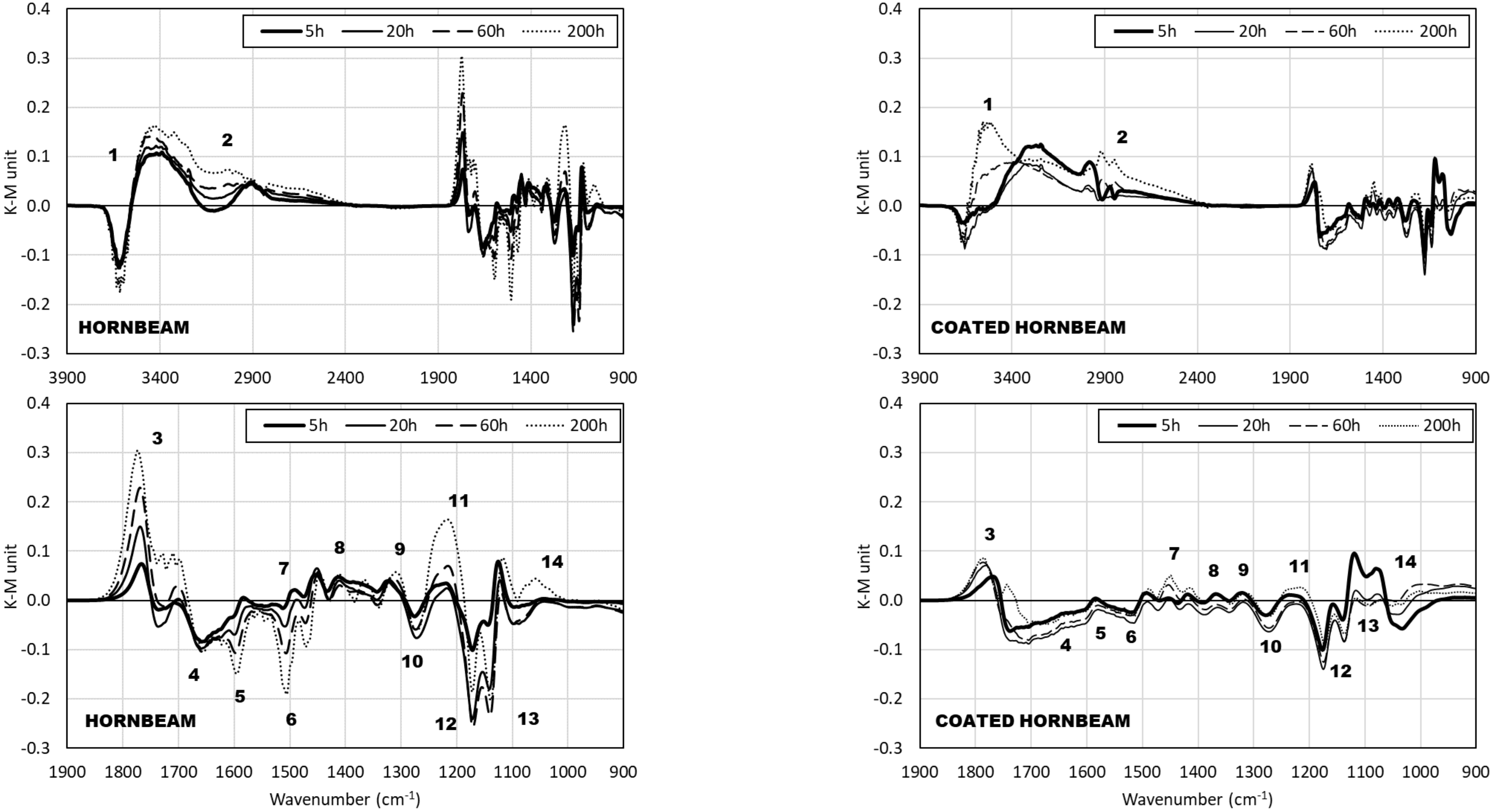

Figure 41. FTIR difference spectra of hornbeam samples with or without boiled-linseed oil coating after 5, 20, 60 and 200 hours of mercury-vapor lamp irradiation.

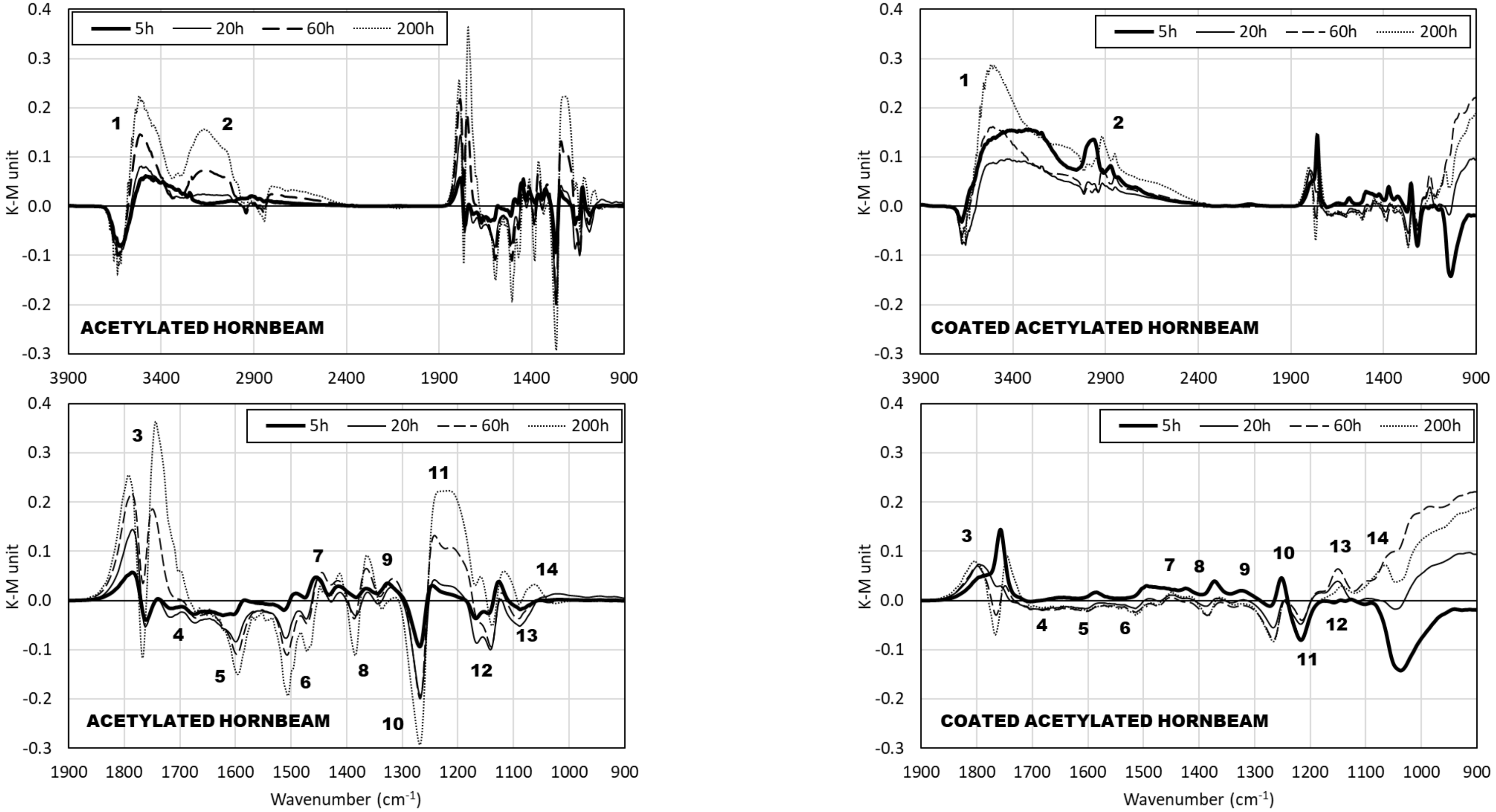

Figure 42. FTIR difference spectra of acetylated hornbeam samples with or without boiled-linseed oil coating after 5, 20, 60 and 200 hours of mercury-vapor lamp irradiation.

In related literature, it has been clarified that linseed oil has drying and degradation mechanism during irradiation. At first, there is an early stage of oxidation of triglycerides where unsaturated fatty acid components autoxidize while conjugated unsaturations form and extensive cross-linking takes place. In the following stage, the labile cross-links are slowly degrading giving rise to a highly stable network with unreacted triglycerides and low molecular weight molecules. In the third stage, progressive oxidation of alkylic segments take place with formation of larger amounts of oxygenated groups (Lazzari and Chiantore, 1999)

6.3.4. Weather exposure

Table A36 lists the weather parameters of this site. Compared to hot and dry territories, the Hungarian field probably accelerates decay. This area has a warm and wet summer season (May-September), with mean temperatures between 15–23 °C, that range up to 37 °C, and the monthly average precipitation is between 31–99 mm. It has a drier winter season (October–April) with 12–75 mm of average precipitation per month, and mean temperatures between -4–12 °C with a maximum of 25 °C. The average annual rainfall during the test period was approximately 541 mm, average annual temperature was 11 °C, and the maximum temperature was 37 °C. The relative humidity ranged from 58 to 84%. The direct normal solar annual radiation index at this site is approximately 3.37 kWh/m^2/day, representing a moderate UV exposure, with a high likelihood that surface microbial activity (mildew) will occur throughout the experiment.

Fungi require oxygen, moderate temperature (25–35 °C), 35-50% of air relative humidity, nutrients, a certain pH, vitamins, and minerals, however water is the main growth factor (Cogulet et al., 2018). This suggests that the summer months were favorable for fungi growth.

According to the ombrothermic diagram (Figure A92), there was a short dry season in May (the area below the temperature line and above the precipitation line). Other than that, the wet season–which is the area below the precipitation line and above the temperature line–was typical for the whole year. In the dry seasons, cracking, insect activity, and UV radiation have a greater degrading effect, while in the wet seasons, fungal activity and leaching are more drastic.

The Scheffer Climate Index of this site was 45.1 (Scheffer, 1971), which indicates intermediately favorable conditions for decay. This index is similar to other reports regarding the SCI of different countries, including Hungary (Brischke et al., 2011; Frühwald Hansson et al., 2012; Niklewski et al., 2021; Niekerk et al., 2022).

The decay rate can be indicated by similar reports that were carried out in this testing field. Untreated species usually start to gray after 2–3 months (Stefanich, 2009; Bak, 2012; Győri, 2012; Csizmadia, 2015; Zöld, 2015; Németh et al., 2016; Nógrádi, 2018; Takács, 2019; Demjén, 2021).

In the study regarding heat-treating hornbeam, L* of heat-treated hornbeam increased, and a* and b* decreased after six months. The samples cracked, grayed, and the untreated ones even molded after two months. Wasp stripping became apparent on untreated samples after five months. Heat-treated hornbeam was more dimensionally stable and durable, but the color difference after weather exposure was greater than that of untreated hornbeam (Csizmadia, 2015).

The highest ΔL* was experienced in the first months of weather exposure (spring and summer of 2018). Then L* decreased at different rates. After about 4 months, the biggest L* change was achieved in every sample. The greatest L* increment was in coated acetylated hornbeam samples. Hornbeam samples experienced the biggest L* reduction, especially (Figure 43). The brightening of acetylated hornbeam and darkening of natural hornbeam was the result of the photooxidation of lignin, hemicelluloses and extractives, which corresponds to the literature (Dawson et al., 2008; Davis et al., 2021).

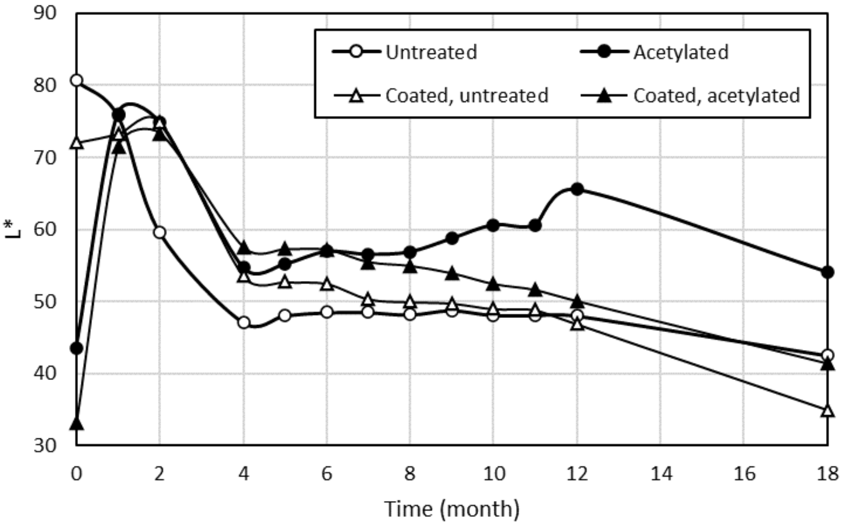

Figure 43. Change of lightness (L) of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 18-month-long weather exposure (July 2016 – January 2018).*

In the first weeks, there was an initial increment of a* in hornbeam samples; their color shifted to a darker yellow. On the other hand, a* decreased in acetylated samples as the surface brightened. After about 4 months, the biggest a* change was achieved in every sample. All of the samples turned gray and a* decreased below 2 (Figure 44).

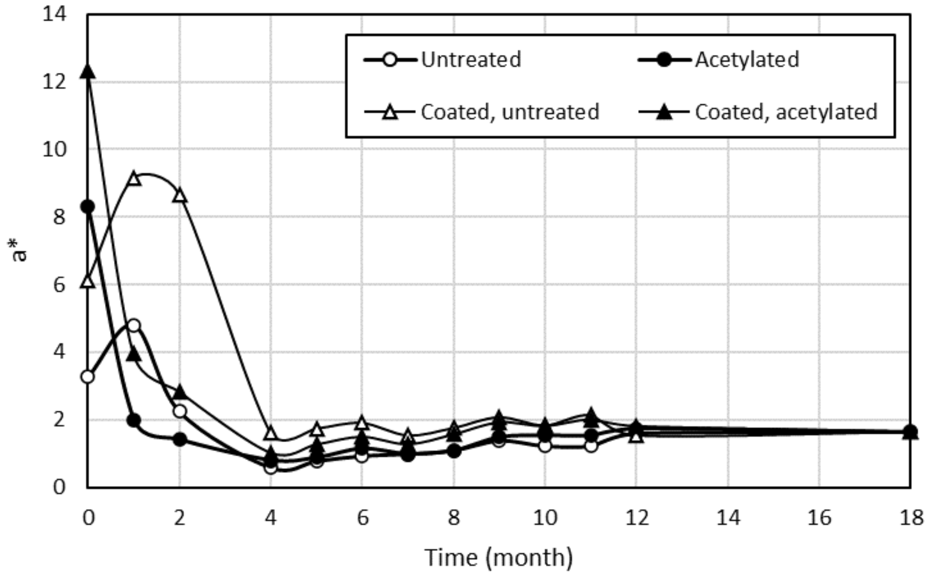

Figure 44. Change of redness (a) of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 18-month-long weather exposure (July 2016 – January 2018).*

Similarly to a*, b* had some initial increment for natural hornbeam samples, but not for acetylated samples. After about 4 months, the biggest b* change was achieved in every sample. All of the samples turned gray and b* decreased below 10 (Figure 45).

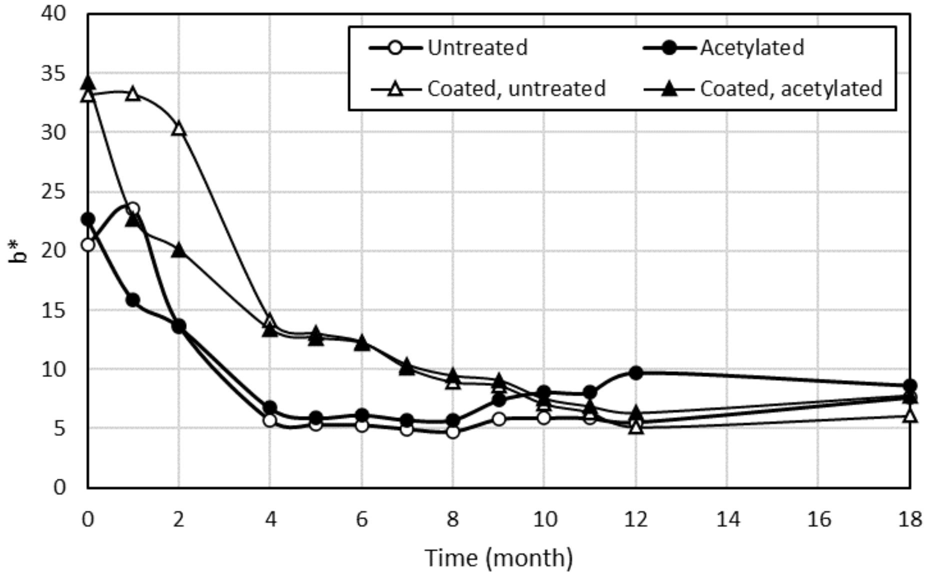

Figure 45. Change of yellowness (b) of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 18-month-long weather exposure (July 2016 – January 2018).*

Figure 46 shows the color data points of tested wood samples on the a* - b* plane during weathering. The filled marks in the upper part of the diagram belong to the first, non-weathered color, followed by the dots of weathered samples after one, two, four months, etc. The diagram shows dotted lines of some relevant hue angles and dashed lines of relevant chroma ranges. Chroma or saturation had some initial increment in untreated samples, but eventually it decreased. The chroma of coated samples was about twice as high than that of uncoated samples until 8th month. After this time, there was no remarkable difference between the chroma of tested samples, and it remained between 5 and 10. As the chroma changed, light untreated wood and deep acetylated wood changed to pale, very pale then finally to grayish color.

The hue angle of tested samples varied during weathering, having higher values for acetylated than untreated samples. The occupied hue interval was 10° for untreated, 12° for coated untreated hornbeam, 14° for acetylated, and 16° for coated, acetylated hornbeam. The hue angle gradually increased as the surface proceeded to gray. The highest values were obtained in the 4th month (83-86°), then it decreased below 80° in the following months.

Acetylated samples had a high rate of ΔE* in the first two months (Figure 47). At about 4 months, the surface started to gray, and the color difference did not change remarkably in the following months. After 18 months, the color difference of untreated samples was higher than that of acetylated samples. Also, the color difference of uncoated samples was lower than that of coated samples. S-Shaped and convex deterioration patterns can also be found in the diagrams (Sandak and Sandak, 2017). On the other hand, as all tested samples became gray, the difference in ΔE* was greatly influenced by the initial color of the samples. Eventually, the color difference between the initial color of untreated hornbeam and the color after 18 months of weathering was 40.25 for untreated hornbeam, 47.88 for coated and untreated hornbeam, 29.10 for acetylated hornbeam, and 41.28 for coated and acetylated hornbeam.

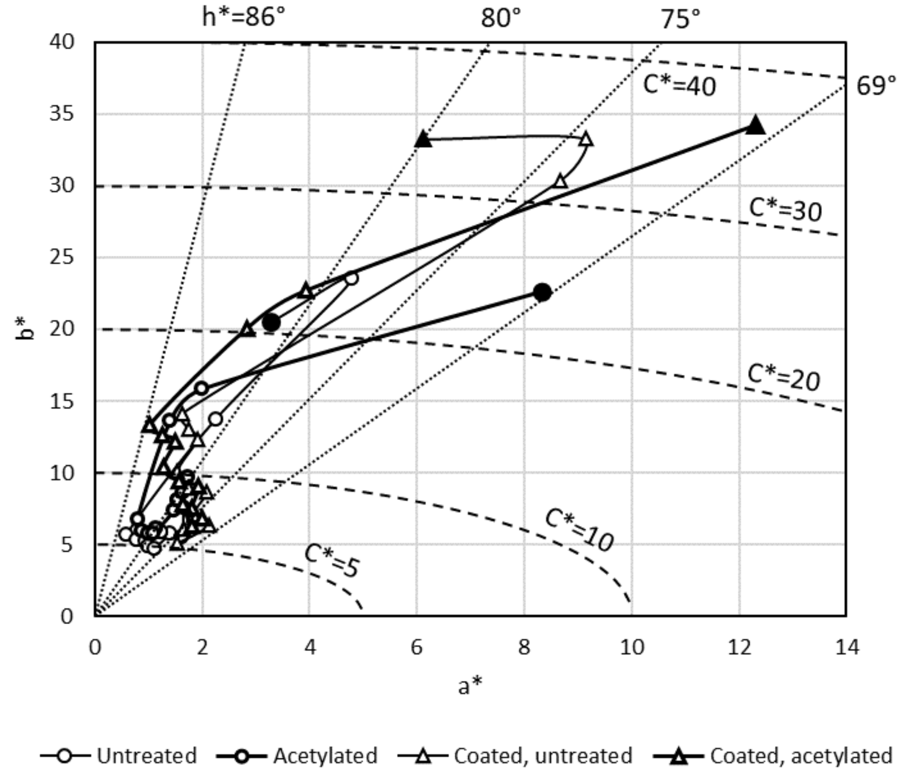

Figure 46. Chromaticity diagram of untreated and acetylated hornbeam, uncoated or coated with boiled-linseed oil, during 18-month-long weather exposure (July 2016 – January 2018). The first, non-weathered points are full, followed by the colors measured in the 1st, 2nd, 4th, etc. month. Redness (a), yellowness (b*), and chroma (C*) gradually decreased, resulting in a grayed surface. The change in hue angle (h*) can be traced by the dotted lines.*

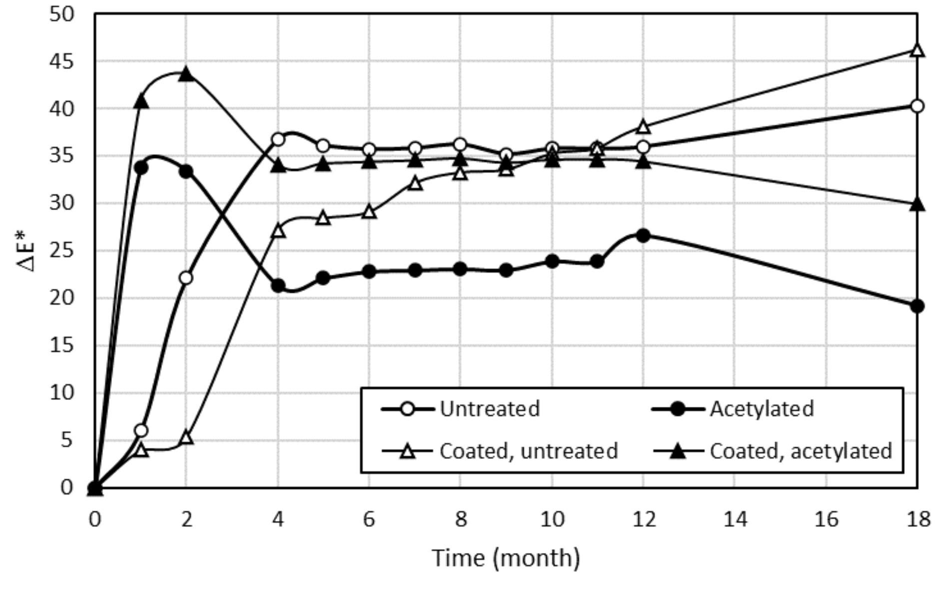

*Figure 47. Change of color difference (ΔE *) of untreated and acetylated hornbeam wood, uncoated or coated with boiled-linseed oil, during 18-month-long weather exposure (July 2016 – January 2018).*

According to the statistical analysis regarding the color after 18 months of weathering, there were no significant differences between a* values of either of the samples (Table 15).

On the other hand, L* values were significantly different between acetylated and untreated samples, and uncoated and coated samples as well. Comparing b* values, acetylation and also coating had significant effect on the photostability of hornbeam wood, but there was no significant difference between uncoated and coated acetylated samples.

Table 15. Summary of color measurement results of untreated, acetylated, and boiled-linseed-oil-coated hornbeam wood before and after 18-month-long weather exposure (July 2016 – January 2018): lightness (L), redness (a*), yellowness (b*) and color difference (ΔE *).*

Wood		Before weathering			18 months of weathering			
		L*	a*	b*	L*	a*	b*	ΔE*
Untreated hornbeam	Uncoated	80.63	3.28	20.52	42.55	1.64	7.61	40.29
	Coated	72.06	6.12	33.23	35.01	1.64	6.08	46.25
Acetylated hornbeam	Uncoated	43.58	8.31	22.66	54.10	1.63	8.66	19.21
	Coated	33.16	12.31	34.21	41.40	1.64	7.79	29.95

Wood already has a perceivable color variation (color difference compared to the average color) before the weather exposure, ranging from 1.15 to 3.14 (Buchelt and Wagenführ, 2012). This color difference can increase during photodegradation (wood degrades in spots, along cracks, wasp stripping occurs, coating fails, mold appears) but also decrease (even photodegradation resulting in complete graying). After 18 months, the color variation ranged between 2.29 and 4.27. Scanned photos of weathered samples are showed in Figure 48.

Figure 48. Series of photos of hornbeam samples exposed to weather. It shows the scans of the untreated (left), acetylated (right), uncoated (up), and coated (bottom) samples before weather exposure, and after 1, 2, 4, 7 and 10 months of weathering (since July 2016).

In the third month (October) heavy rain occurred which affected the color change of the samples. Here the measured data has big variation because of the moist surface, so it was excluded from the results. According to various studies (Hon and Minemura, 2001; Teischinger et al., 2012; Németh et al., 2013; Tolvaj, 2013) the increase of moisture content and the wetting of the surface makes the wood more vivid, as it reduces L* and increases a* and b*. The rain leaches out the water-soluble extractives, which define the color of wood, and also the photodegradation products. The hornbeam samples started cracking, molding and fading in the first month of exposure (Figure 48). The surfaces gradually grayed and molded in the following months. In the last months, long and deep cracks appeared on the end grain and sides as well. The shape and dimensions of the samples changed. Small wasp strippings are visible in some cases.

In case of the weather exposure, the color is influenced by many other factors besides UV radiation. The exposure to real conditions is more useful for the industry than laboratory tests, which lack these factors. On the other hand, the weathering tests are non-repeatable and uncontrollable, which makes it difficult to compare results. The sunlight (UV radiation) causes the greatest change in the color and the surface. The mercury-vapor lamp can help study the photodegradation mechanism in wood but it cannot simulate natural sunlight (Tolvaj and Persze, 2011; Tolvaj and Varga, 2012). During irradiation, the leaching of extractives does not take place, which grays the surface. The color of irradiated wood after 200 hours is obtained in less than 1 month of weather exposure (in this testing field, in July 2016) (Table 16). Compared to irradiation, the color changes similarly only in the first months of weathering as a* and b* increases. After that, a* and b* is reduced due to leaching and graying caused by weather conditions.

Table 16. Lightness (L), redness (a*) and yellowness (b*) of untreated and acetylated hornbeam uncoated or coated with boiled linseed-oil, after 200-hour-long irradiation and 1-month-long weather exposure (July - August 2016)*

Wood		Irradiation (200 hours)			Weathering (1 month)			
		L*	a*	b*	L*	a*	b*	ΔE*
Untreated hornbeam	Uncoated	72.64	7.77	33.10	75.79	4.79	23.51	10.52
	Coated	64.69	11.17	38.24	73.26	9.14	33.25	10.12
Acetylated hornbeam	Uncoated	67.99	3.40	18.23	76.07	2.01	15.86	8.53
	Coated	55.65	8.18	27.05	71.38	3.94	22.72	16.86

6.4. Conclusions

The purpose of this research was to analyze the weathering behavior of acetylated hornbeam and to see how does acetylation and coating with boiled-linseed oil change the photostability of natural hornbeam wood. During UV irradiation hornbeam yellowed, darkened, the redness (a*) and yellowness (b*) increased. During weather exposure, where the fluctuation of temperature and moisture is frequent, hornbeam wood cracked, discolored, and grayed in the end. The graying of wood is due to the leaching of lignin breakdown products leaving the gray cellulose chains on the surface. Acetylated hornbeam did not crack during the exposure to frequently changing weather, but it had worse color stability than native hornbeam. The dark, grayish brown color of acetylated hornbeam lightened during UV irradiation because of the transformation of extractives and degradation of lignin. Unlike hornbeam, its L* increased while the redness and yellowness decreased. Coating the samples with boiled-linseed oil decreased the rate of color change and cracking. It is best to use it as a sealant and combine it with other outdoor finish. According to the FTIR spectra, lignin did degrade during mercury-vapor lamp irradiation. The absorption of functional groups in lignin decreased while that of methane, methylene, methyl and carbonyl groups increased. The rate of degradation and structural changes were highest in case of acetylated samples, but the strengthening polymers did not degrade to a significant extent.

Chapter 7. Photostability after coating

7.1. Introduction

Wood modification and coating can be used to protect wood from performance loss caused by photodegradation and weathering (Jones and Brischke, 2017). Coating is widespread because it is more convenient and less expensive. On the other hand, its disadvantages include leachability, susceptibility to mechanical damage, and the need for renewing its application. Coating usually performs better on low-density wood than on high-density wood because of the lower swelling-shrinking rate. A higher swelling-shrinking rate and higher stresses can occur between earlywood and latewood, which can create stresses in the coating of high-density wood and lead to coating failure (Nejad and Cooper, 2017).

The ideal finish allows the natural visual characteristics to be visible, minimizes UV discoloration, reduces water exchange between the atmosphere and the material, and accommodates the dimensional changes of the material to reduce cracking and peeling from the wood surface for the longest possible time, thereby reducing maintenance expense.

Coatings can be film-forming or non-film forming; this study tested the latter. Non-film forming coatings are stains (pigmented or clear), which resist UV and water penetration while highlighting some visual characteristics but are less effective than film-forming paints. Easy but more frequent maintenance is required (Jones and Brischke, 2017). Penetrating oil finishes can reduce dimensional changes, thereby decreasing cracking and checking; however, the oil degrades over time, and the protective characteristics of the coating are diminished. After the coating has either peeled or been destroyed, the natural process of color change will begin to occur (Nejad and Cooper, 2017; Cogulet et al., 2018).

Oil-based coatings are mainly triglycerides including different fatty acids in esters. Wood impregnating oils and binders in paint are usually drying oil or semi-drying oils. Vegetable oils can be efficiently used in wood protection for their antifungal, antibacterial, water-repellency, and UV stability. The downside of oil coatings is that they only fill the wood cavities by capillarity, without chemically bonding to the cell walls. Thus, it is necessary to ensure high oil retention in order to acquire the required protection. Drying oils (often mixed with oil-modified polyester resins or alkyds) undergo first an auto-oxidation reaction under air exposure, form a structural tri-dimensional network through cross-linking, then a radical chain reaction takes place. Some of the highly conjugated polymeric networks are UV-sensitive, they are prone to yellowing and discoloration. Higher amounts of linoleic acid with two double bonds increase the speed of drying, but also the rate of photochemical degradation. Linseed oil contains 48-60 w% linolenic acid, 14-19 w% linoleic acid, 14-24 w% oleic acid, 6-7 w% palmitic acid, and 3-6 w% stearic acid. Ether bridges increase the resistance to water and alkali. Linseed, tall, orange, soybean, nut, and hemp oil are efficient for wood preservation, mainly against decay and termites while tall, linseed oil and tung oil are very efficient against water uptake (Kataoka et al., 2007).

The rate of surface degradation is typically related to UV intensity, time of exposure, wood species, and climatic factors (Hon, 1995; Mohebby and Saei, 2015; Teaca et al., 2019; Tolvaj and Faix, 1995). In the early stages of weathering, dark wood tends to become light, and light wood tends to darken or turn silver (Dawson et al., 2008; Davis et al., 2021). Natural and modified natural resins are also important components of natural wood coatings. Plant resins are usually synthesized by coniferous plants and contain terpenes and derivatives. They are transparent and have an amorphous chemical structure. The most frequently used resins in coatings are shellac, colophony, and dammar (Lazzari and Chiantore, 1999). In the case of colored coatings, pigments and dyes are also degraded.

Some pigments can be more photo-resistant than the binder, so they become non-bound to each other after the destruction of the binder, which leads to “chalking” (Cogulet et al., 2018). Due to chemical changes during photodegradation, the coating can become more brittle, cracks can appear, and the coating film becomes thinner. Wood and coatings age according to the same phenomena (Jones and Brischke, 2017; Cogulet et al., 2018). With clear coatings, the loss of protection is due to delamination rather than the destruction of the polymeric matrices (Evans et al., 2015). Exposing the coating to water flow causes the leaching of pigments, hydrolysis of organic compounds, fungal degradation, and wood dimensional changes, which reduce coating performance and service life (Cogulet et al., 2018). When the coating is penetrated into the wood, the moisture starts to build up at the interface between the wood and the coating film, then the coating is delaminating from the wood due to different dimensional changes, which leads to further dimensional changes and fungal decay (Rowell and Bongers, 2015).

The lower shrinking and swelling rate enable a longer-lasting coating film. The higher the WPG, the more durable the coating of acetylated wood will be (Plackett et al., 1992).

Water-based paints penetrate less and a form thinner film on acetylated wood than on untreated wood. Flaking can be a problem because of increased acidity and buffering capacity (Accsys PLC, 2020). Case studies have shown that while outdoor paints and stains need to be repainted every 2–6 years, Accoya requires 10-12 years (Alexander, 2007). Various case studies addressed the topic of coating acetylated wood and have highlighted the durability of alkyd and acryl coating systems. The maintenance time or service life of coated acetylated wood can be three or four times longer with appropriate surface preparation, surface treatment and a well-chosen coating system (Beckers et al., 1998; Schaller and Rogez, 2007; Rowell and Bongers, 2015, 2017). Alkyd and acrylic stains were tested at 13 years of exposure, with the best results being the alkyd primary and acrylic topcoats, which did not need to be repainted after 13 years. If a suitable coating system is used, it may be sufficient to maintain the coating every 10 years or even less frequently (Rowell and Bongers, 2015).

The present work tested various environmentally friendly, waterborne oil-based coatings on natural and acetylated hornbeam during natural weather exposure and xenon lamp irradiation. Then, the coating performance of acetylated hornbeam and the photostability properties of tested coatings were evaluated to determine suitable and less-suitable coatings for exterior use of acetylated hornbeam.

7.2. Materials and Methods

7.2.1. Preparation

Samples of untreated and industrially acetylated hornbeam (average WPG 15.3%) were manufactured with dimensions of 20 × 20 × 100 mm^3 (t × w × l). The average density of hornbeam and acetylated hornbeam were 745 ± 42 kg/m^3 and 795 ± 55 kg/m^3, respectively. Acetylation was carried out the same way as seen in Paragraph 1.8.

There were nine different oils and stains tested in this comprehensive research: Uncoated (marked as 0 throughout), Oli-Natura oil-colorless (OO0), Auro stain-colorless (AS0), -umbra (ASU), Biopin stain-colorless (BS0). -Swedish red (BSR), -palisander (BSP), Auro oil-teak (AOT), Biopin oil-teak (BOT), and -red (BOR) (Table A37, Table A38). OO0, AS0, AOT and ASU coatings were linseed oil-based coatings; the rest were mainly polymer made from natural oils, fatty acids and resins. The finishes were applied using a paintbrush according to the manufacturer’s instructions. The products originated from three different companies: Stoki Ltd. (Oli-Natura), Sixay Furniture Ltd. (Auro), and Orange Ltd. (Biopin). Overall, 10 samples were made of each type of coating and wood. Of these, five samples were used for weather exposure and five for irradiation.

The sample weight was determined before and after coating to define weight gain (%, g/m^2) and observe the uptake difference between non-acetylated and acetylated wood.

7.2.2. Irradiation with xenon lamp

The UV irradiation test was performed in an artificial ageing chamber. The test used two xenon lamps with 482 W/m^2 average radiant power density. The lamps were 64 cm above the samples and the equipment temperature was set to a maximum of 50 °C.

7.2.3. Weather exposure

The samples were exposed to weathering without soil contact on the roof of The Central Library of the University of Sopron (47°40’54.3”N 16°34’40.6”E) in April 2018 (Figure 49). They were placed on a wood stand tilted at 45 degrees. The time of exposure was 24 months. The weather parameters of the testing field were obtained and Scheffer Climate Index was calculated the same way as described in Paragraph 4.2.3.

Figure 49. Weather exposure of untreated and acetylated hornbeam wood coated with various oils and stains.

7.2.4. Color measurement

Each sample had four measuring points, which equals 20 for each type per test. The color was expressed in CIE L*a*b* color space with a Konica Minolta 2600d spectrophotometer. The colorimeter’s sensor head was 8 mm. The color was measured and calculated based on the D65 illuminant and 10° standard observer. The color coordinates were calculated according to ISO 11664:2019.

The color measurement and visual inspection of the xenon lamp-irradiated samples were completed after 0-5-10-20-30-60-120-200 hours of irradiation. The color measurement and visual inspection of the weathered samples were conducted at the beginning, then every 10 days (less frequently later) in their current state without conditioning. A color chart was also created by converting CIE L*a*b* coordinates to values of RGB (Red Green Blue) for a video display screen (Nobbs, 2023). The conversion was based on the sRGB (Standard Red Green Blue) definitions of the light emitted from the display screen. Photos and scans were taken of the samples in their current state to compare visual appearance.

7.2.5. Statistical analysis

Statistical analysis was performed using the Dell Statistica software (version 13, Dell Inc., Round Rock, TX, USA). Factorial analyses of variances (ANOVA) combined with the Fisher’s LSD test was conducted, and the differences were considered significant at $p < 0.05$.

7.3. Results and Discussion

7.3.1. Coating

Figure 50 shows the color data points of untreated and acetylated hornbeam when uncoated and after coating with the tested oils and stains. The diagram shows dotted lines of some relevant hue angles and dashed lines of relevant chroma ranges.

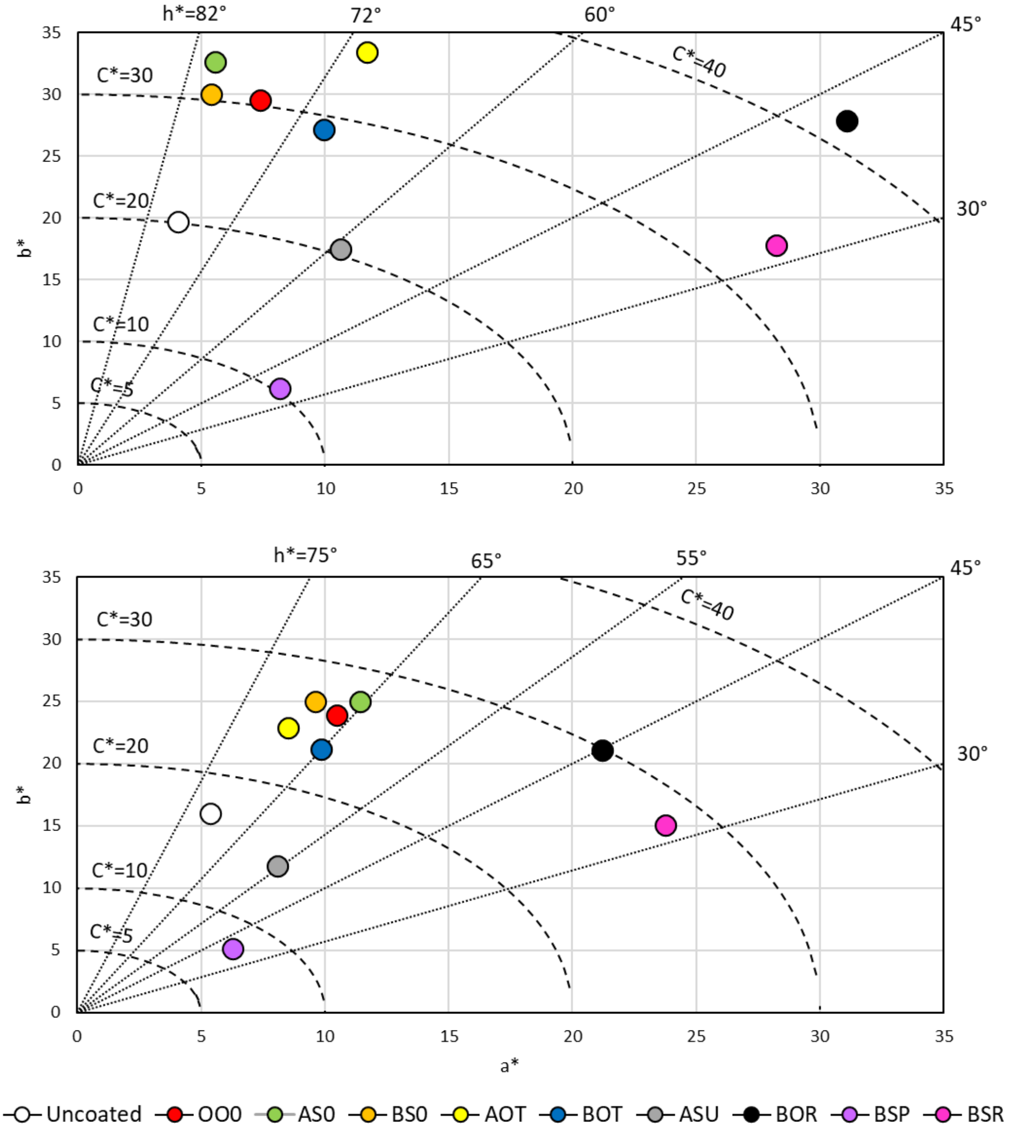

Figure 50. Chromaticity diagram of untreated (above) and acetylated (below) hornbeam wood, coated with various oils and stains. Redness (a) was higher and hue angle (h*) was lower after coating in every case. Yellowness (b*) and chroma (C*) was lower for ASU and BSP stains.*

Table 17 shows the color measurement results. The natural color became darker, lightness (L*) decreased. Redness (a*) was higher and hue angle (h*) was lower after coating in every case. The occupied hue interval was higher for untreated (48°) than for acetylated wood (39°). In most cases, yellowness (b*) increased and the color became more vivid as the chroma increased. Dark colored stains ASU and BSP had lower b* and C* compared to uncoated wood, and the grain structure was less prominent.

Table 17. Color coordinates of hornbeam and acetylated hornbeam, uncoated and coated with various oils and stains. Color parameters include lightness (L), redness (a*), yellowness (b*), C* (chroma), and h* (hue angle).*

	Untreated					Acetylated				
Coating	L*	a*	b*	C*	h*	L*	a*	b*	C*	h*
Uncoated	78.7	4.1	19.7	20.1	78.4	58.3	5.4	15.9	16.8	71.3
OO0	73.1	7.4	29.5	30.4	75.9	47.4	10.5	23.9	26.1	66.3
AS0	76.1	5.6	32.7	33.1	80.4	49.4	11.4	25.0	27.5	65.4
BS0	75.6	5.4	30.0	30.4	79.8	49.9	9.6	25.0	26.8	68.9
AOT	67.3	11.7	33.4	35.4	70.7	50.5	8.5	22.9	24.4	69.6
ASU	40.6	10.6	17.5	20.5	58.8	36.9	8.1	11.8	14.3	55.5
BSP	32.9	8.2	6.2	10.2	37.1	30.3	6.3	5.1	8.1	38.7
BSR	38.5	28.2	17.8	33.4	32.3	35.5	23.7	15.1	28.1	32.5
BOT	69.6	9.9	27.1	28.9	69.9	47.4	9.9	21.2	23.4	65.0
BOR	49.6	31.1	27.9	41.7	41.9	42.2	21.2	21.1	29.9	44.8

According to the weight gain results, hornbeam absorbed less coating after acetylation, except for AOT and BSP (Figure A93). This means that the coating penetrated the wood less and formed thinner film compared to natural hornbeam. In the cases of AS0, ASU, BOT and BOR, the weight gain did not reach the application amount given by the manufacturer, which can be explained by its dense and less porous structure. According to statistical analysis, the coating uptake was significantly different after acetylation for AOT, BOT, AS0 and ASU.

Acetylated hornbeam takes up less moisture, which indicates lower uptake of water-borne coatings. After 49 days, the maximum water uptake of hornbeam was 5513 g/m^2, which decreased to 4559g/m^2 after acetylation (Paragraph 1.8). In wettings studies, the contact angle of hornbeam increased from 43-44° to 61-62°, and the surface energy decreased from 55 to 64 mJ/m^2, which makes acetylated hornbeam less wettable and less coatable (Chapter 5). The coating performance of hornbeam also depends on its chemical properties. After acetylation, its pH decreased from 5.11 to 4.73, and its buffering capacity increased from 1.11 to 2.15 mg/g (Chapter 2), which can lead to coating flaking (Accsys PLC, 2020).

7.3.2. Irradiation with xenon lamp

The highest L* change was experienced in the first 5 hours of irradiation, especially for acetylated hornbeam samples. L* of untreated samples decreased, while that of acetylated samples increased. After 200 hours of irradiation, OO0 experienced the most prominent ΔL*: 18.27 for untreated, and 34.16 for acetylated hornbeam. BS0 had the smallest ΔL* among the colorless coatings: 13.10 for untreated, 21.17 for acetylated hornbeam. Dark, pigmented stains had the smallest ΔL* of all coatings tested (ASU, BSP, BSR): ~0.87 for untreated, ~3.88 for acetylated hornbeam (Figure 51). Dark woods usually brighten and light woods darken during UV exposure. (Dawson et al., 2008; Davis et al., 2021),

Consequently, a* of untreated hornbeam increased, while that of acetylated hornbeam decreased, except for dark, pigmented stains. OO0 and BS0 had the biggest a* change. AS0 had the smallest Δa* among the colorless coatings: 9.99 for untreated, 6.33 for acetylated hornbeam. Coating with teak oil showed a* changes that were similar to the control: 6.14 – 7.04. Dark, pigmented stains had the smallest a* change of all coatings tested (ASU, BSR, BOR): ~0.77 for untreated, ~2.26 for acetylated hornbeam. Unlike uncoated and coated with colorless and teak-colored coatings, acetylated hornbeam had a* increment when coated with dark, pigmented stains, especially with BSP (Figure 52).

Compared to the other color coordinates, b* changed less consistently. Coating hornbeam with colorless oils and stains (11.62-21.11) had higher Δb* during irradiation compared to dark, pigmented stains (1.61-5.89). Coating with teak oil showed similar results to the uncoated samples, for both untreated and acetylated hornbeam. The b* of acetylated hornbeam changed less compared to untreated hornbeam (Figure 53).

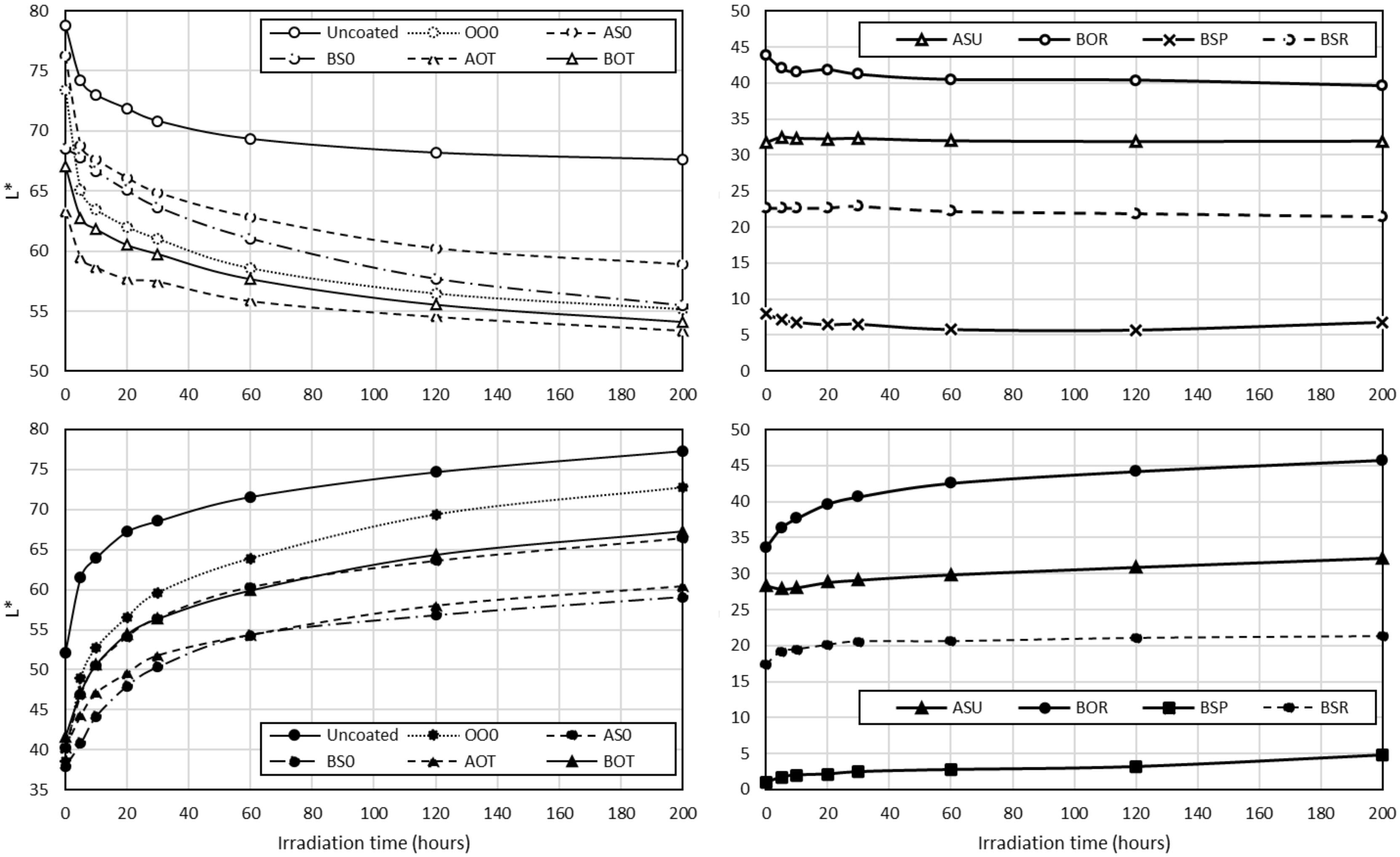

Figure 51. Change of lightness (L) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during 200-hour-long xenon lamp irradiation.*

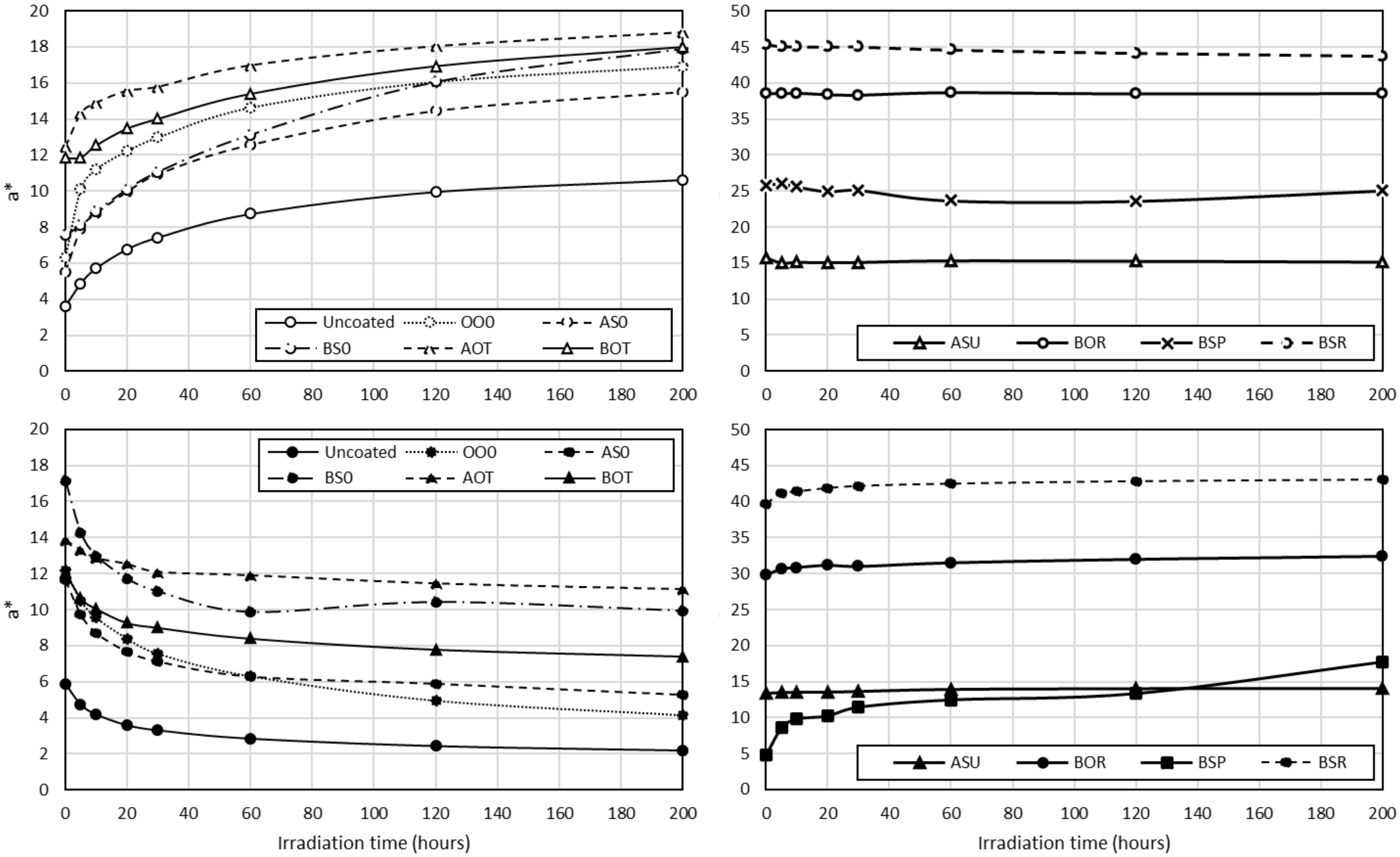

Figure 52. Change of redness (a) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during 200-hour-long xenon lamp irradiation.*

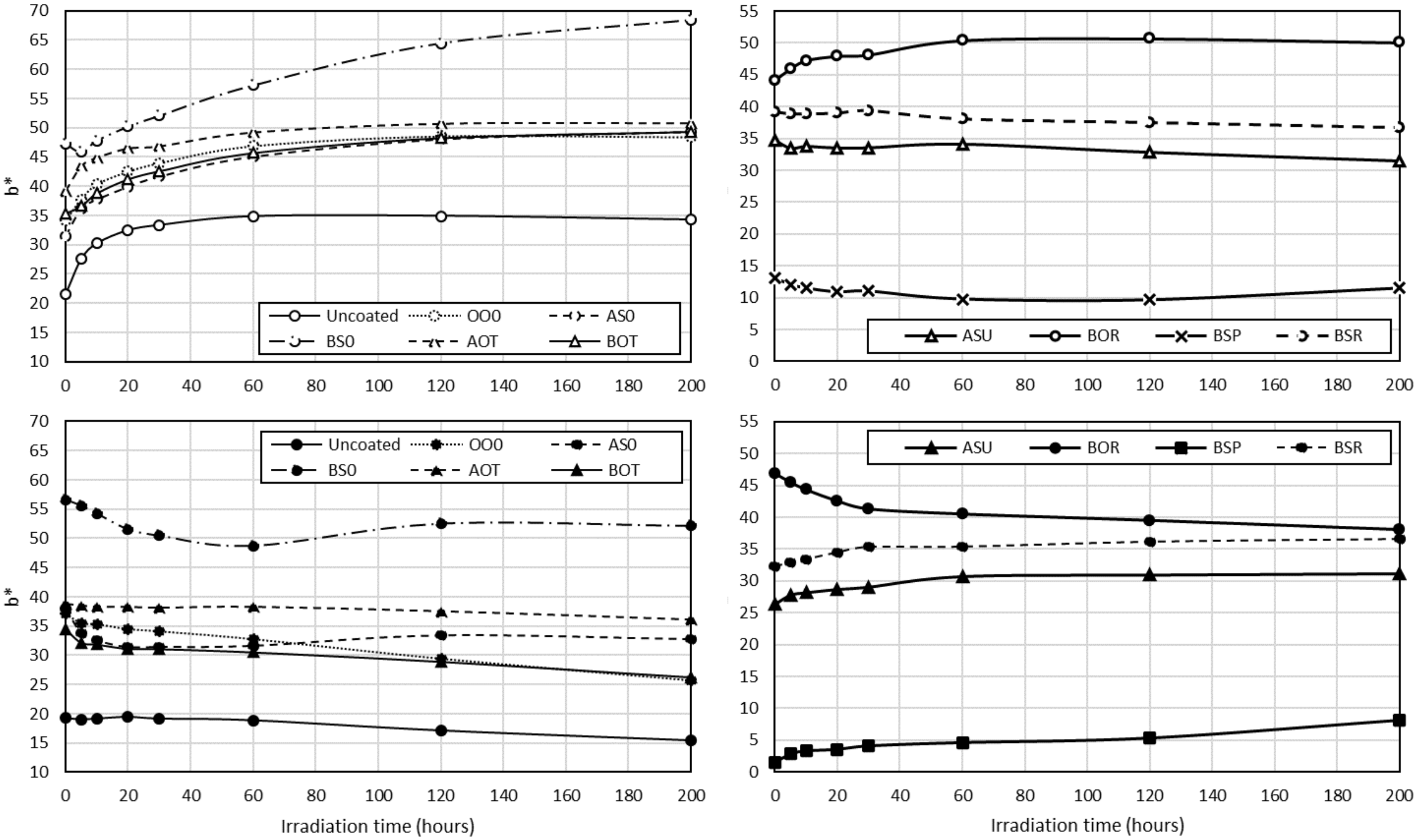

Figure 53. Change of yellowness (b) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during 200-hour-long xenon lamp irradiation.*

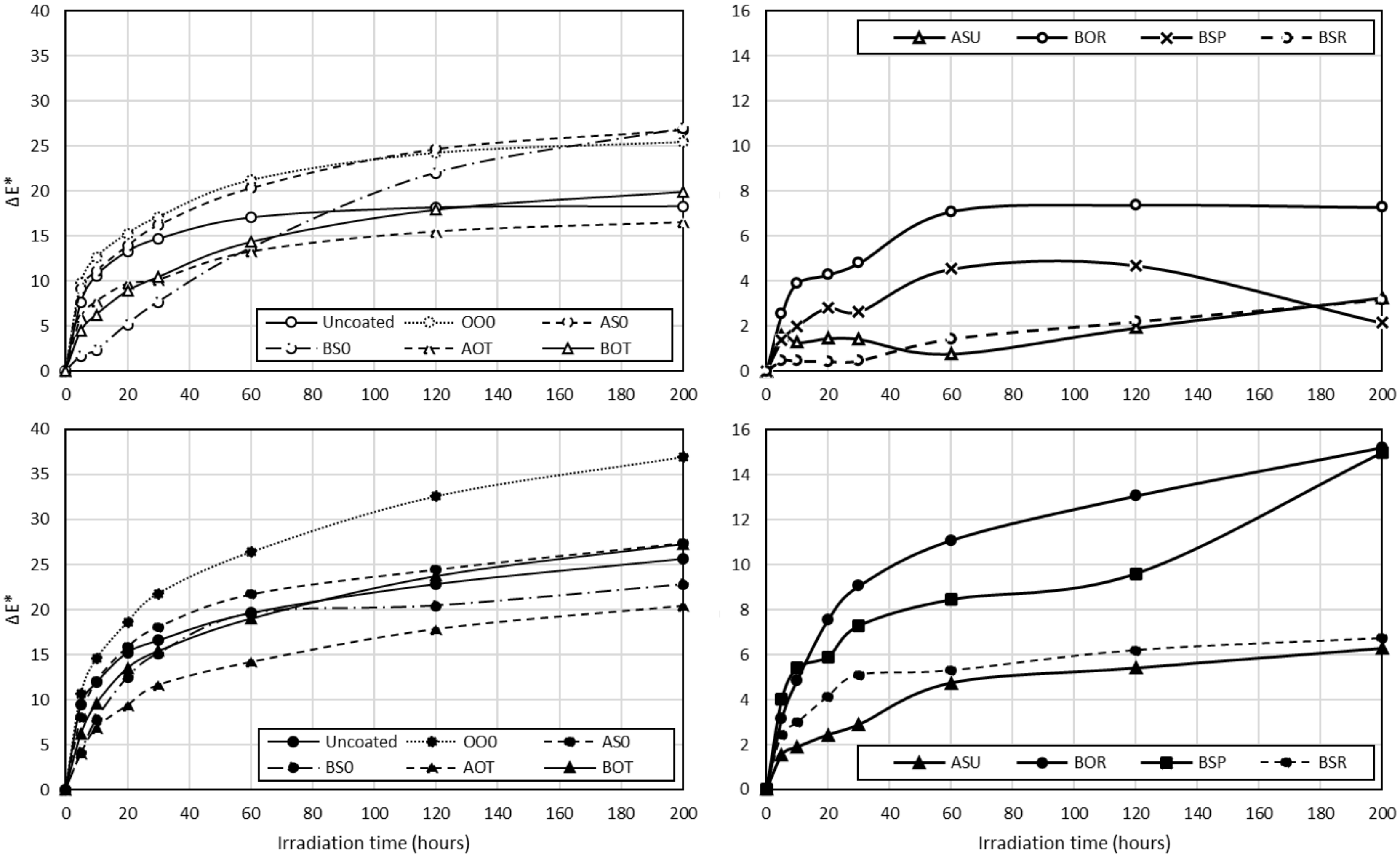

Figure 54. Change of color difference (ΔE) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during 200-hour-long xenon lamp irradiation.*

In every case, the color difference after 200 h of irradiation was perceivable ($\Delta E^*>2$) (Buchelt and Wagenführ, 2012) (Figure 54). ASU, BSR, and BSP achieved the lowest ΔE^* in hornbeam and acetylated hornbeam. Untreated hornbeam had a lower ΔE^* after irradiation than acetylated hornbeam. The use of non-pigmented oils and stains exhibited the greatest ΔE^* after irradiation. Coating with teak-colored oils showed about the same photostability as uncoated wood. The change of color parameters during irradiation had a concave deterioration pattern (Sandak and Sandak, 2017).

Figure 55 and Figure 56 show the color data points of tested wood samples on the a* - b* plane during xenon lamp irradiation. The first, non-irradiated color is marked with a triangle, which is followed by the dots of irradiated samples after 5, 10, 30 hours, etc. The diagram shows dotted lines of some relevant hue angles and dashed lines of relevant chroma ranges.

During irradiation, a*, b*, and C* increased for hornbeam samples which were uncoated, or coated with colorless or teak-colored coatings. Its color became more vivid and light, as C* increased by 13.06-22.82. On the other hand, dark pigmented stains did not change C* remarkably. On the contrary, a*, b*, and C* of acetylated hornbeam decreased gradually during irradiation of uncoated samples, or samples coated with colorless or teak-colored coatings. Their color changed from deep, dark to pale as C* decreased by 3.36-13.06. Untreated hornbeam had greater C* change than acetylated hornbeam using the same colorless or teak-colored coatings. In comparison with them, dark pigmented coatings had remarkably lower C* differences during irradiation, and C* changed exactly the opposite way (Table 18).

The highest hue angles (80-81°) were of untreated hornbeam, especially uncoated and those coated with colorless coatings. It decreased gradually during irradiation as the surface darkened. On the other hand, acetylated hornbeam exhibited hue angle increase due to lightening. The occupied hue interval was higher for acetylated samples than for untreated samples, having the widest hue interval for uncoated and colorless coatings (6-9°).

The value of color variation (the color difference calculated compared to the average color) indicated how variable the initial color is. The color variation ranged between 1.23 and 4.07 for untreated hornbeam and between 1.09 and 5.10 for acetylated hornbeam (Table A39). The highest differences were measured when both of them were coated with OO0 or BOT. After irradiation, the color variation decreased for hornbeam wood, except for dark pigmented coatings (ASU, BSP, BSR, BOR). The lowest value was found in AS0-coated samples. There was significant difference between the color variation of the initial and the irradiated samples when they were coated with OO0, BSP, BSR or BOT. In most cases, the color variation of acetylated hornbeam increased after irradiation, and it had the lowest value in uncoated samples. Except for uncoated and ASU-coated acetylated wood, all of the samples had significant change in color variation after irradiation.

According to the statistical analysis, there were significant changes in L*, a* and b* after 200 hours of irradiation, except for untreated hornbeam coated with ASU, BSP and BSR, and acetylated hornbeam coated with ASU and BSR. There was no significant difference between the color coordinates of untreated and acetylated hornbeam coated with ASU or BSR. The color of OO0 and BOT-coated hornbeam was not significantly different after 200 hours or irradiation.

Artificial aging only incurs UV light degradation and eliminates the impact of other weather elements and microorganisms. Consequently, the color coordinates mostly increase. The changes caused by light irradiation is highly dependent on the used light source. Xenon light can simulate the effect of sunlight during weathering, but only at long exposure times, as the yellowing will be about three times more intensive in the short term (Tolvaj and Mitsui, 2005).

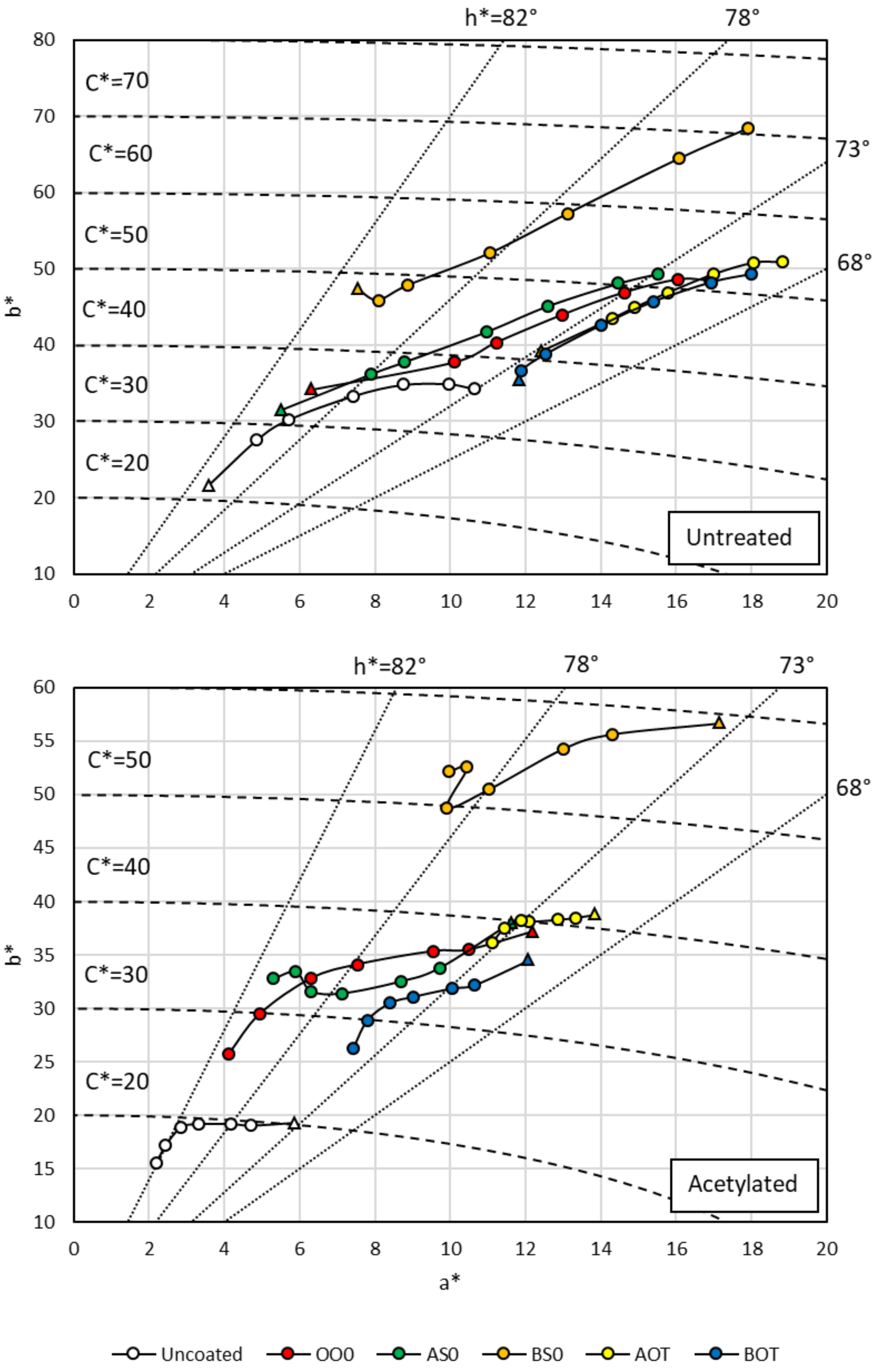

Figure 55. Chromaticity diagram of untreated and acetylated hornbeam wood, coated with various colorless and teak-colored oils and stains, exposed to 200-hour-long xenon lamp irradiation. The first, non-irradiated points are triangle-shaped, followed by the colors measured at 5, 10, 30 hours, etc. The change in redness (a), yellowness (b*), chroma (C*) and hue angle (h*) can be traced at the same time on this diagram.*

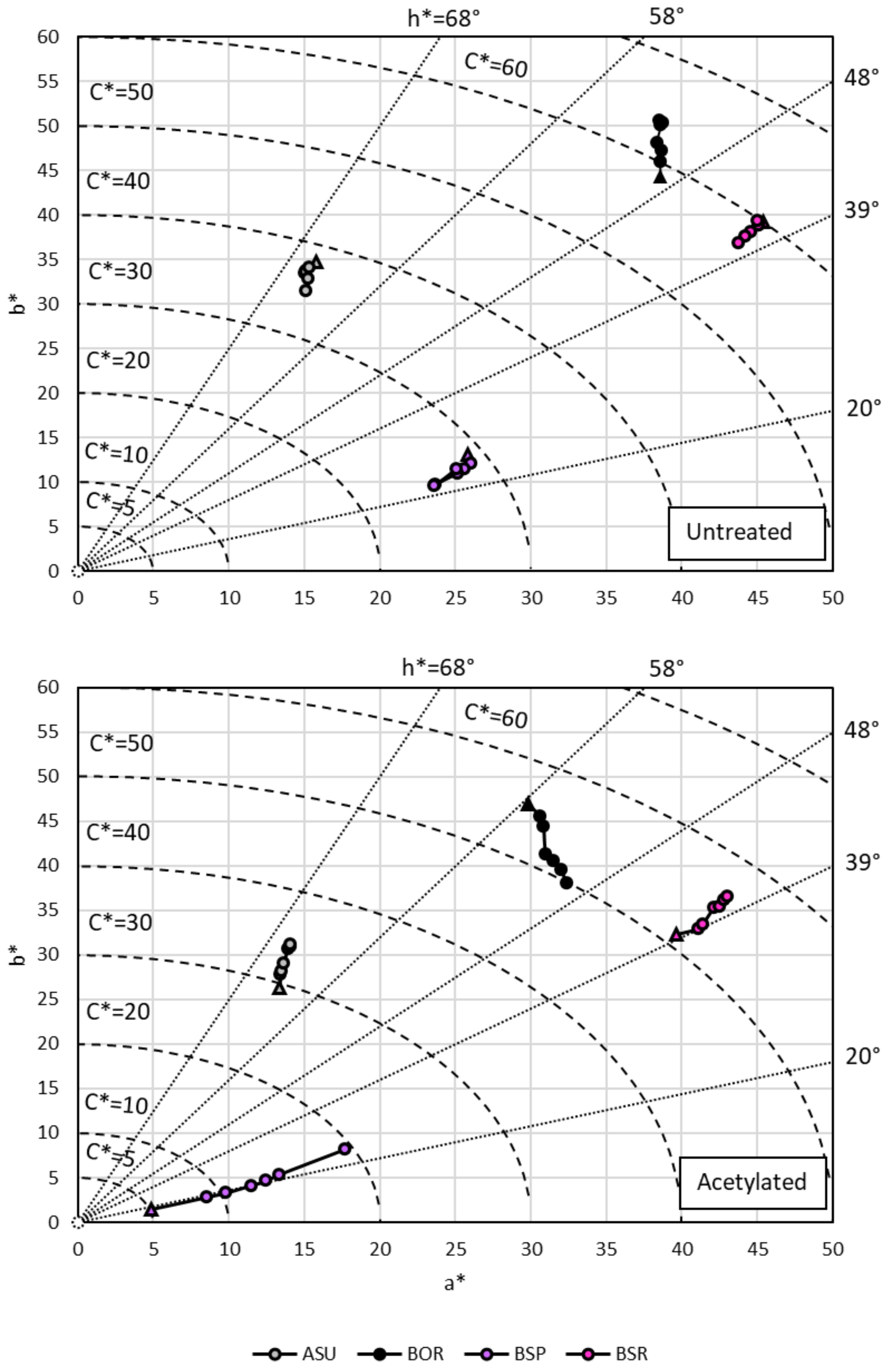

Figure 56. Chromaticity diagram of untreated and acetylated hornbeam wood, coated with various dark oils and stains, exposed to 200-hour-long xenon lamp irradiation. The first, non-irradiated points are triangle-shaped, followed by the colors measured at 5, 10, 30 hours, etc. The change in redness (a), yellowness (b*), chroma (C*) and hue angle (h*) can be traced at the same time on this diagram.*

Table 18. Color coordinates of hornbeam and acetylated hornbeam after 200 hours of xenon lamp irradiation. The samples were uncoated or coated with various oils and stains. Color parameters include lightness (L), redness (a*), yellowness (b*), C* (chroma), h* (hue angle), and color difference compared to initial color (ΔE*). Coatings, which had significant color changes after irradiation are marked by an asterisk if* $p < 0.05$*.*

			Untreated			
Coating	L*	a*	b*	C*	h*	ΔE*
Uncoated*	67.59	10.64	34.27	35.88	72.76	18.30
OO0*	55.14	16.91	48.41	51.28	70.74	25.47
AS0*	58.92	15.52	49.36	51.74	72.55	26.78
BS0*	55.45	17.91	68.43	70.73	75.34	26.92
AOT*	53.41	18.82	50.86	54.23	69.69	16.53
BOT*	54.12	17.98	49.27	52.45	69.95	19.95
ASU	31.93	15.14	31.48	34.93	64.31	3.27
BOR*	39.60	38.57	50.08	63.21	52.40	7.28
BSP	6.76	25.07	11.50	27.58	24.63	2.14
BSR	21.42	43.76	36.78	57.17	40.04	3.16
			Acetylated			
Coating	L*	a*	b*	C*	h*	ΔE*
Uncoated*	77.32	2.20	15.51	15.67	81.94	25.70
OO0*	72.74	4.12	25.71	26.04	80.90	36.92
AS0*	66.39	5.29	32.76	33.19	80.82	27.41
BS0*	59.15	9.97	52.19	53.14	79.18	22.80
AOT*	60.41	11.12	36.13	37.80	72.89	20.46
BOT*	67.30	7.42	26.20	27.23	74.20	27.32
ASU	32.21	14.09	31.19	34.22	65.68	6.27
BOR*	45.75	32.43	38.06	50.00	49.56	15.22
BSP*	4.81	17.72	8.13	19.49	24.64	14.98
BSR	21.28	43.05	36.54	56.47	40.33	6.72

The results are comparable to those of mercury-vapor lamp irradiation (Chapter 6). The xenon lamp emits UV light in only the UV-A region (400-340 nm). The average radiant power density of a mercury vapor lamp and a xenon lamp are 76 and 482 W/m^2, respectively. Comparing the xenon lamp results to the results of mercury vapor lamp irradiation reveals that xenon lamp exposure had a greater impact on the color of both wood types (Table 13, Table 18). The reason for this could be the higher radiant power density of the xenon lamp.

Wood and coating change according to the same phenomena (Jones and Brischke, 2017; Cogulet et al., 2018). During irradiation, photo oxidation and cross-linking reactions take place in coated wood (polymer). First, the polymer absorbs photons, which generates free radicals. Then, reactions take place between the oxygen and free radicals which create peroxy radicals. Peroxy radicals react with the polymer to form a polymer hydroperoxide and a polymer alkyl radical. Following this, hydroperoxides are broken into oxy and hydroxyl radicals. Finally, cross-linking reactions take place between the free radicals (Williams, 2005; Cogulet et al., 2018). In colored coatings, pigments and dyes degrade during irradiation as well, with a varying time course or durability depending on its nature.

The lower photostability of acetylated wood can be explained by the fact that water-based paints penetrate less and a form thinner film on it (Accsys PLC, 2020), and the varying WPG can also influence the color homogeneity. During the irradiation of oil-coated wood, the oil inhibits the photodegradation mechanism, but over time it degrades and the natural process of wood color change begin to occur (Nejad and Cooper, 2017; Cogulet et al., 2018).

According to these results, acetylation did not increase the photostability of hornbeam wood. On the other hand, ASU and BSR significantly increased the photostability of both untreated and acetylated hornbeam wood.

7.3.3. Weather exposure

Table A40 lists the weather parameters of this site. Compared to hot and dry territories, the Hungarian field probably accelerates decay. This area has a warm and wet summer season (May-September), with mean temperatures between 13–23 °C, that range up to 36 °C, and the monthly average precipitation is between 42–154 mm. It has a drier winter season (October–April) with 7–79 mm of average precipitation per month, and mean temperatures between 1–16 °C with a maximum of 29 °C. The average annual rainfall during the test period was approximately 636 mm, average annual temperature was 13 °C, and the maximum temperature was 36 °C. The relative humidity ranged from 45 to 88%. The direct normal solar annual radiation index at this site is approximately 3.65 kWh/m^2/day, representing a moderate UV exposure, with a high likelihood that surface microbial activity (mildew) will occur throughout the experiment. Fungi require oxygen, moderate temperature (25–35 °C), 35-50% of air relative humidity, nutrients, a certain pH, vitamins, and minerals, however water is the main growth factor (Cogulet et al., 2018). This suggests that the summer months were favorable for fungi growth.

According to the ombrothermic diagram (Figure A94), there was a short dry season in February and in April (the area below the temperature line and above the precipitation line). Other than that, the wet season–which is the area below the precipitation line and above the temperature line–was typical for the whole year. In the dry seasons, cracking, insect activity, and UV radiation have a greater degrading effect, while in the wet seasons, fungal activity and leaching are more drastic.

The Scheffer Climate Index of this site was 42.1 (Scheffer, 1971), which indicates intermediately favorable conditions for decay. This index is similar to other reports regarding the SCI of different countries, including Hungary (Brischke et al., 2011; Frühwald Hansson et al., 2012; Niklewski et al., 2021; Niekerk et al., 2022).

The highest ΔL* was experienced in the first months of weather exposure (spring and summer of 2018). In the first weeks, there was an initial increment, then L* decreased at different rates depending on the wood and coating type. After about 5–9 months, the biggest L* reduction was achieved in every sample. The greatest L* increment was in acetylated hornbeam samples, especially those that were coated with colorless coating (OO0, AS0, BS0) and BOT. Hornbeam samples experienced the biggest L* reduction, especially those coated with AOT and BS0. Dark pigmented coatings like ASU, BSP, and BSR had the lowest ΔL* (Figure 57).

In the first weeks, there was an initial increment of a* in hornbeam samples; before they started graying, their color shifted to a darker yellow. Then a* decreased at different rates depending on the wood and coating type. The greatest a* increment was in BS0 before the coating failed, and the surface began to gray as with the other colorless coatings. BSP coated acetylated hornbeam also had a great increment of a*. The biggest a* reduction was in BOR, BOT and AOT. In addition, ASU exhibited the lowest Δa* (Figure 58).

Initial increment was also the case of b*, but only for natural hornbeam samples and not for acetylated samples. Among colorless coatings, BS0 maintained the wood color for the longest period, but after the coating failed, the surface began to gray, resulting in an even larger color difference than that of the uncoated wood itself. The b* of every coating–except for BSP and BSR–decreased over time during weather exposure. AOT, BOT, and BOR experienced the biggest reductions. Also, ASU, BSR and BSP had the lowest Δb* (Figure 59).

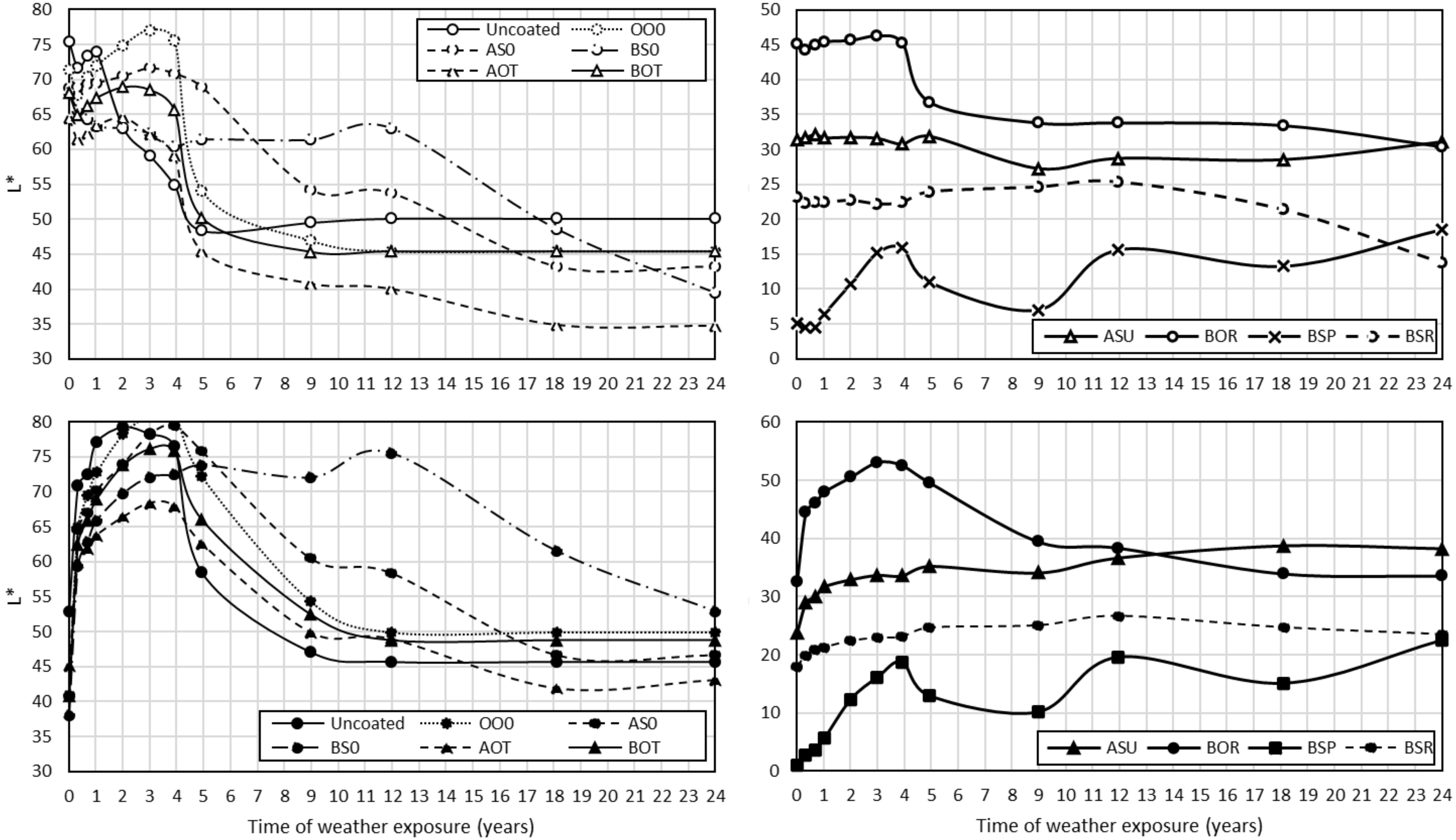

Figure 57. Change of lightness (L) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during two-year-long weather exposure.*

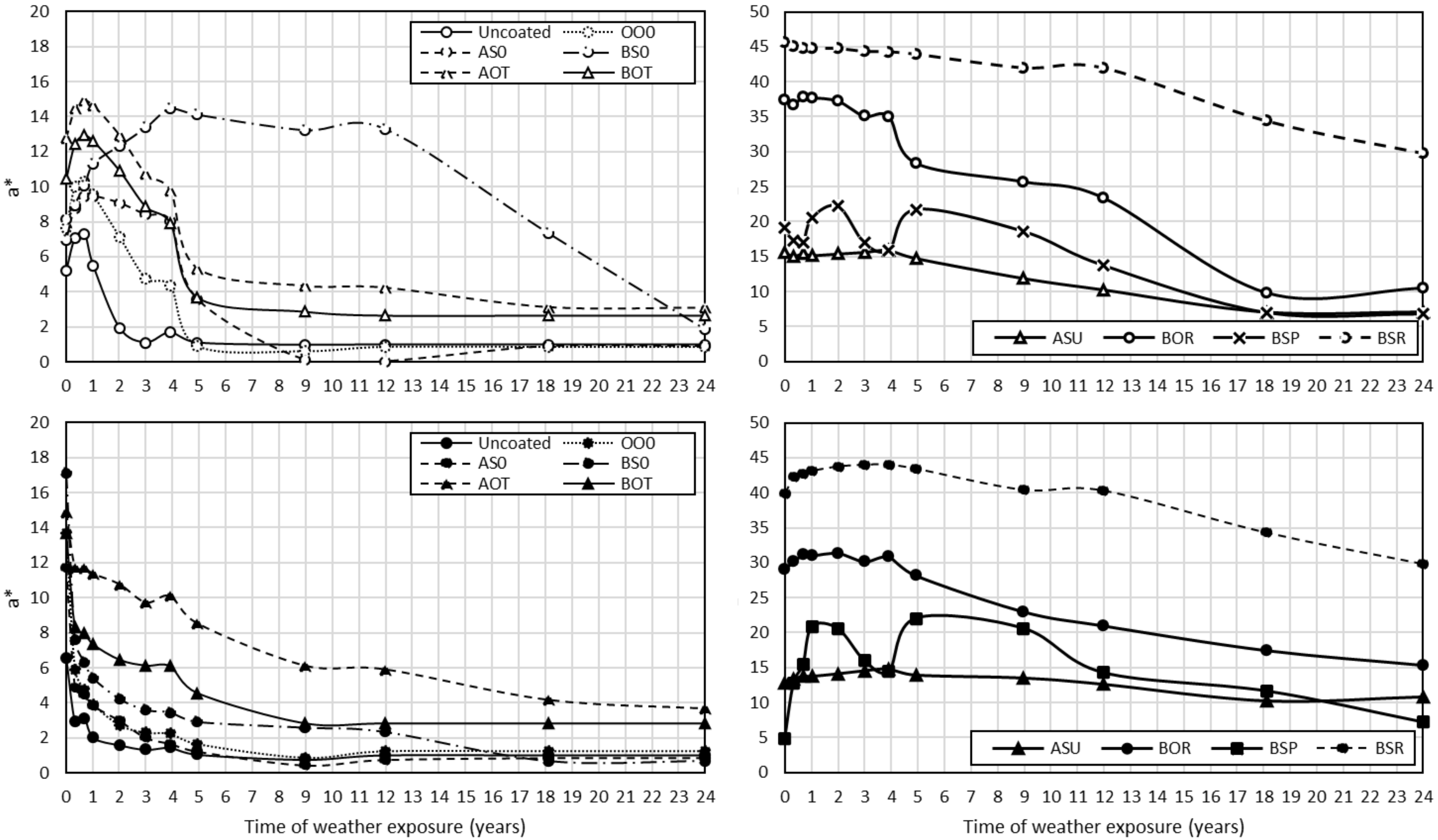

Figure 58. Change of redness (a) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during two-year-long weather exposure.*

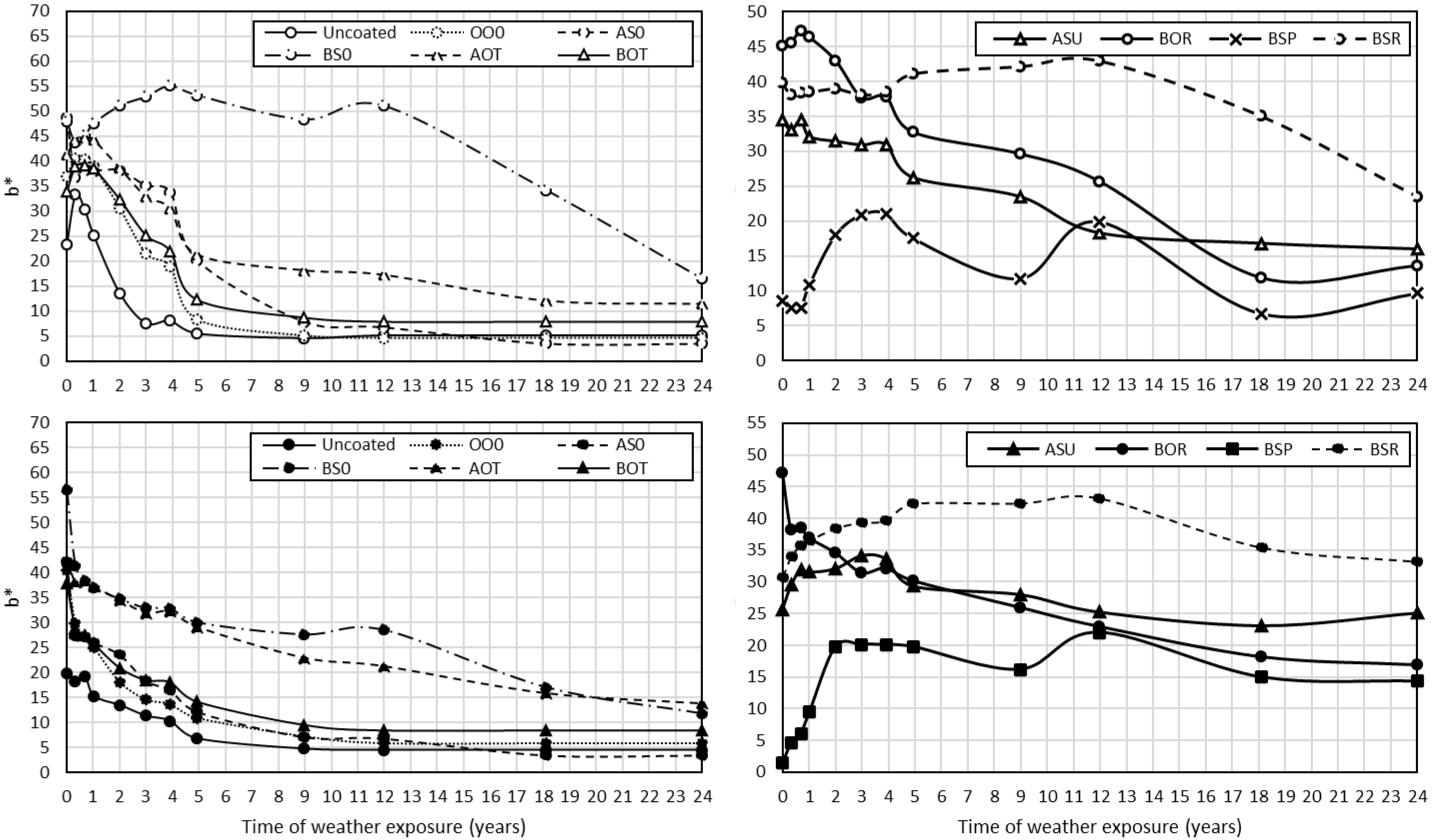

Figure 59. Change of yellowness (b) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during two-year-long weather exposure.*

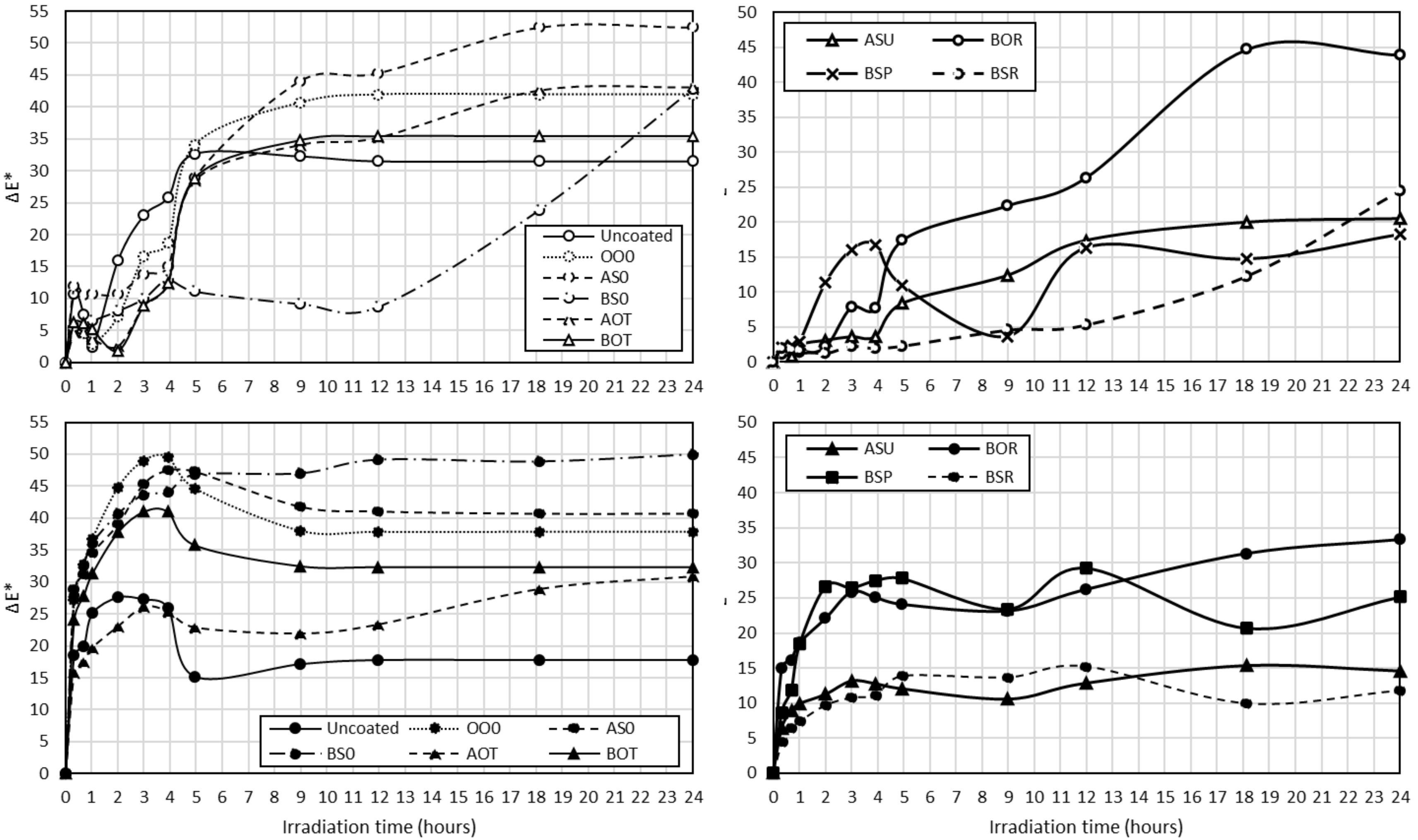

Figure 60. Change of color difference (ΔE) of untreated (no fill) and acetylated (solid fill) hornbeam, with different coatings, during two-year-long weather exposure.*

Colorless coatings had a high rate of ΔE* in the first five months. At about 5–9 months, the surface started to gray, and the rate of change decreased greatly after one year. The greatest ΔE* in colored coatings was in BOR, BOT and AOT. In most cases, coated acetylated hornbeam had lower ΔE* than hornbeam at the end of the exposure. Moreover, its trend curve was flatter. BSR, BSP and ASU achieved the lowest ΔE* (Figure 60). S-Shaped and convex deterioration patterns can also be found in the diagrams (Sandak and Sandak, 2017).

According to the statistical analysis, there were significant changes in L*, a* and b* after two years of weathering for all tested samples**.** The color of OO0 and AS0-coated hornbeam, uncoated and AS0-coated acetylated hornbeam was not significantly different after two years of weathering. This means, these coatings had no significant effect on the color stability of hornbeam and acetylated hornbeam for the test period and in these weather conditions (Table 19).

Table 19. Color coordinates of hornbeam and acetylated hornbeam after 2 years of weathering (April 2018 – April 2020). The samples were uncoated or coated with various oils and stains. Color parameters include lightness (L), redness (a*), yellowness (b*), C* (chroma), h* (hue angle), and color difference compared to initial color (ΔE*). All of the coatings had significant color changes after weathering (if $p < 0.05$).*

			Untreated			
Coating	L*	a*	b*	C*	h*	ΔE*
Uncoated	50.1	0.98	5.09	5.19	79.08	31.52
OO0	45.4	0.85	4.63	4.71	79.57	41.96
AS0	43.3	0.89	3.46	3.57	75.62	52.46
BS0	39.5	1.89	16.51	16.62	83.48	42.81
AOT	34.8	3.10	11.52	11.93	74.96	43.11
BOT	45.4	2.65	7.89	8.33	71.46	35.39
ASU	31.1	7.06	15.96	17.46	66.13	20.47
BOR	30.4	10.52	13.56	17.16	52.20	43.91
BSP	18.5	6.80	9.65	11.81	54.82	18.26
BSR	13.7	29.77	23.51	37.94	38.30	24.52
			Acetylated			
Coating	L*	a*	b*	C*	h*	ΔE*
Uncoated	45.71	1.03	4.54	4.65	77.24	17.78
OO0	49.88	1.25	5.88	6.02	77.97	37.80
AS0	46.67	0.87	3.48	3.59	76.04	40.73
BS0	52.89	0.70	11.88	11.90	86.62	50.01
AOT	43.13	3.68	13.78	14.26	75.06	30.82
BOT	48.76	2.82	8.45	8.91	71.56	32.33
ASU	38.19	10.84	25.07	27.31	66.62	14.54
BOR	33.58	15.30	16.85	22.76	47.75	33.29
BSP	22.44	7.22	14.35	16.06	63.29	25.15
BSR	23.52	29.85	33.19	44.64	48.04	11.78

Figure 61 and Figure 62 shows the color data points of tested wood samples on the a* - b* plane during weathering. The first, non-irradiated color is marked with a triangle, which is followed by the dots of weathered samples after 10, 20, 30, 60 days, etc. The diagram shows dotted lines of some relevant hue angles and dashed lines of relevant chroma ranges.

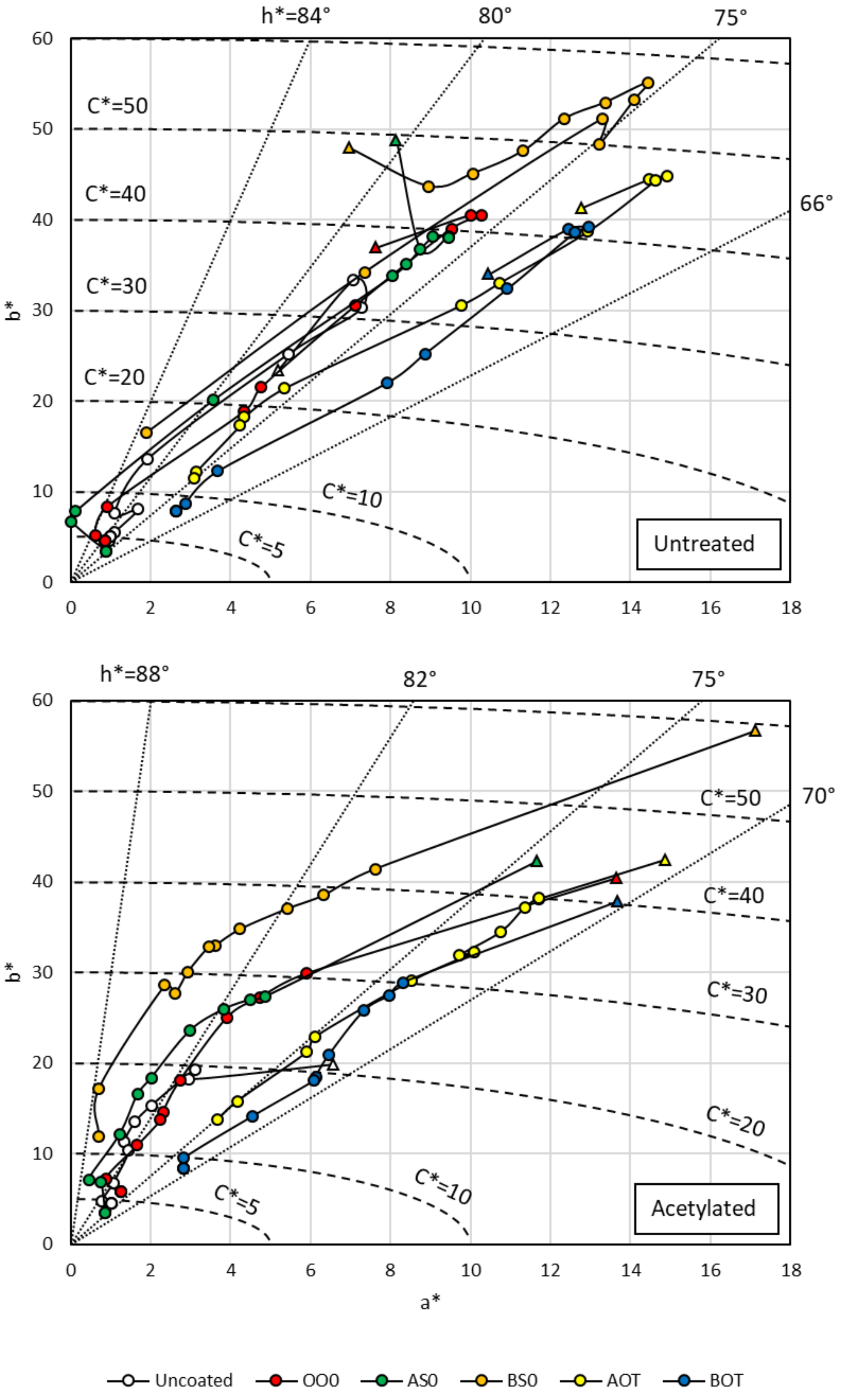

Figure 61. Chromaticity diagram of untreated and acetylated hornbeam wood, coated with various colorless and teak-colored oils and stains, during two-year-long weather exposure (April 2018 – April 2020). The first, non-irradiated points are triangle-shaped, followed by the colors measured at 10, 20, 30, 60 days, etc. The change in redness (a), yellowness (b*), chroma (C*) and hue angle (h*) can be traced at the same time on this diagram.*

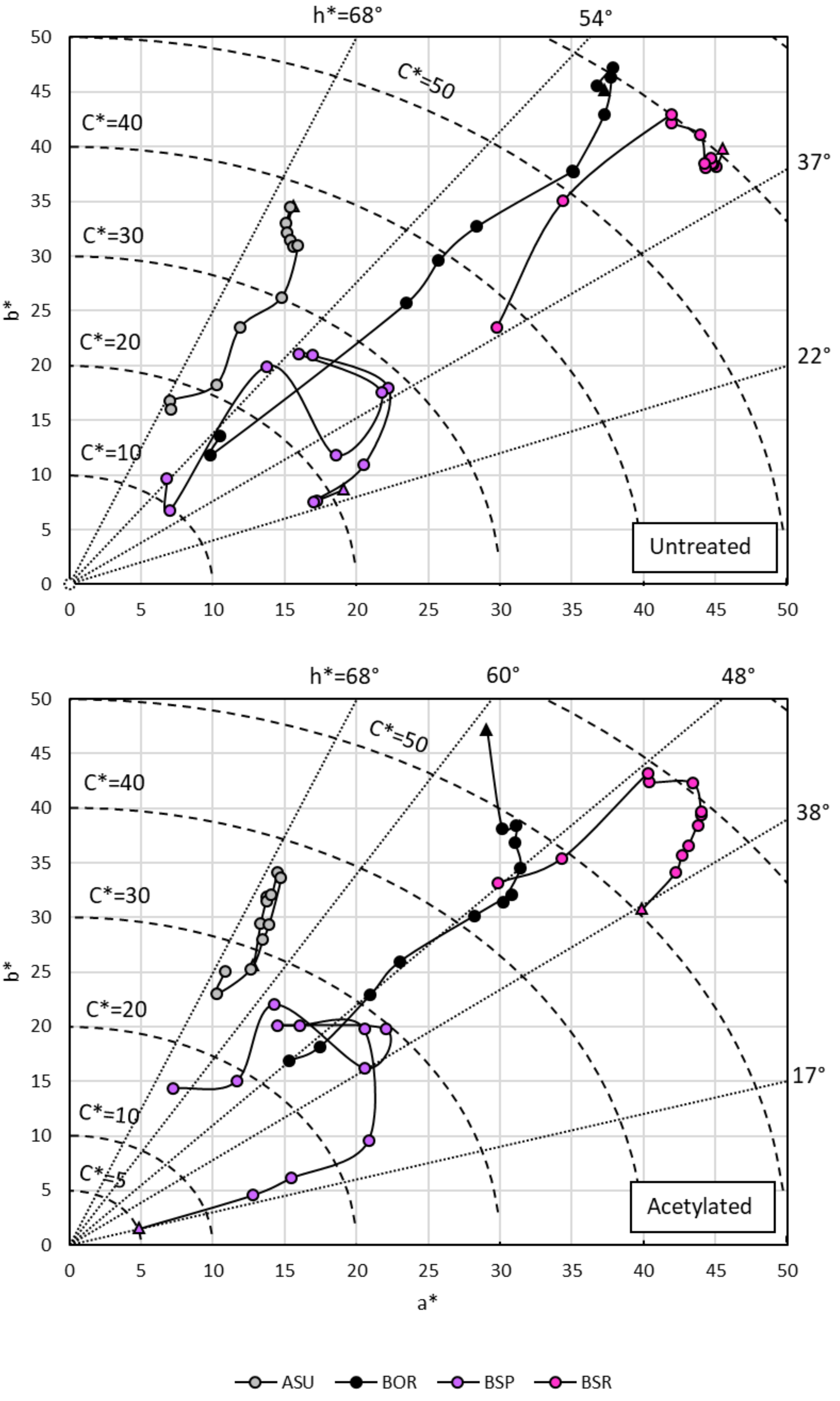

Figure 62. Chromaticity diagram of untreated and acetylated hornbeam wood, coated with various dark oils and stains, during two-year-long weather exposure (April 2018 – April 2020). The first, non-irradiated points are triangle-shaped, followed by the colors measured at 10, 20, 30, 60 days, etc. The change in redness (a), yellowness (b*), chroma (C*) and hue angle (h*) can be traced at the same time on this diagram.*

During weathering, a*, b*, and C* increased for most of the untreated hornbeam samples until the first month. Its color became more vivid and light, as C* increased. Then, as a* and b* decreased, C* also decreased and the surface started to gray. On the contrary, a*, b*, and C* of acetylated hornbeam decreased from the beginning. Their color changed from deep, dark to grayish, dark as C* decreased. Acetylated hornbeam had greater C* change than untreated hornbeam using the same coatings, except for OO0, BS0 and BOT. After 2 years of exposure, the lowest C* was of AS0 for both untreated and acetylated hornbeam. Acetylated wood had the lowest change in C* when coated with ASU or BSR.

The highest hue angles were of untreated hornbeam, especially uncoated (78°) and those coated with colorless coatings (78-82°). Among acetylated samples, uncoated (72°) and those coated with colorless coatings had the highest initial hue angle as well (71-75°). The occupied hue interval was higher for acetylated samples than for untreated samples, having the widest hue interval for those coated with BSP (46°). As the surface darkened or lightened, then grayed, the hue angle changed varyingly.

The value of color variation (the color difference calculated compared to the average color) indicated how variable the initial color is. The color variation ranged between 2.08 and 9.93 for untreated hornbeam and between 1.77 and 6.07 for acetylated hornbeam (Table A41). It shows that the samples already had a perceptible color difference or variation (greater than 2) before the weather exposure. This color difference can increase during photodegradation (wood degrades in spots, along cracks, wasp stripping occurs, coating fails, mold appears) but also decrease (even photodegradation resulting in complete graying). Acetylated hornbeam had lower color variation than untreated hornbeam after weathering. For both untreated and acetylated hornbeam, there was significant difference between the color variation of the initial and the irradiated samples when they were coated with AOT, BS0, BSP and BOR.

The time course of the photodegradation process is listed below:

- Uncoated hornbeam was the first to start graying among the tested samples–after about 21 days. Acetylated hornbeam started to gray after two months.
- Coated acetylated samples started graying later than coated unmodified samples, which corresponds to the literature (Kalnins, 1984; Plackett et al., 1992; Hon, 1995; Torr et al., 1996; Ota et al., 1996, 1997; Ohkoshi, 2002; Mitsui and Tolvaj, 2004, 2005). Black stain fungi could attack the delignified surface of acetylated wood (Plackett et al., 1992; Cogulet et al., 2018).
- OO0, AOT and BOT-coated samples started graying after three months due to no or low amount of pigments, and not chemically bonding to the cell walls (Lazzari and Chiantore, 1999).
- AS0-coated samples started to gray and crack after five months.
- BS0 and BSP-coated samples had a stable color for about one year and had a flaking surface after 1.5 years when the binder degraded, similarly to the literature (Evans et al., 2015; Cogulet et al., 2018).
- BOR-coated samples cracked after six months. It had a brightening interval until about five months, after which it started to darken again while graying.
- Cracks, flaking, chalking, and wasp marks became more apparent after nine months. Chalking was due to the photodegradation of the coating. The binder degraded where the film became thinner, and cracks appeared. Other researchers observed a similar process (Jones and Brischke, 2017; Cogulet et al., 2018). Wasps use the cellulose they strip from the wood surface to create nests. These marks were visible on almost all samples after one year of exposure.

- After a shorter or longer period of time, the coating film thinned or peeled, and the natural process of color change took place as seen in literature (Nejad and Cooper, 2017; Cogulet et al., 2018).
- BSR and ASU-coated samples withstood the weather exposure for two years.

The results can be observed on the photo scans (Figure A95), and color chart (Figure A96). BSR and ASU were the most photostable coatings. Among the colorless coatings, BS0 was the most durable. BSP had better durability during only UV exposure, without other weathering factors. The brightening of acetylated hornbeam was very apparent. On the other hand, the coating of untreated hornbeam failed in many cases earlier than that of acetylated hornbeam, due to lower dimensional stability and durability.

Acetylation did not improve the photostability of hornbeam, but it was less susceptible to decay and dimensional changes. Using ASU or BSR coating, acetylated wood had the most photostable color, which lasted at least two years of weathering. It is important to keep maintaining the coating to have long-lasting color. On the other hand, customers may want the silvery-gray patina of acetylated wood which develops during weathering without any quality reduction.

Color change in coating takes place due to photo oxidation, cross-linking, and leaching, where pigments and hydrophobic compounds are leached by precipitation. Light filters through clear coatings, which lead to photodegradation similarly to uncoated wood. During lignin degradation, free radicals are formed which affect the wood-coating interface. Free radicals degrade the linkages between wood and coating, which can cause delamination while the coating itself is not degraded (Cogulet et al., 2018). Coatings made of linseed oil (OO0, AS0, AOT, ASU) and those that were mainly polymer (made from natural oils, fatty acids and resins) had different photostability. According to artificial weathering studies, linseed oil has an early stage of photodegradation, where the oxidation of triglycerides, autoxidation of unsaturated fatty acid components, formation of conjugated unsaturations, and the development of extensive cross-linking takes place. In the next phase, the labile cross-links are consumed, and a network with higher stability is formed with unreacted triglycerides and low molecular weight molecules formed by fragmentation. After years of ageing, a progressive oxidation of the alkylic segments take place, leading to partial fragmentation and growth of oxygenated groups (Kataoka et al., 2007). Linseed oil provides nutrition for mildew which is especially discernable on hornbeam samples. In wet and damp areas, when coated with oil, acetylated hornbeam is likely to be attacked by mildew (Mohebby and Saei, 2015).

The high photostability of coatings BS0, BSP, and BSR is probably due to its pigments, fillers, and additives like vegetable-based emulsifier, lead- and barium-free stabilizers and drying agents, methyl cellulose, film treaters (3-iodine-2-propynyl butylcarbamate (max. 0.2%), and 2-octyl-2H-isothiazol-3-one (<0.01%)). Their film thickness was also somewhat greater compared to other coatings, but this was not measured in this study.

The color of wood irradiated for 200 hours with xenon lamp was obtained in less than 1 month of weather exposure (in this testing field, in April 2018) (Table A42). Compared to irradiation, the color changed similarly only in the first months of weathering as a* and b* increased. After that, a* and b* was reduced due to leaching and graying caused by weather conditions. All the acetylated samples had the same or similar color after 200-h-long irradiation as one-month-long weather exposure, which suggests 3–4 times faster aging. The results of untreated hornbeam varied. In many cases, only L* was similar because a* and b* changed in different ways.

A similar research study reported strong linear relationships between the first 70 days of natural sunlight to 60 h under artificial xenon light irradiation (180 W/m^2), suggesting a 30 times faster aging process in the artificial xenon light. After that, the linear relationship vanished (Liu et al., 2019). The results of color changes show that among the weathering factors, sunlight (UV radiation) caused the greatest color and surface changes. Irradiating with a mercury vapor lamp or a xenon lamp can help to study the photodegradation mechanism in wood and provide results in shorter time. On the other hand, laboratory tests cannot precisely predict the level of color change caused by sunlight (Tolvaj and Mitsui, 2005; Kržišnik et al., 2018).

FTIR studies confirmed that during the photodegradation of acetylated hornbeam caused by mercury-vapor lamp irradiation, the absorption of functional groups in lignin decreased. On the other hand, functional groups of methane, methylene, methyl and carbonyl groups had greater absorption. The rate of degradation and structural changes were higher in acetylated hornbeam than untreated hornbeam, but the strengthening polymers did not degrade notably. Transformation and degradation of lignin and extractives resulted in the color brightening of acetylated hornbeam. This is confirmed by our results, where acetylated hornbeam had greater color difference values, but it was more dimensionally stable, more durable and less susceptible to structural changes caused by weathering (Chapter 6).

7.4. Conclusions

According to the results of the present study, acetylation decreased the non-film forming coating uptake of hornbeam, which could lead to lower photostability properties. On the other hand, the coating system demonstrated better quality due to the lower dimensional stability of acetylated hornbeam. These findings corresponded to literature. Thus, longer service life is achieved, and less maintenance is required with the use of acetylated hornbeam wood. The color of acetylated hornbeam is not photostable. As was the case during ultraviolet degradation, it also undergoes chemical changes that results in surface brightening and eventual graying outdoors. This was the result of the degradation and transformation of lignin and extractives, together with leaching caused by rain and wasp stripping. Coating systems can hinder the effects of photodegradation, but long-lasting results require regular maintenance. Dark pigmented stains last longer and have a lower color difference compared to the initial color. However, they cover and hide the wood grain more than colorless and brighter pigmented coatings do.

Among the tested colorless coatings, Biopin colorless stain provided the most photostable coating film. Among all tested coatings, Auro umbra-colored stain and Biopin Swedish red-colored stain obtained the best results. We recommend using these coatings (or those with similar properties) to finish products made from acetylated hornbeam wood in order to have long-lasting color during its service life.

Color change was greater with the xenon lamp irradiation than with the mercury vapor lamp irradiation because the xenon lamp possessed higher radiant power density. In acetylated samples, 3-4 times faster aging was achieved, because the results after 200-hour-long irradiation and after one month of weather exposure (April to May 2018) were the same or similar. Oli-natura colorless oil and Auro colorless stain had no significant effect on the photostability of hornbeam and acetylated hornbeam wood. Based on these findings, irradiating with a xenon lamp can help manufacturers and users predict the color change of acetylated hornbeam wood under similar exposure conditions as in this research.

Chapter 8. Acetylated hornbeam as a product

The supply of European hornbeam was examined in Paragraph 1.5, where the price and amount per country was listed. This list indicates that the most optimal countries (price, amount and distance from acetylation plant) to acquire 3 or 4-sides-clear hornbeam boards could be France, Germany and Poland. To ease procurement, it could be obtained from the same place where beech is obtained by the plant (Schwarzwald, Germany). Romania and Iran have large quantity of hornbeam as well, but the transportation makes the material more expensive. In order to make precise conclusion and decision in this regard, material, insurance and transporting costs need to be calculated and compared. As hornbeam of Hungarian origin was tested, the material properties may vary depending on the site conditions.

The price (range) of acetylated hornbeam wood would be the same as Accoya®, because the raw material is similar or cheaper than the raw material used for Accoya® radiata pine, beech or alder production (Paragraph 1.3, Table A28, Table A30). Hornbeam has similar density and pore-structure to beech, it can be optimized to similar acetylation settings.

The properties of acetylated hornbeam are similar to acetylated beech, and in some cases, even better. It has lower water uptake and greater MOR, MOE, and hardness (Paragraph 1.8). It was acetylated with process parameters optimized for Radiata pine, which means these properties can be improved further with process parameters optimized for hornbeam wood.

Based on the results of this dissertation, acetylated hornbeam can be used in Use Classes 1, 2, and 3 according to EN 335: 2013 (Table A23, Table A24). It can be classified possibly in even higher use classes as well, if resistance to termites (UC 4) and marine borers (UC 5) had been examined (Paragraph 1.4).

Product groups of acetylated hornbeam may include: indoor furniture (P1), floor and non-structural interior uses (P2), exterior joinery (P3), decking (P5), fencing (P6). It could possibly be used for outdoor furniture (P7), and in-ground timber (P9), but less likely for cladding (P4) and some construction elements (P8) due to its high density. Construction elements of acetylated hornbeam can be steps, stairs, flooring, and thresholds, etc. On the other hand, acetylated wood is less promoted for indoor utilization due to its smell of acetic acid, especially when uncoated.

In a report on the life cycle assessment (LCA) of Accoya® Radiata pine, Scots pine, and beech (Vogtländer, 2010), acetylated beech generally has lower ecocosts of emissions (EUR/m^3) compared to Accoya® Radiata pine. On the other hand, beech raw material grows more slowly, having about one-third of Radiata pine's mean annual increment (m^3/ha/yr). As it is sourced in Germany, only a truck is needed for transportation, no sea transport is required as for Radiata and Scots pine. The expected life span of acetylated beech decking was estimated to be 35-37.5 years without maintenance, higher than Accoya® Radiata pine and Scots pine decking (25 years) due to its lower hardness. The Service Life Planning (SLP) of Accoya timber window frames revealed that the estimated service life (ESL) was between 77 and 90 years, depending on exposure conditions (Menzies, 2013). This value is greater than that of timber treated with preservatives and PVC-U (polyvinyl chloride) windows. Further studies regarding is embodied energy (EE) and global warming potential (GWP) data from forest to factory gate were examined according to published environmental product declarations (EPD) (Hill et al., 2021). The GWP could be lowered in many ways, particularly when European-sourced wood was used. However, care should be taken with life cycle analysis and whole life costs, as the data could be manipulated to give the desired result (Jones et al., 2009).

SWOT analysis (Strengths, Weaknesses, Opportunities, Threats) of acetylated hornbeam was established in Table 20 , based on Jones (2007) and Gamache and Espinoza (2017).

Table 20. SWOT analysis of acetylated hornbeam.

Strengths	**Weaknesses**
- hornbeam regenerates easily, has good shade tolerance and at young age grows faster than oaks - high dimensional stability - high hardness - homogeneous modification throughout cross sections - good mechanical properties in wet conditions - enhanced durability indoors and outdoors, in and above ground - use of native European, deciduous, underutilized species - sustainable, from sustainably managed forests - similar color to tropical species - extended maintenance intervals for coatings - stores CO_2 for many years (not firewood) - recyclable - barefoot-friendly	- dependency on timber supplies - lower availability of timber in adequate quality, size and quantity, from on region - not common practice and goal to produce high-quality hornbeam logs - hornbeam is regarded as firewood - storage and drying of hornbeam has to be done with great care due to risk of splitting, twisting and low durability - treatment adversely affected dynamic material strength, photostability (or patina), and flexibility - heavy compared to competitors - smell of acetic acid - limited or no long-term performance data - lack of dedicated standards - limited public perception, low awareness - lack of knowledge in market and manufacturers - high investment costs in equipment - high cost of modified wood - potential for waste due to wood splitting
Opportunities	**Threats**
- increasing species diversity and stability by growing more hornbeam - increasing consumer preference for environmentally-friendly products - growing concerns over use of toxic chemicals - growing concerns over illegal logging - recovery of markets lost to wood - establishment of new markets for wood - greater use of FSC timber (or equivalent) - increased liaison with affiliated industries - potential market of high-end users preferring high-quality high-end products - competitive price compared to tropical species - growing preference for low-maintenance materials for decking products	- supply and cost of wood and chemicals - unfavorable climate change scenarios - aggressive marketing of competing materials - customers not willing to change - new cheaper products entering the market

The main competitors of acetylated hornbeam are:

- Naturally high-durability (mainly) tropical wood species: A number of them have outstanding physical, mechanical, and durability properties, which makes a huge demand for them worldwide. In Europe alone, more than 6 million m^3 of tropical timber is sold per year. They are used mainly for furniture (26%), windows (26%), doors (16%), stairs (6%), flooring (3%), and other uses, like decking (6%). However, the consumption of tropical wood species is not sustainable from an environmental perspective (Larsson-Brelid, 2013).
- Preservative (copper-) impregnated wood: The most common method to protect wood from biological degradation, approximately 6 million m^3 of preservative treated wood is produced in Europe per year. The demand is rather for its low price rather than its performance.

  The reduction of its market share could be achieved by an environmental tax, bans, or restrictions on copper (Larsson-Brelid, 2013). Pressure treated lumber is usually chosen by users because of its affordability and high availability (Gamache and Espinoza, 2017).

- Wood-plastic composites (WPC): WPC consists of 50-60% of wood fiber or particles and the rest is a thermoplastic polymer, biocides (usually zinc borate), coupling agents, UV-absorbers, and other additives. The global production is about 1 million m^3 per year. It is used for decking, which is about double or triple cost of preservative treated wood, and it does not have a better carbon footprint either (Larsson-Brelid, 2013; Gamache and Espinoza, 2017). WPC is usually chosen by users because of its low maintenance requirements, high durability, aesthetics and wide availability (Gamache and Espinoza, 2017).
- Further competitors are listed in Figure 63.

Total budget competitors	**Generic competitors**	**Product competitors**	**Direct competitors**
wood-based panels fake grass stairs railing outdoor furniture pergola fence doors and windows	PVC vinyl rubber composite aluminum concrete stone	thermo softwood bamboo charred wood WPC fiber cement	thermo hardwood furfurylated wood naturally durable hardwood tropical hardwood

Figure 63. Competitors, market share of acetylated hornbeam decking.

The range of competitors was defined for a certain product rather than the material itself, as the competitors may vary based on the fields of use. Here, decking was chosen as a realistic product made of acetylated hornbeam, and four groups of competitors have been identified on the market:

- direct competitors: who sell the same products and services to customers by targeting the same goals in the market (e.g. furfurylated wood decking)
- product and brand competitors: who sell similar products and services to customers, having similar features, benefits and uses for customers, but prices are comparable (e.g. WPC decking);
- generic competitors: who sell completely different products and services which satisfy the similar needs of customers as their competitors’ products do (e.g. composite decking);
- total budget competitors: who sell completely different products and services in the same price range, where customers use the same amount of money, and it matters where the customer spends it (e.g. stairs).

One of the main advantages of modified wood is its sustainability, thus meeting the European and national regulations on wood protection (The European Construction Products Directive (CPD) (1988) 89/106/EEC, The Biocidal Products Directive (BPD) (1998) 98/8/EC, The EU Marketing and Use Directive for Arsenic (76/769/EEC), BPD and focus on end-of-life disposal issues, national approvals and certification for treated wood and wood treatments, European Standards Committees (CEN) and International standards committees).

Acetylated hornbeam, and modified wood in general, needs to find its niche market, where it is appreciated, and recognized as a superior product. It can even enter new non-wood markets as well. Once the general public sees the use of modified wood in niche markets, the chance of market diversification increases. It is important to keep in mind that modified wood is not a replacement for preservative-treated wood; it is ideally a replacement for non-timber materials. In order to reach wider markets, there needs to be collaboration with timber companies in affiliated sectors, like the Finnish ThermoWood Association. Examples of where other partners may provide necessary expertise are in timber supply, transportation, sales, marketing, coating, and maintenance (Jones et al., 2009).

Some key performance indicators of materials, all or most of which are necessary to be accepted as a suitable material for use: fire retardancy, flammability, biological durability, dimensional stability, color stability, weathering resistance, hardness, abrasion resistance, workability, mechanical properties, and appearance (Jones et al., 2009). Properties underlined characterize acetylated hornbeam.

For non-wood materials, the higher volume of operation has led to reduced prices, which is difficult for modified wood to compete against. Customers mainly decide on the suitability of products by their quality and unit price. Thus, modified wood, including acetylated hornbeam, should aim for niche markets. Later, as the production levels and availability increase, the price can gradually decrease, but still remain in the price range of tropical hardwoods. Here, the longer service life (cradle to grave life) can be emphasized, with the opportunity to extend it by regular maintenance cycles. Unlike preservative-treated wood, it is not contaminated waste, it can be reused, recycled, composted, or burned at the end of its life. This means there is lower volume of material disposed, less product enters landfills, and less resource is wasted (Jones et al., 2009).

The properties of acetylated hornbeam can be compared to those of other common materials used for decking (Table 21) (Material Properties, 2023). Acetylated hornbeam – as other natural wood – absorbs less heat, which is favorable e.g. to go barefoot on decking and stairs. It also has better strength to density ratio than concrete, porcelain, PVC, and rubber. Its hardness is comparable to some other commonly used materials as well.

Table 21. Properties of acetylated hornbeam and other commonly used materials (Material Properties, 2023).

	Acetylated hornbeam	Aluminum (AL 6061)	Concrete	Porcelain	PVC	Rubber
Density (kg/m3)	660 – 825 – 870	2700	2400	2400	1220	1100
Strength (compression) (MPa)	84	290	2	29	48	5
Strength/density ratio	0.103	0.107	0.001	0.012	0.039	0.005
MOE (GPa)	15	69	60	n/a	3.4	0.05
Brinell hardness (MPa)	39-50-101	105	-	-	35	n/a
Mohs scale mineral hardness	-	-	6	7	-	-
Thermal conductivity (W/m.K)	0.230 (untreated)	150	0.5	1.5	0.2	0.5

There were attempts to utilize acetylated hornbeam and design products of it during this research, which are shown in Appendix 2. Based on its improved dimensional stability and durability, a knife handle (Figure A97), a pack of beach toys (Figure A98), and an outdoor bench was made (Figure A99) in 2022 through collaborations. The description of these prototypes are not elaborated here.

Chapter 9. Summary

In the past decades, there has been an increased awareness of the fragility of the environment. Sustainable forestry, using native wood species and minimizing transportation are just part of the solutions for reducing greenhouse gas emissions. Many European wood species, including hornbeam (*Carpinus betulus* L.), have low natural durability which makes them unable to be used for exterior applications without additional protection. For decades, this has been done using biocide preservatives which are toxic for both environment and humanity. Today, non-toxic methods are preferred for wood preservation, among which are the wood modification methods, including acetylation.

In previous work, European hornbeam wood was industrially acetylated in order to improve its properties and widen its usage. There were promising results concerning its physical and mechanical properties. In this work, its product-related properties were targeted in order to evaluate its potential in the market. An extensive literature research was thoroughly carried out on the availability and future of European hornbeam wood, from both the forestry and wood industry point of view. A distribution map was drawn according to standing stock information on hornbeam in the world. Then, the current state of research was explained regarding the modification of this species. This investigation about improving the properties of hornbeam wood by industrial acetylation has been a unique form of research since 2014.

Chemical investigation showed that the proportional increase of the hemicellulose content (+11.10%) was compensated for by the decrease of cellulose (-8.55%) and of lignin (-2.86%) contents. The extractive content increased to 1.91%, while the pH decreased to 4.73. HPLC analysis, which monitors main indicators of cleavage and breakdown products, determined that during the acetylation of hornbeam wood it is the hemicellulose fraction that gets acetylated and which is primarily responsible for the WPG, while it slightly degrades. The structure of lignin is altered as an effect of heat and the acidic medium and is also possibly acetylated to a small extent. The slightly darker, walnut-like color of acetylated hornbeam was due the alterations in the structure of lignin (oxidation, reaction with furfural) as well as the increase of the extractive content. According to Fourier Transform Infrared Spectroscopy studies, the increase of absorption of methine (CH), methylene (CH_2) and methyl (CH_3) groups at 2970 cm^{-1} is due to the exchange of OH groups (WOOD-OH) into acetyl groups (WOOD-O-C(=O)-CH_3), which corresponds to the decrease of moisture sorption in acetylated hornbeam. The hemicellulose fraction was acetylated by the higher absorption of the C=O (carbonyl) groups at 1769 cm^{-1} and of the C-O stretching at 1270 cm^{-1} in xylan. The absorption of the conjugated carbonyl groups at 1597 cm^{-1} decreased slightly in the acetylated wood, probably due to minor degradation of xylans in the acidic medium. Lignin degraded during acetylation by decrease of the aromatic skeletal vibration in syringyl at 1597 cm^{-1} and guaiacyl lignin at 1505 cm^{-1}, of the asymmetric C-H deformation in lignin at 1464 and 1432 cm^{-1}, and of the aromatic C-H skeletal vibration at 1136 cm^{-1}. As the total phenolic content decreased, the real decrease of the lignin content is only minor, and changes in the FTIR spectra indicate only internal structural changes of the lignin matrix. FTIR studies of lignin samples also confirmed this. During UV irradiation of acetylated hornbeam, the absorption of functional groups in lignin at ~1600, 1500, 1470, 1270, 1150 cm^{-1} decreased while that of methane, methylene, methyl and carbonyl groups increased at ~2900 cm^{-1}. The rate of degradation and structural changes were highest in acetylated samples, but the strengthening polymers did not notably degrade.

When preparing microscopy sections, the cutting of smooth, undamaged sections of acetylated hornbeam was possible only after swelling and softening in acetone, not water as in untreated wood. Successful acetylation was confirmed by minimal staining effect of safranin. Acetylation did not damage the wood microstructure and increased the cell-wall thickness by 7.0%.

Although the increase was statistically significant, it was too small to be visible in the micrographs. The pits of acetylated hornbeam were much narrower, probably due to permanent cell-wall swelling. New brown deposits were found in parenchyma cells of acetylated hornbeam. Each cell contained a small amount of an insoluble substance, which led to the hypothesis that a natural component of the living cells became insoluble during acetylation. Microscopic studies showed that fungi were able to colonize acetylated cell lumina without visible degradation and mass loss (~1%) in laboratory studies against *Coniophora puteana, Rhodonia (Poria) placenta,* and *Trametes (Coriolus) versicolor.* In soil burial tests, one acetylated hornbeam stake out of 12 was attacked locally by brown rot decay according to visual and microscopical studies. It had lower acetyl content which was confirmed by FTIR. This locally decayed acetylated hornbeam stake lost 6% of mass in 5.5 years, while untreated hornbeam, beech, and Scots pine had 23-39% of mass loss and broke in 6 years or less. The other acetylated hornbeam stakes are still in the soil for further testing, without any signs of decay or insect damage so far.

Hornbeam became more hydrophobic after acetylation. Its surface energy decreased from 64 to 55 mJ/m^2, due to the decrease of polar component. The dispersive component did not change. The water contact angle increased by 18° after acetylation. There was no significant difference between the wettability of radial and tangential surfaces. The shear strength of the conditioned samples decreased after acetylation, but due to its lower water uptake, acetylated hornbeam exhibited enhanced shear strength after soaking in cold water, and boiling water compared to untreated hornbeam. Similar to the shear tests, acetylated hornbeam retained its bonding strength after soaking in cold water and boiling water, unlike untreated hornbeam. PUR adhesive had better results than PVAc adhesives, and it is more optimal to be used with acetylated hornbeam. During microscopy studies, the higher PUR bonding strength of acetylated hornbeam wood was due to the lack of overpenetration, while it had lower PVAc bonding strength due to overpenetration. With overpenetration, high maximum penetration values are obtained, while the effective penetration values (which affect bonding strength more) are lower.

Acetylated hornbeam undergoes surface brightening during UV irradiation, and eventual graying outdoors, which results in a “natural patina” of wood. During graying of acetylated hornbeam, the lightness (L*) increased, while red (a*) and yellow (b*) hue decreased, which was due to transformation of the extractives and degradation of the lignin, which were leached out during weathering. Acetylated hornbeam resisted dimensional changes caused by changing climate and precipitation, but it was susceptible to wasp stripping and was stained by mold during weather exposure as untreated wood, but to a lower extent. The color change of acetylated hornbeam irradiated with a xenon lamp was greater than with a mercury-vapor lamp due to its higher radiant power density. The color achieved in 200 hours of aging was achieved in one month or less when exposed to weather. For hornbeam, the absorbance of tested coatings decreased after acetylation due to its lower water uptake. The photostability was improved by coating with dark stains for at least two years. On the other hand, colorless stains, and colorless or colored oils did not have a long-lasting effect on its photostability.

According to these results, acetylated hornbeam was characterized further in the discussions. Its price range was expected to be the same as Accoya®, its properties were similar or better than acetylated beech. It was classified in Use Class 1-3 according to EN 335:2013. Its product groups were identified as indoor furniture (P1), flooring and non-structural interior uses (P2), exterior joinery (P3), decking (P5), and fencing (P6). SWOT analysis was established, its competitors were identified, and its position on the market was extensively described.

Chapter 10. Novel findings

There are seven novel findings of this dissertation, which are listed below. They were published in research articles, trade articles and conference papers, which are listed in Appendix 3.

Thesis 1. The chemical structure of hornbeam after acetylation

I concluded that the proportional increase of the hemicellulose content (+11.10%) was compensated by the decrease of cellulose (-8.55%) and of lignin (-2.86%) contents. I proved that the extractive content increased to 1.91% and the pH decreased to 4.73. I concluded that the slightly darker, walnut-like color of acetylated hornbeam was due to the alterations in the structure of lignin (oxidation, reaction with furfural) as well as the increase of the extractive content. By HPLC analysis, I concluded that during the acetylation of hornbeam wood it is the hemicellulose fraction that gets acetylated and which is primarily responsible for the WPG, while a slight degradation also occurs to it.

Thesis 2. FTIR studies of chemical changes after acetylation, and after UV irradiation

I proved that the increase of absorption of methine, methylene and methyl groups at 2970 cm^{-1} is due to the exchange of OH groups into acetyl groups, which corresponds to the decrease of moisture sorption in acetylated hornbeam. I proved that the hemicellulose fraction was acetylated by the higher absorption of the C=O (carbonyl) groups at 1769 cm^{-1} and of the C-O stretching at 1270 cm^{-1} in xylan. The absorption of the conjugated carbonyl groups at 1597 cm^{-1} decreased slightly in the acetylated wood, probably due to a minor degradation of xylans in acidic medium. I proved that lignin degraded during acetylation by decrease of the aromatic skeletal vibration in syringyl at 1597 cm^{-1} and guaiacyl lignin at 1505 cm^{-1}, of the asymmetric C-H deformation in lignin at 1464 and 1432 cm^{-1}, and of the aromatic C-H skeletal vibration at 1136 cm^{-1}. I proved that as the total phenolic content decreased, the real decrease of the lignin content is only minor, and changes in the FTIR spectra only indicate internal structural changes of the lignin matrix. FTIR studies of lignin samples also confirmed this finding.

I concluded that during UV irradiation of acetylated hornbeam, the absorption of functional groups in lignin at ~1600, 1500, 1470, 1270, 1150 cm^{-1} decreased while that of methane, methylene, methyl and carbonyl groups increased at ~2900 cm^{-1}. The rate of degradation and structural changes were the highest in case of acetylated samples, but the strengthening polymers did not degrade significantly.

Thesis 3. Microscopic studies of acetylated hornbeam

I concluded that the cutting of smooth, undamaged sections of acetylated hornbeam was only possible after swelling and softening in acetone, not water as in case of untreated wood. I proved that native hornbeam wood was sufficiently acetylated due to the minimal staining effect of safranin. I concluded that acetylation did not damage the wood microstructure and increased the cell-wall thickness by 7%. The pits of acetylated hornbeam were much narrower, due to permanent cell-wall swelling. I found new brown deposits in parenchyma cells of acetylated hornbeam. Each cell contained a small amount of an insoluble substance, which led to the hypothesis that a natural component of the living cells (e.g. lignans) became insoluble during acetylation.

Thesis 4. Durability of acetylated hornbeam in field test

In a long-term field test, acetylated hornbeam exhibited high resistance against fungal decay, mold, insects, and moisture, while control samples of hornbeam, beech and Scots pine failed after 0.5-6 years with 23-39% of their mass lost. The remaining acetylated hornbeam stakes are still in the soil for further testing, without any signs of decay or insect damage up to this point. Microscopic studies showed that fungi were able to colonize acetylated cell lumina in field test studies and in laboratory studies against *Coniophora puteana*, *Rhodonia (Poria) placenta,* and *Trametes (Coriolus) versicolor.*

Thesis 5. Wetting, shear strength and bonding strength of acetylated hornbeam

I proved that acetylated hornbeam is less wettable, its surface energy decreased from 64 to 55 mJ/m^2, due to the decrease of the polar component. The dispersive component did not change. The water contact angle increased significantly by 18° after acetylation. I proved that there is no significant difference between the wettability of radial and tangential surfaces. I proved that the shear strength of conditioned samples decreased after acetylation, but due to its lower water uptake, acetylated hornbeam exhibited significantly enhanced shear strength after soaking in cold and boiling water, compared to untreated hornbeam. I proved that acetylated hornbeam retained its bonding strength after soaking in cold and boiling water, unlike untreated hornbeam. I concluded that PUR adhesive had better results than PVAc adhesives, and it gave better results when used with acetylated hornbeam. I proved during my microscopic studies that the higher PUR bonding strength of acetylated hornbeam wood was due to the lack of overpenetration, while it had lower PVAc bonding strength due to overpenetration. With overpenetration, high maximum penetration values are obtained, while the effective penetration values (which affect bonding strength more) are lower.

Thesis 6. Color stability of acetylated hornbeam exposed to UV irradiation

I proved that acetylated hornbeam undergoes surface brightening during UV irradiation, and eventual graying outdoors. I proved that during graying of acetylated hornbeam, the lightness (L*) increased, while red (a*) and yellow (b*) hue decreased. I concluded that it was due to transformation of extractives and degradation of lignin. These breakdown products were leached out during weathering. I proved that acetylated hornbeam resists dimensional changes caused by changing climate and precipitation, but it is susceptible to wasp stripping and can be stained by mold during weather exposure, but to a lower extent than untreated wood. The color resulted in 200 hours of aging was achieved in one month or less when exposed to weather.

Thesis 7. Coating of acetylated hornbeam to improve color stability

I proved that the coating absorbance of hornbeam decreased after acetylation due to its lower water uptake. I proved that its photostability can be largely improved by coating it with dark stains like Auro Wood stain No. 160 or Biopin Weather Protection Stain (for at least two years). On the other hand, colorless stains, and colorless or colored oils did not have a long-lasting effect on its photostability. Oli-Natura colorless oil and Auro colorless stain had no significant effect on the color stability under tested conditions.

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APPENDICES

Appendix 1. Supplementary materials

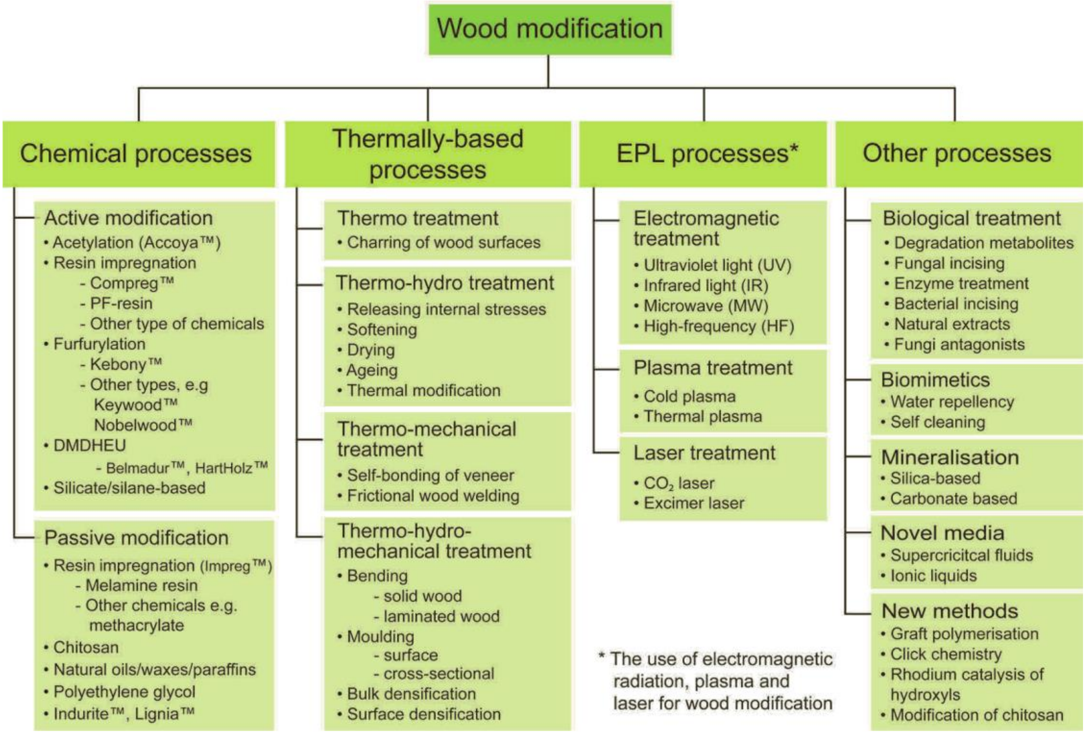


Figure A64. Classification of wood modification processes (Sandberg et al., 2021). The trademark of a process is marked with the ™ sign in general.

Table A22. Properties of Accoya® Radiata pine wood (Accsys PLC, 2020).

Durability (EN 350, EN 113, ENV 807)	Class 1
Density (65% RH 20°C)	515 ± 80 kg/m^3
Shrinkage (wet to 65% RH 20°C)	0.4% (radial), 0.8% (tangential)
Shrinkage (wet to oven dry)	0.7% (radial), 1.5% (tangential)
Equilibrium moisture content (65% RH 20°C)	3-5%
Thermal conductivity (EN 12667)	0.12 W/m·K
Janka hardness (ASTM D143)	4,100 N (side), 6,600 N (end)
Brinell hardness (EN 1534)	24.0 N/mm^2

Table A23. Overview of Use Classes (UC), as defined according to EN 335:2013, and typical ranges and their associated risks according to the WPA report (WPA, 2012).

Use Class	Biological risk	Typical service exposure	Examples of product ranges
UC 1	Insect	Internal, with no risk of wetting.	All timbers in normal pitched roofs except tiling battens and valley gutter members.
UC 2	Fungi/Insect	Internal, with risk of occasional wetting.	Floorboards, architraves, internal joinery, skirtings. All timbers in upper floors not built into solid external walls.
UC 3.1	Fungi/Insect	External, above damp-proof course, coated.	Tiling battens, frame timbers in timber frame houses, timber in pitched roofs with a high condensation risk, timbers in flat roofs, ground floor joists, sole plates (above the damp proof course), timber joists in upper floors built into external walls.
UC 3.2	Fungi/Insect	External, above damp-proof course, uncoated.	External joinery including roof soffits and fascias, barge boards, etc., cladding, valley gutter timbers, external structural load-bearing timbers.
UC 4	Fungi/Insect (incl. termites)	Timbers in permanent contact with the ground or below a damp-proof course. Timbers in permanent contact with fresh water. Cooling tower packing. Timbers exposed to the particularly hazardous environment of cooling towers.	Cladding, fence rails, gates, fence boards, agricultural timbers not in soil/manure contact and garden decking timbers that are not in contact with the ground.
UC 5	Marine borers/Fungi	All components with permanent contact with sea water.	Fence posts, gravel boards, agricultural timbers in soil/manure contact, poles, sleepers, playground equipment, motorway and highway fencing/sound barriers and garden decking timbers that are in contact with the ground. Lock gates and canal linings. Cooling tower infrastructure (fresh water).

Table A24. Product groups and their associated Use Classes (UC), modified based on WPA report (WPA, 2012; Jones and Sandberg, 2020).

Group	Identifier	Use Classes					
P1	Indoor furniture	UC 1					
P2	Floor and non-structural interior uses	UC 1	UC 2				
P3	Exterior joinery			UC 3.1	UC 3.2		
P4	Cladding			UC 3.1	UC 3.2		
P5	Decking			UC 3.1	UC 3.2		
P6	Fencing			UC 3.1	UC 3.2		
P7	Outdoor furniture			UC 3.1	UC 3.2	UC 4	
P8	Construction elements			UC 3.1	UC 3.2	UC 4	
P9	In-ground timber					UC 4	
P10	Products exposed to water					UC 4	UC 5

Table A25. Application of different wood modification methods into products in different Use Classes (UC) (Jones and Sandberg, 2020). Green indicates that the modified wood has been commercially demonstrated in that Use Class, and yellow marks that it can be according to research studies.

Modification	UC 1	UC 2	UC 3.1	UC 3.2	UC 4	UC 5
Acetylation	🟨	🟩	🟩	🟩	🟩	🟨
Thermal modification	🟨	🟩	🟩	🟩		
Compreg-type	🟩	🟩	🟩	🟩		
Impreg-type	🟩	🟩	🟩	🟩	🟩	
Kebony®, Nobelwood®	🟨	🟩	🟩	🟩	🟩	🟨
DMDHEU (Belmadur®/Hartholz™)	🟨	🟨	🟩	🟩		
Silicates and silanes		🟩	🟩	🟩		
Chitosan			🟨	🟨		
Inudrite™/Lignia®		🟩	🟩	🟩	🟩	🟨
Oil/wax		🟨	🟩	🟩		
PEG	🟩	🟨				

Table A26. Availability in the world: Hornbeam forests and wood price in 2022 spring.

Country	Price (EUR/m^3)	Coverage (K ha)	Standing stock (m m^3)	Harvested volume (K m^3/yr)
Armenia	N/A	N/A	0.45	N/A
Luxembourg	1280	N/A	0.73	N/A
Albania	N/A	N/A	1.98	N/A
Belarus	N/A	N/A	3.00	N/A
Republic of Moldova	500	N/A	3.13	N/A
Belgium	N/A	N/A	3.30	N/A
Turkey	N/A	20	2.00	N/A
Czech Republic	735	35	5.37	106
Austria	310	<69	9.00	205
Sweden	N/A	71	9.00	252
Slovenia	N/A	<88	9.89	62
Hungary	400-600	97	18.28	168
Serbia	N/A	119	21.00	N/A
Georgia	N/A	N/A	24.60	N/A
Slovakia	460	116	25.42	408
Azerbaijan	N/A	184	26.22	N/A
Bulgaria	560	157	29.40	N/A
Croatia	260	238	34.65	682
Poland	420	N/A	37.00	N/A
Germany	650-1100	N/A	37.11	N/A
Ukraine	270	208	39.00	N/A
Romania	500	476	113.57	N/A
France	550	587	115.00	731
Iran	N/A	N/A	150.00	N/A

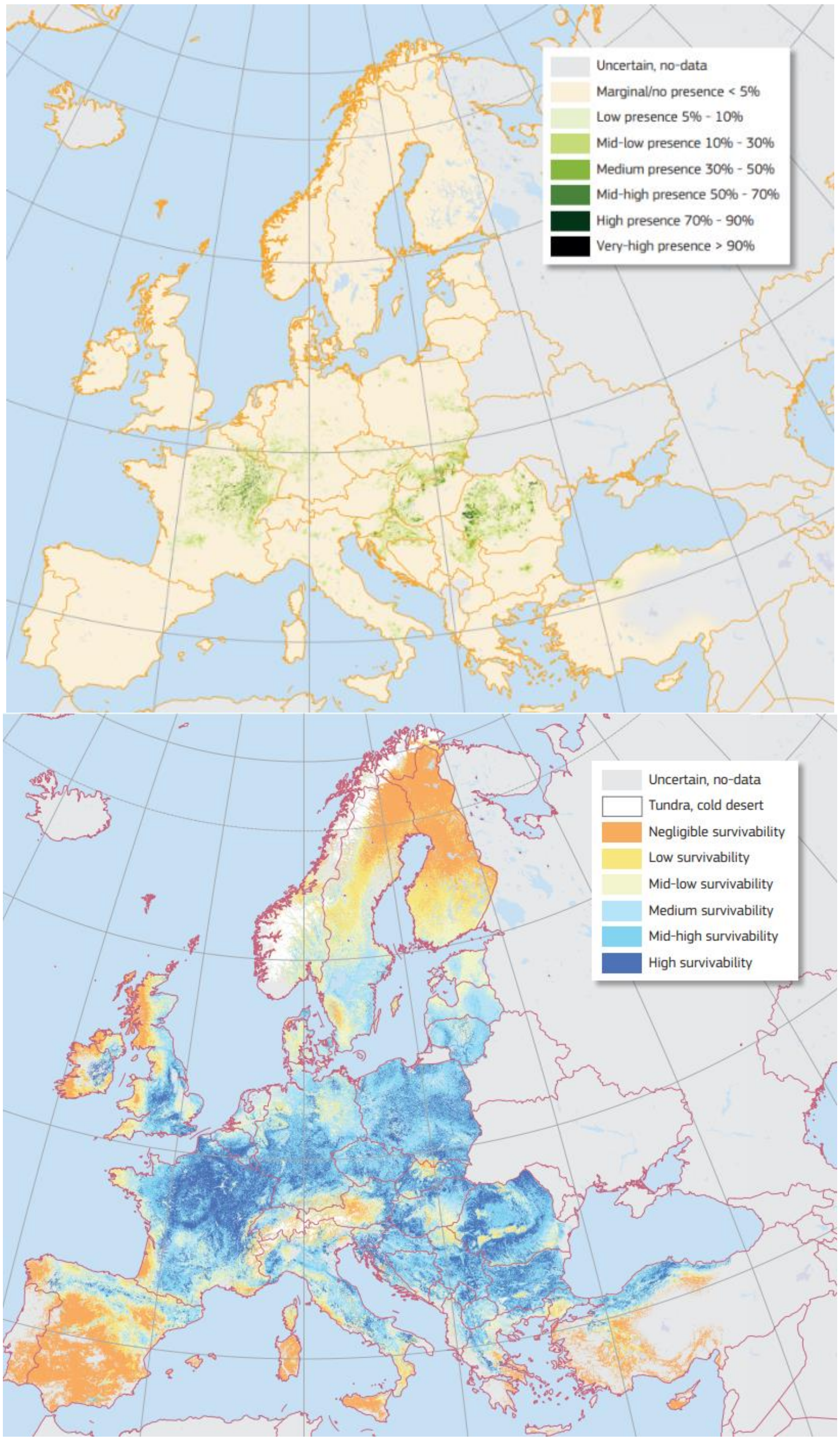


Figure A65. High resolution distribution map estimating the relative probability of presence of Carpinus betulus (up), and the maximum habitat suitability of Carpinus betulus (bottom) (Sikkema et al., 2016).

Table A27. Physical and mechanical (air-dry) properties of hornbeam wood (Molnár and Bariska, 2002).

Density	- oven-dry: 500-790-820 kg/m^3 - air-dry (12% moisture content): 540-830-860 kg/m^3 - green: 660-970-1,200 kg/m^3
Porosity	48 %
Shrinkage	- tangential: 11.5 % - radial: 5.2-6.8 % - longitudinal: 0.5 % - volumetric: 18.8 %
Fiber saturation point	32-35 %
Calorific value	14,467 kJ/kg; 12,008 MJ/m^3 (at 15% moisture content)
Compression strength	54-82-99 MPa
Tensile strength	47-135-200 MPa
Shear strength	8.5-16.0 MPa
Bending strength	58-160-200 MPa
Impact bending or shock strength	8.0-12.0 J/cm2
Cleavage	- radial: 0.62 MPa - tangential: 1.50 MPa
Brinell hardness	- end grain: 71 MPa - side grain: 29-32-36 MPa
Bending modulus of elasticity	7,000-16,200-17,700 MPa

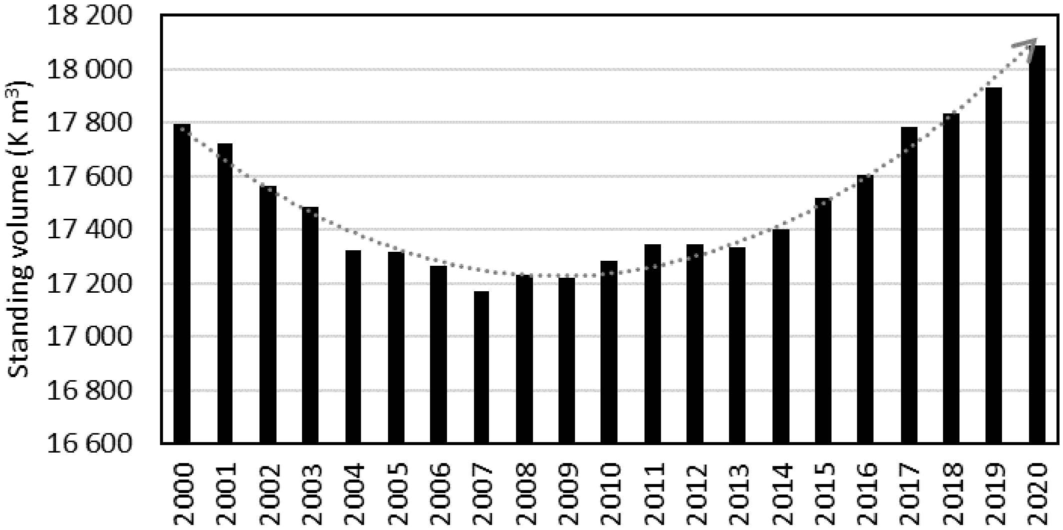


Figure A66. Standing volume of hornbeam timber in Hungary over the past 20 years (NFK, 2021).

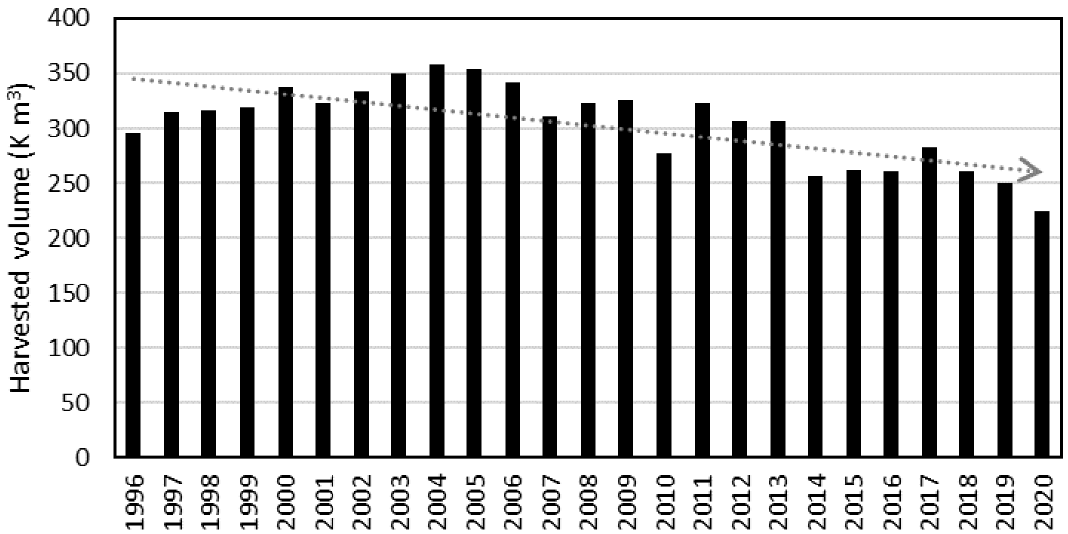


Figure A67. Harvested volume of hornbeam in Hungary (NFK, 2021).

Table A28. Physical properties of untreated (CO) and acetylated (AC) hornbeam, beech and Radiata pine. Average values are given with standard deviation in brackets (Pozsgayné Fodor, 2015). Data for beech and radiata pine were added from Accsys technologies (AT) and related literature (MB, W) (Molnár and Bariska, 2002; Wagenführ, 2007)

Property / Material		Hornbeam		Beech		Radiata pine	
		AC	CO	AC	CO	AC	CO
Moisture content (%)	Fiber saturation point	24 *(2.3)*	37 *(1.9)*	n.a.	32-35 [MB]	n.a.	n.a.
	Equilibrium at 20°C, 65% RH	3 *(0.3)*	10 *(0.5)*	n.a.	n.a.	3-5 [AT]	n.a.
Density (kg/m^3)	Dried	801 *(66.3)*	689 *(15.9)*	n.a.	680 [W]	n.a.	400 [W]
	Conditioned	823 *(53.6)*	761 *(53.5)*	800 [AT]	720 [W]	515 [AT]	510 [W]
	Saturated	982 *(58.2)*	942 *(35.5)*	n.a.	1070 [W]	n.a.	800 [W]
Shrinkage (%)	Radial	1.2 *(0.5)*	6.5 *(0.7)*	1.3 [AT]	5.9 [AT]	0.7 [AT]	2.3 [W]
	Tangential	2.0 *(0.8)*	10.89 *(0.8)*	2.2 [AT]	12.9 [AT]	1.5 [AT]	4.5 [W]
	Longitudinal	0.3 *(0.2)*	0.4 *(0.3)*	n.a.	0.3 [MB]	n.a.	0.3 [W]
Max. water uptake (g/m^2)		4559 *(1035)*	5513 *(1137)*	5,600 [AT]	n.a.	23,442 [AT]	n.a.

Table A29. Average weight loss of untreated and acetylated samples exposed to wood-decay fungi for 16 weeks, with standard deviation in brackets (Pozsgayné Fodor, 2015)

Fungus	Vessel	Sample	Weight loss (%)
Coniophora puteana	Virulence	Untreated	45.64 *(± 3.68)*
	Reference	Untreated	18.58 *(± 1.07)*
		Acetylated	0.84 *(± 0.17)*
Poria placenta	Virulence	Untreated	20.78 *(± 1.54)*
	Reference	Untreated	21.19 *(± 6.61)*
		Acetylated	0.20 *(± 0.21)*
Coriolus versicolor	Virulence	Untreated	34.00 *(± 1.91)*
	Reference	Untreated	32.66 *(± 2.09)*
		Acetylated	0.83 *(± 0.12)*

Table A30. Mechanical properties of untreated (CO) and acetylated (AC) hornbeam, beech and Radiata pine. Average values are given with standard deviation in brackets (Pozsgayné Fodor, 2015). Data for beech and radiata pine were added from Accsys technologies (AT) and related literature (MB, W) (Molnár and Bariska, 2002; Wagenführ, 2007)

Property / Material		Hornbeam		Beech		Radiata pine	
		AC	CO	AC	CO	AC	CO
Compression strength parallel to grain (N/mm^2)		84 *(6.6)*	59 *(4.3)*	n.a.	62[MB]	n.a.	51[W]
Modulus of rupture (N/mm^2)	Conditioned	173 *(25.2)*	144 *(9.8)*	114[AT]	127[AT]	39[AT]	78[W]
	Saturated	141 *(15.2)*	73 *(6.4)*	107[AT]	60[AT]	n.a.	
Modulus of elasticity (kN/mm^2)	Conditioned	15.37 *(1.5)*	15.39 *(1.2)*	12.15[AT]	13.03[AT]	8.79[AT]	11[W]
	Saturated	14.11 *(1.4)*	10.36 *(1.0)*	11.68[AT]	7.81[AT]	n.a.	n.a.
Impact bending strength (kJ/m^2)		159 *(37.0)*	84 *(10.8)*	n.a.	100[MB]	50[AT]	94[W]
Janka hardness (conditioned) (N/mm^2)	Radial	114 *(17.9)*	73 *(4.8)*	79[AT]	71[AT]	41[AT]	28[AT]
	Tangential	124 *(21.4)*	80 *(6.8)*	n.a.	n.a.	42[AT]	28[AT]
	End grain	-	95 *(7.3)*	107[AT]	84[AT]	66[AT]	36[AT]
Janka hardness (saturated) (N/mm^2)	Radial	83 *(10.9)*	39 *(2.9)*	n.a.	n.a.	n.a.	n.a.
	Tangential	105 *(15.3)*	41 *(5.7)*	n.a.	n.a.	n.a.	n.a.
	End grain	-	46 *(3.5)*	n.a.	n.a.	n.a.	n.a.
Brinell hardness (conditioned) (N/mm^2)	Radial	39 *(5.6)*	26 *(2.4)*	n.a.	34[MB]	n.a.	13[W]
	Tangential	50 *(9.1)*	29 *(2.7)*	n.a.		n.a.	
	End grain	101 *(12.7)*	67 *(10.4)*	n.a.	72[MB]	n.a.	n.a.
Brinell hardness (saturated) (N/mm^2)	Radial	32 *(4.7)*	14 *(1.2)*	n.a.	n.a.	n.a.	n.a.
	Tangential	40 *(7.8)*	15 *(1.5)*	n.a.	n.a.	n.a.	n.a.
	End grain	74 *(15.8)*	30 *(3.1)*	n.a.	n.a.	n.a.	n.a.

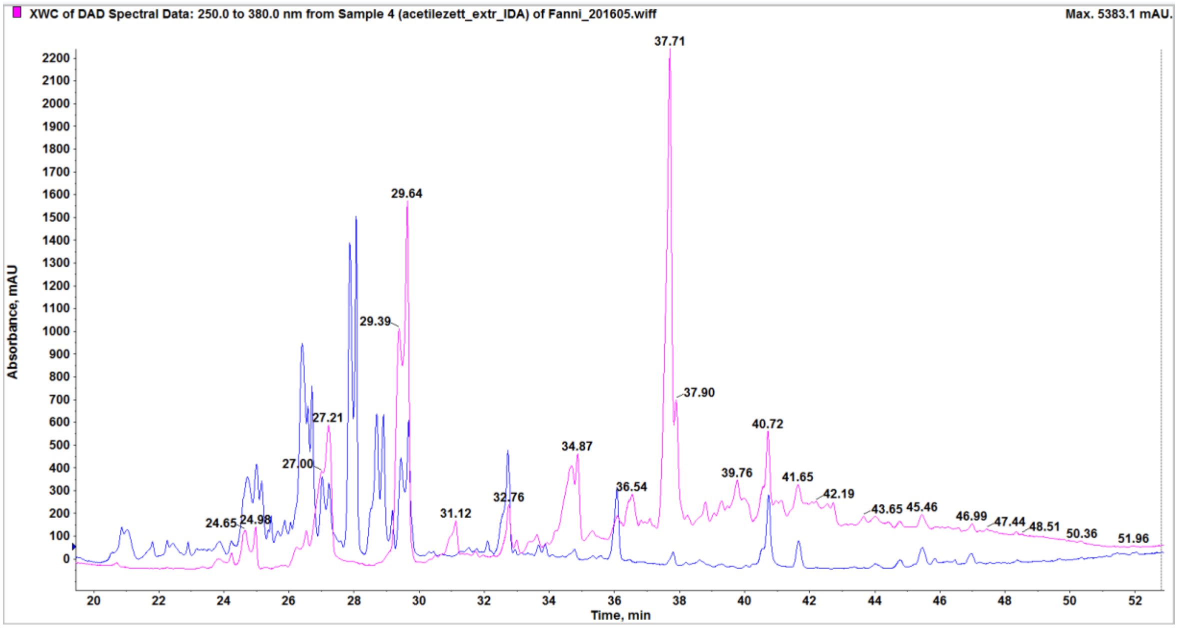


Figure A68. HPLC-PDA (250-380 nm) chromatogram of the untreated (blue) and acetylated (magenta) hornbeam extracts.

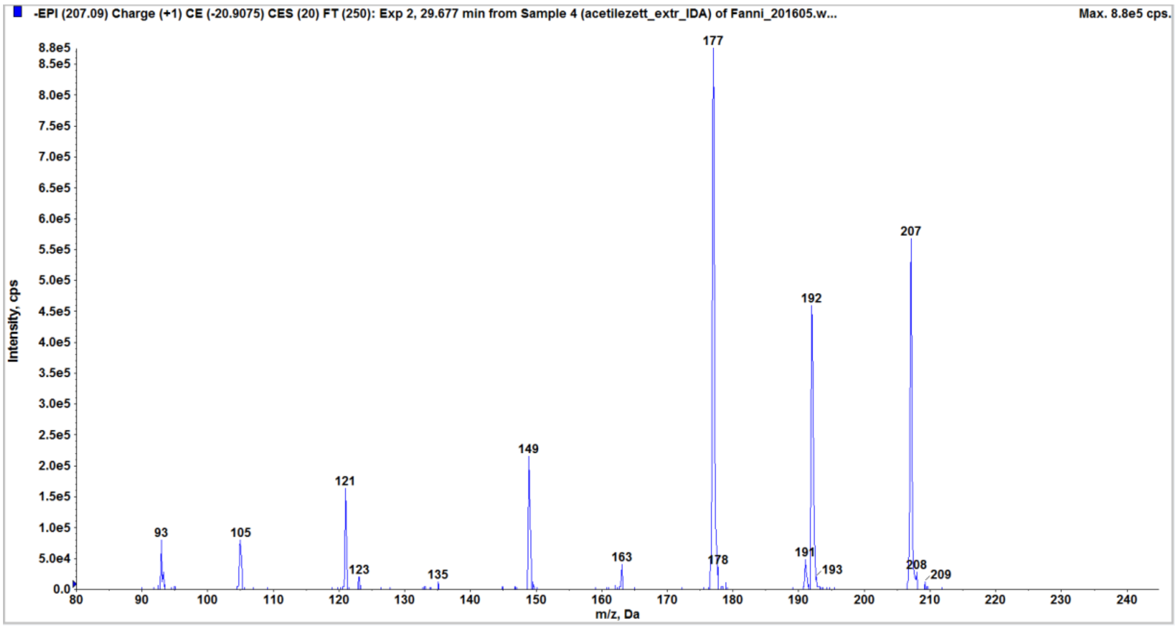


Figure A69. The MS/MS spectrum of the compound at 29.39 and 29.65 min. retention time. The peaks were identified as isomers of sinapaldehyde.

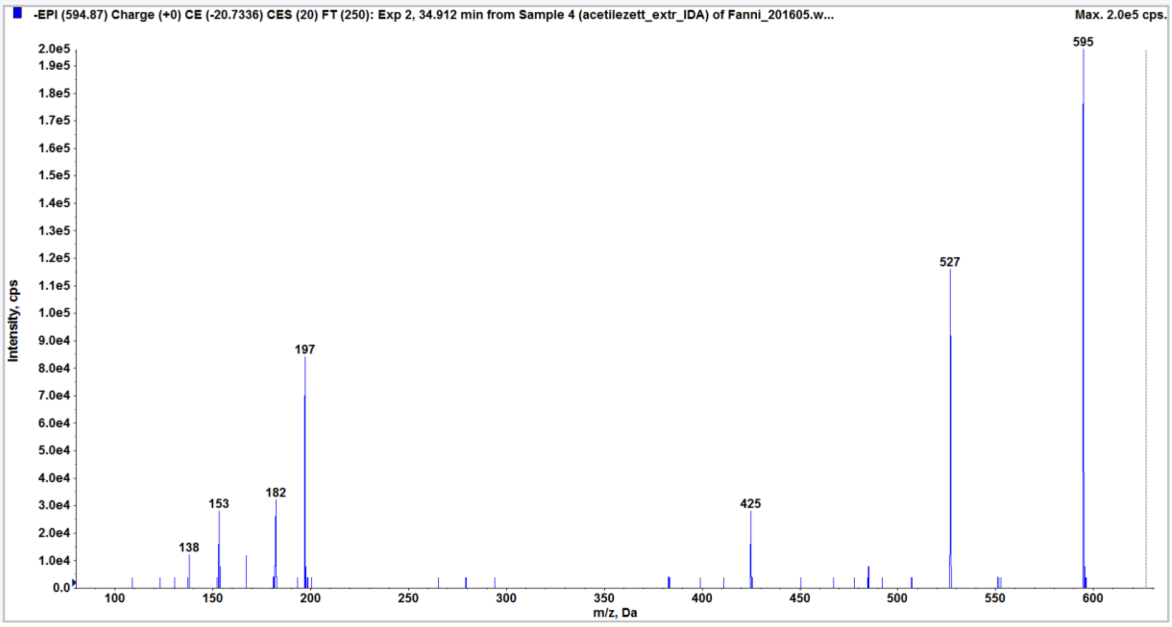


Figure A70. The MS/MS spectrum of the compound at 34.87 min. retention time. It was identified as a derivative of syringic acid.

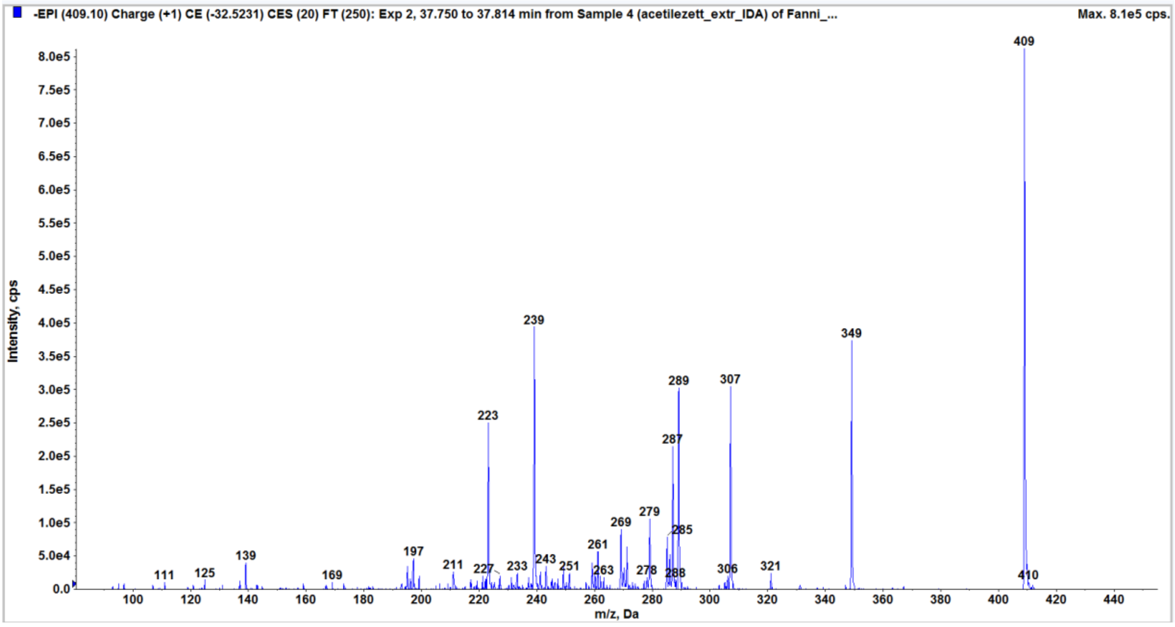


Figure A71. The MS/MS spectrum of the compound at 37.73 min. retention time.

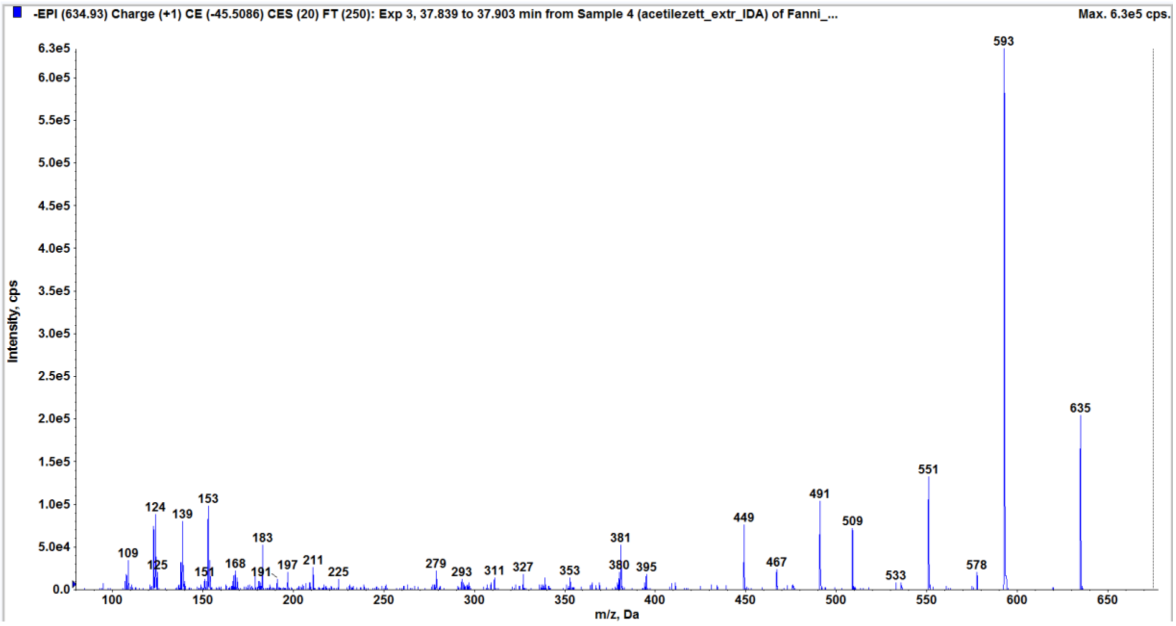


Figure A72. The MS/MS spectrum of the compound at 37.85 min. retention time.

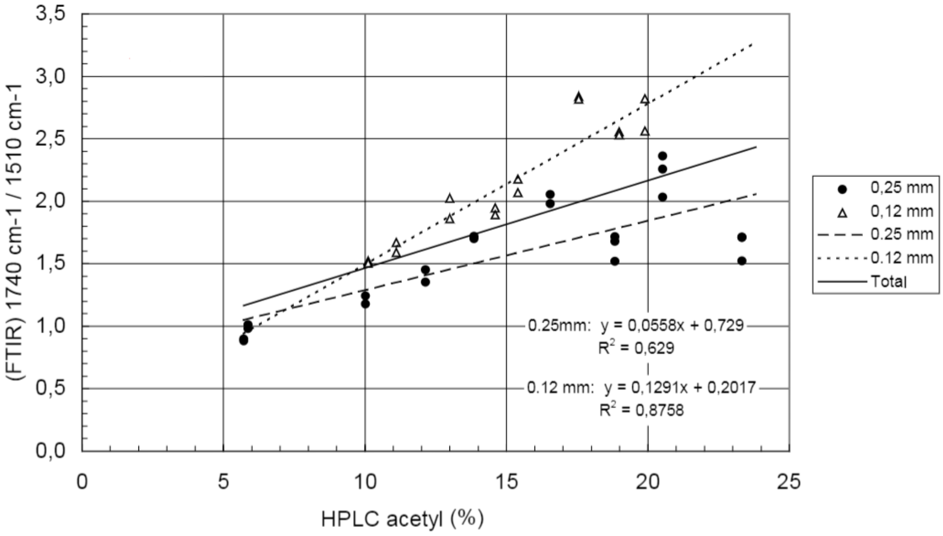


Figure A73. Correlation between FTIR and HPLC acetyl content of acetylated beech of various grinding sizes during sample preparation (Beckers et al., 2003).

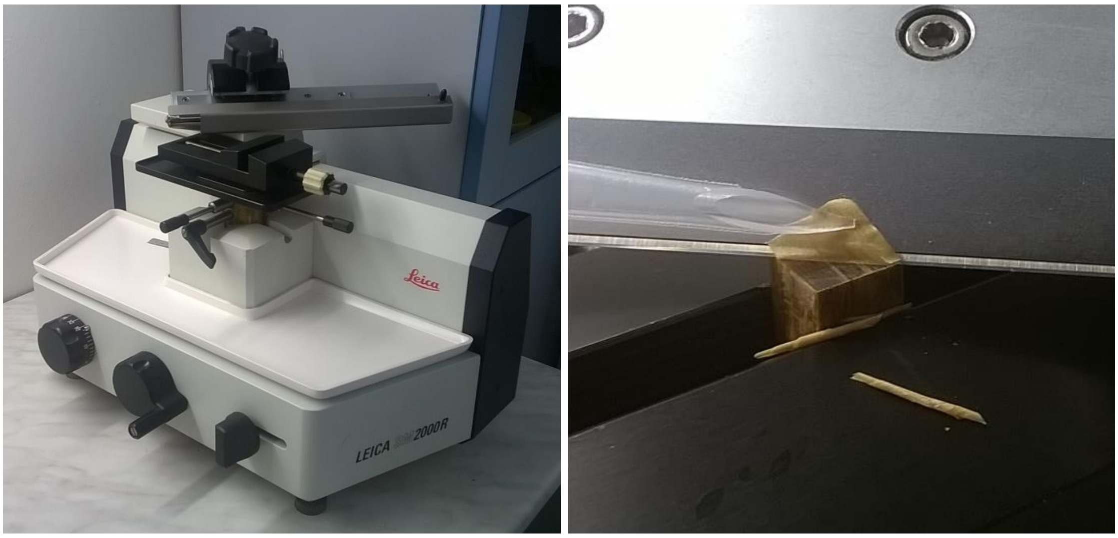
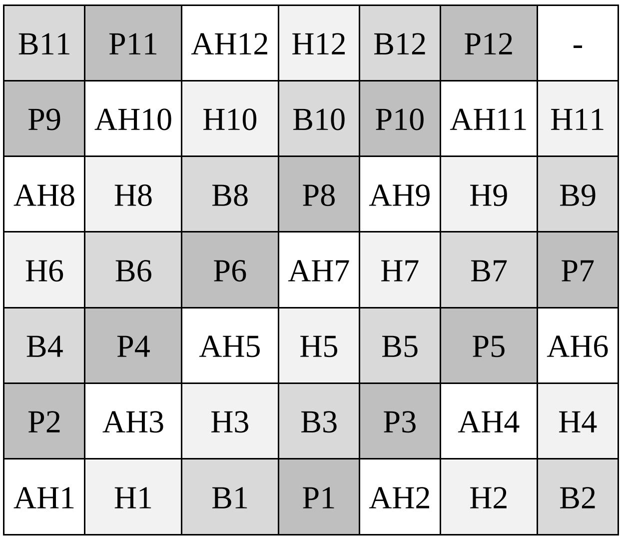


Figure A74. Microtome (left) and section cutting of acetylated wood (right).



B11	P11	AH12	H12	B12	P12	-
P9	AH10	H10	B10	P10	AH11	H11
AH8	H8	B8	P8	AH9	H9	B9
H6	B6	P6	AH7	H7	B7	P7
B4	P4	AH5	H5	B5	P5	AH6
P2	AH3	H3	B3	P3	AH4	H4
AH1	H1	B1	P1	AH2	H2	B2

Figure A75. Map of stakes in soil (AH: acetylated hornbeam, H: untreated hornbeam, B: beech, P: pine sapwood).

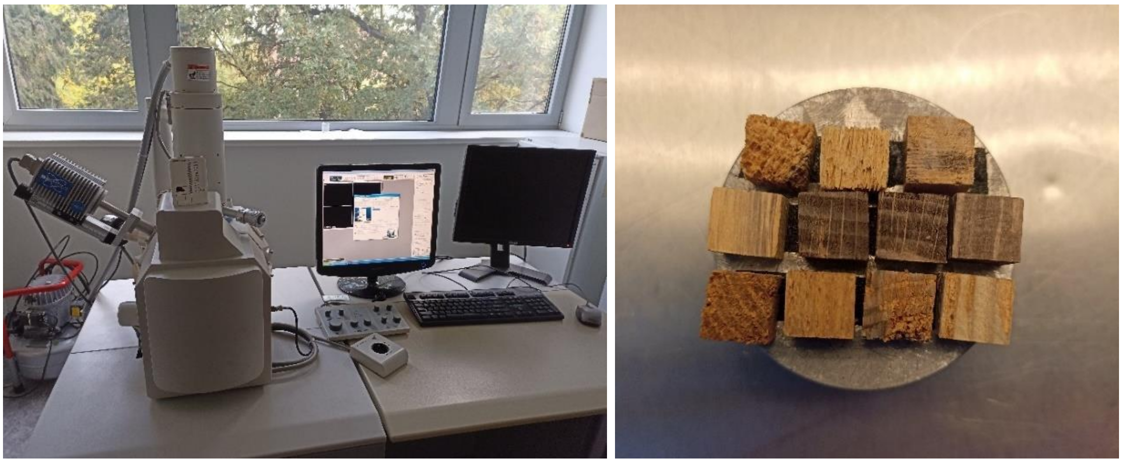


Figure A76. Hitachi S-3400N Scanning Electron Microscope (left) and samples on stage (right).

Table A31. Average monthly breakdown of weather parameters during the test period (between April 2016 and March 2023). Months are marked with numbers (1-12), AVG denotes average values, SUM denotes sum of monthly values.

Monthly data	1	2	3	4	5	6	7	8	9	10	11	12
Mean temperature (°C) AVG: 12	1	4	7	12	15	21	22	22	17	12	6	3
Maximum temperature (°C) AVG: 25	13	19	22	26	29	34	35	35	30	24	18	14
Precipitation (mm) SUM: 573	26	26	26	26	82	64	71	61	62	48	47	35
Number of days with precipitation above 0.25mm SUM: 109	10	7	6	7	13	9	11	8	8	9	9	10
Sunshine duration (hours/ month) SUM: 2,377	87	134	178	248	262	315	316	277	230	166	91	74
Relative humidity (%) AVG: 70	78	70	61	58	68	63	62	65	70	77	84	81
Solar irradiance (MJ/m^2) SUM: 4,779	119	209	388	523	613	714	703	591	430	266	129	96

Table A32. Annual breakdown of weather parameters during the test period (between April 2016 and March 2023). Years are marked with numbers (1-7).

Annual data	1	2	3	4	5	6	7	Average
Mean temperature (°C)	11	11	13	12	12	12	13	12
Maximum temperature (°C)	24	24	24	26	25	26	26	25
Precipitation per year (mm)	578	617	662	603	607	485	430	569
Number of days per year with precipitation above 0.25mm	97	133	113	102	113	92	106	108
Annual sunshine duration (hours)	78	74	85	81	80	85	63	78
Relative humidity (%)	71	71	70	70	71	65	69	70
Annual solar irradiance (MJ/m^2)	4,674	4,631	4,947	4,776	4,797	5,016	4,226	4,724

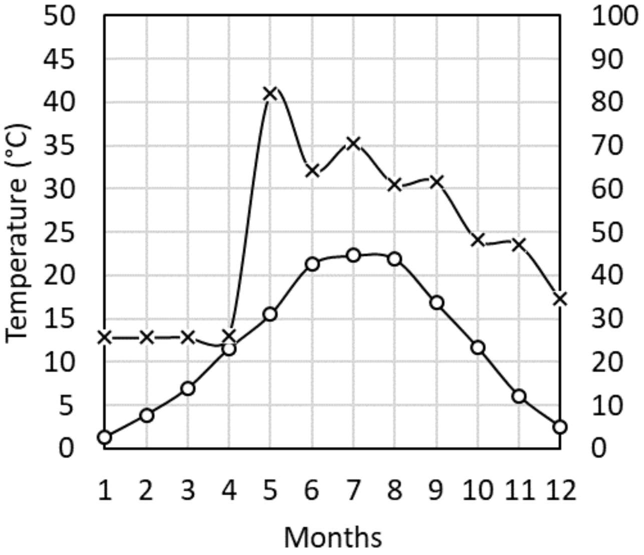


Figure A77. Ombrothermic diagram, which summarizes trends in temperature (O) and precipitation (X) of 6 years of exposure (2016–2023). The wet period is typical for the whole year; there is no dry period.

Figure A78. Wood degradation during exposure from left to right: wasp stripping (untreated hornbeam no.1, 11 months), algae (untreated Scots pine stake no.1, 11 months), mushroom of Coprinellus micaceus (untreated hornbeam stake no.12, 5 months), mycelium (untreated Scots pine stake no.1, 5 months).

Figure A79. Sound acetylated hornbeam stakes (left) and untreated hornbeam stakes with wasp stripping, cracks, graying (right) after one year.

Figure A80. Failed untreated stakes from left to right: hornbeam stake no.3, beech stake no.6, and Scots pine stake no.1. after 6 months of exposure.

Figure A81. Smoky polypore or smoky bracket (Bjerkandera adusta) on beech stake no. 7 (left) and Coprinellus micaceus on beech stake no.3 (right) after 15 months.

Figure A82. Brown rot in acetylated hornbeam stake no. 7 (left), decayed and insect-damaged untreated hornbeam (middle) and beech stakes (right) after 1.5 years of exposure.

Figure A83. Smoky polypore or smoky bracket (Bjerkandera adusta) on beech stake no.7 after 16 and 18 months.

Figure A84. Severely damaged Scots pine stakes after 3.5 years (left), and sound acetylated hornbeam stakes after 4 years of exposure.

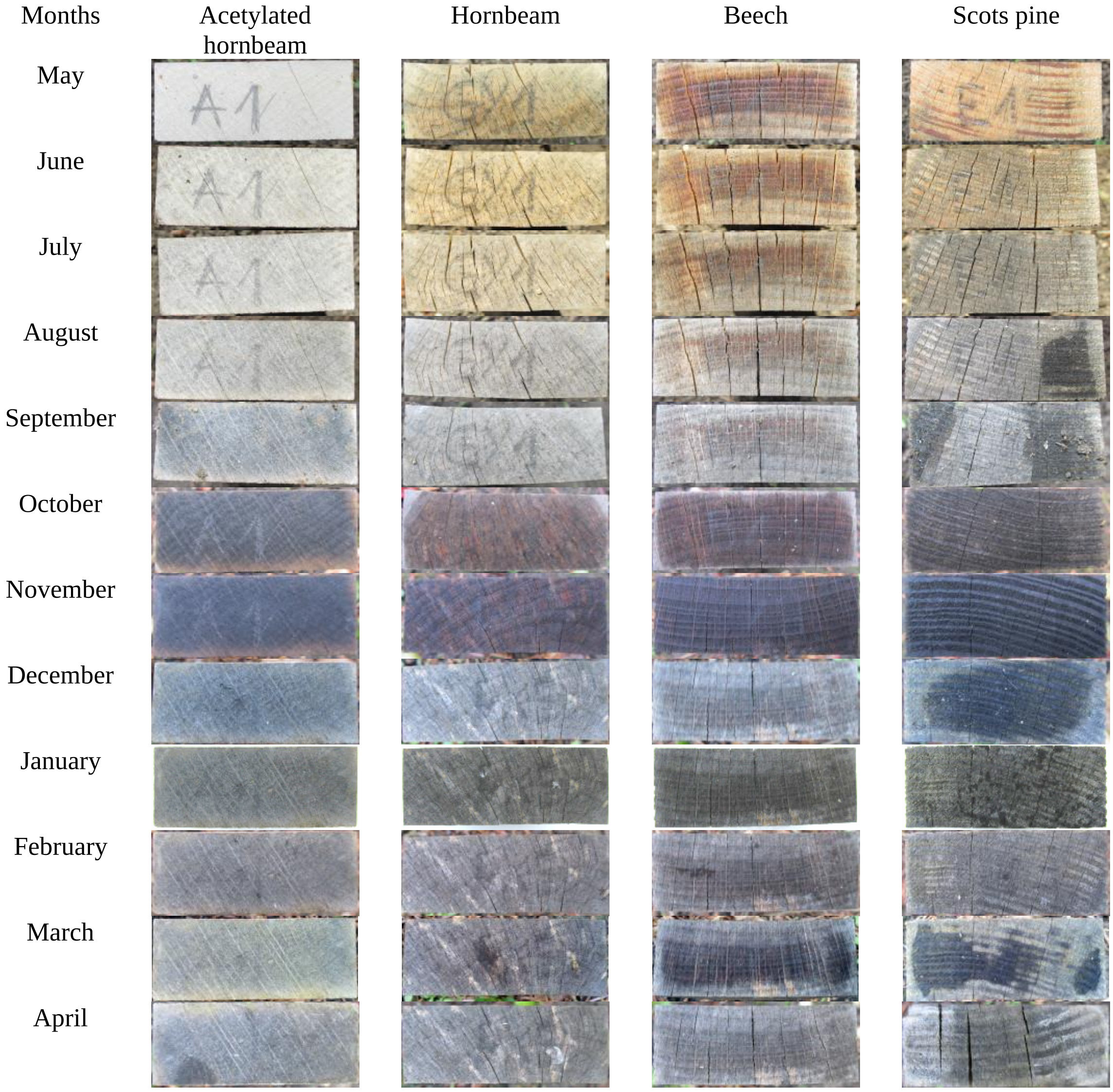


Figure A85. Photo series of stake top cross section surfaces in the first year of exposure.

*Table A33. Summary of results of field soil trial: dry mass and dry density loss of tested wood species after 6 years. Average values are presented with standard deviation in brackets. * no failure occurred, but it was taken from the test for examination.*

Wood Species	Dry Mass Loss (%)	Dry Density Loss (%)
Acetylated hornbeam *	6.05	5.72
Hornbeam	28.01 (11.79)	27.57 (11.65)
Beech	29.67 (6.53)	29.38 (6.22)
Scots pine sapwood	38.91 (9.18)	22.83 (9.88)

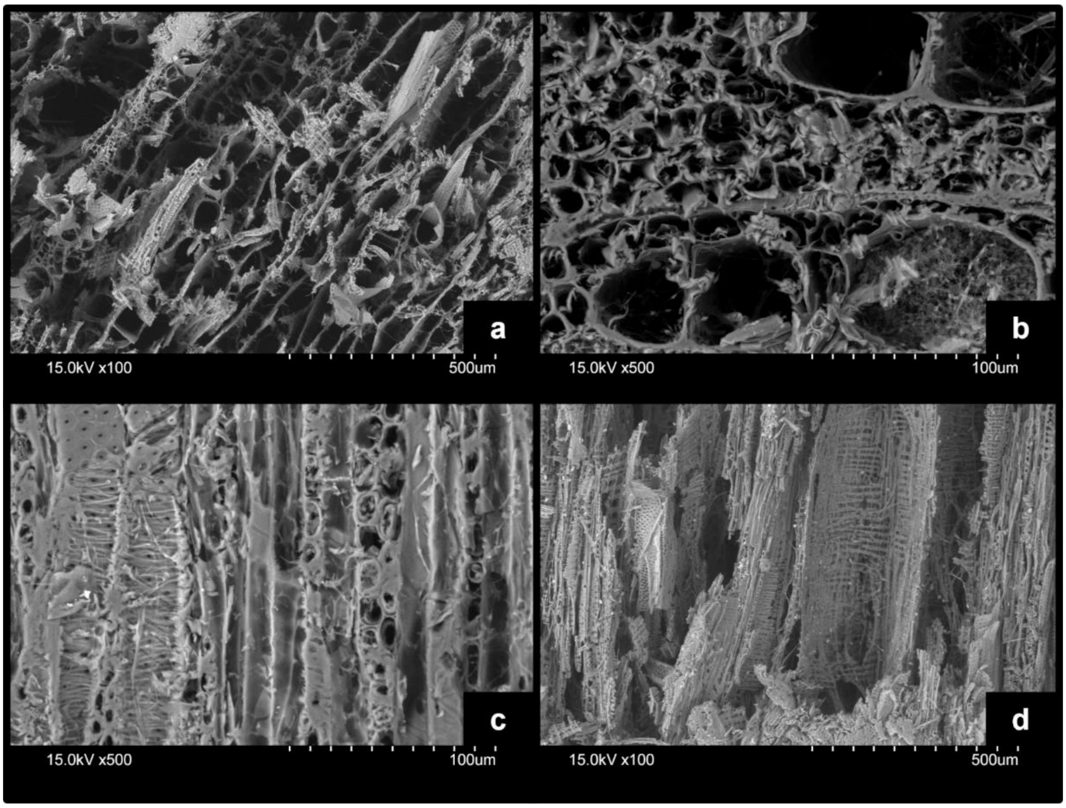


Figure A86. SEM pictures of cross section (above) and longitudinal section (below) of decayed hornbeam wood: (a) cell wall thinning, (b) fungal hyphae in lumen, (c) gradual disappearance of bordered pits, (d) fibrous tissue.

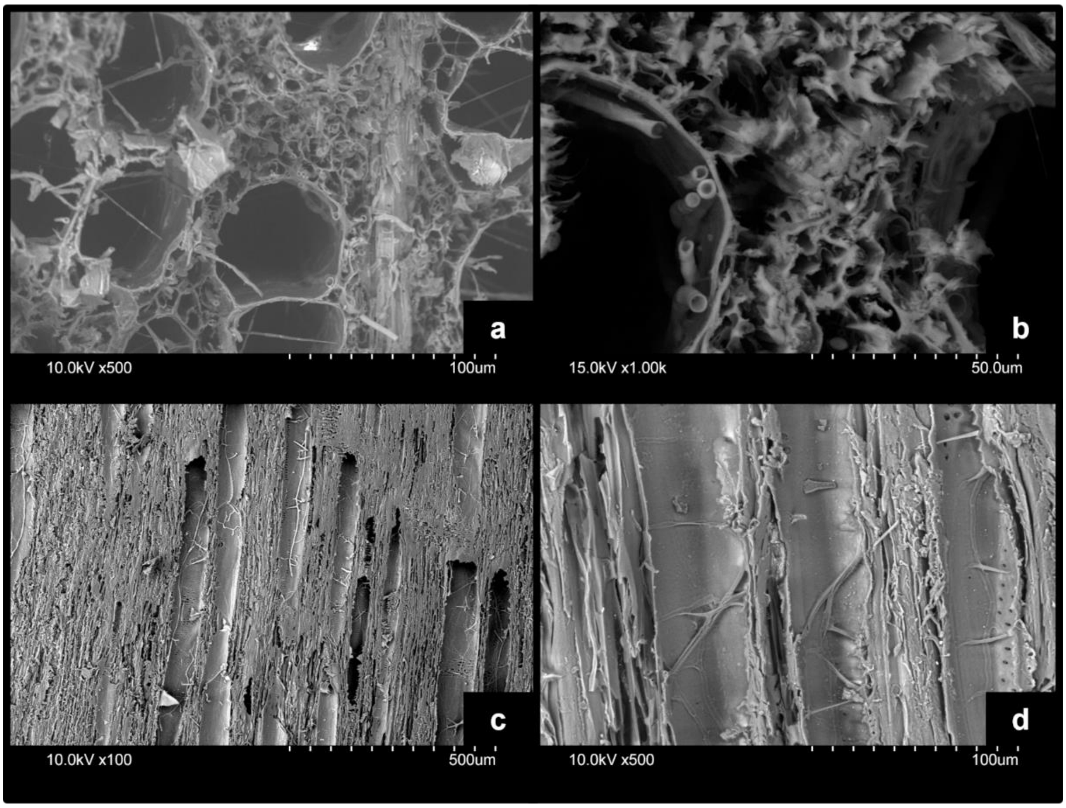


Figure A87. SEM pictures of cross section (above) and longitudinal section (below) of decayed beech wood: (a) fibrous tissue, (b) hyphae in lumen, (c) damaged bordered pits, (d) growing hyphae along vessels.

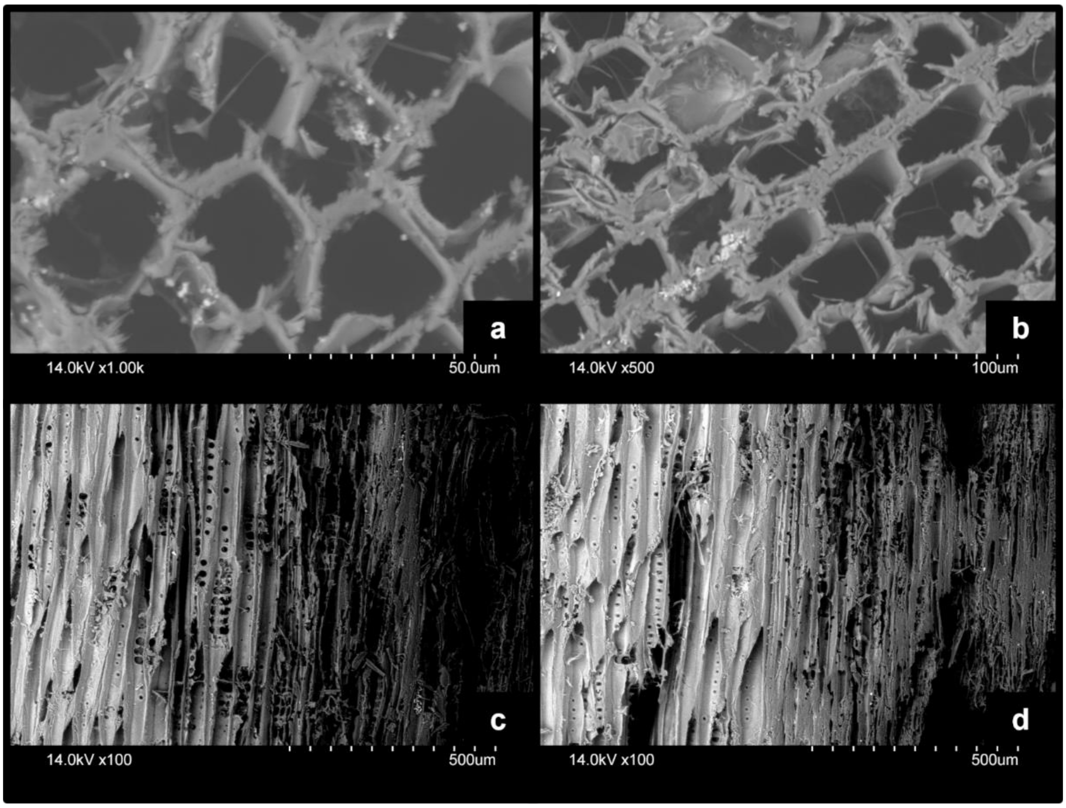


Figure A88. SEM pictures of cross section (above) and longitudinal section (below) of decayed Scots pine wood: (a) thinned cell wall structure, (b) fungal hyphae in lumina, (c) fibrous structure, (d) gradual disappearance of bordered pits on decay border.

Table A34. Technical information on tested adhesives (B: beech, H: hornbeam, and AH: acetylated hornbeam).

Tested adhesives	Brookfield Viscosity (20 °C) (MPa.s)	Density (kg/m^3)	pH	Consumption (g/m^2)
PVAc D3 adhesive (one-component, water-based polyvinyl acetate dispersion)	9,000–15,000	1,060–1,100	2.8–3.6	(B) 175–190 (H) 175–190 (AH) 130–150
PVAc D4 adhesive (two-component adhesive, PVAc D3 adhesive +5% modified aliphatic polyisocyanate)	2,800–4,000	1,140–1,180	n.a.	(B) 145 (H) 150–160 (AH) 150
One-component PUR adhesive (one-component, polyurethane prepolymer with free 4,4′-methylenediphenyl diisocyanate)	9,000–14,500	1,070–1,140	n.a.	(B) 120 (H) 120–145 (AH) 160

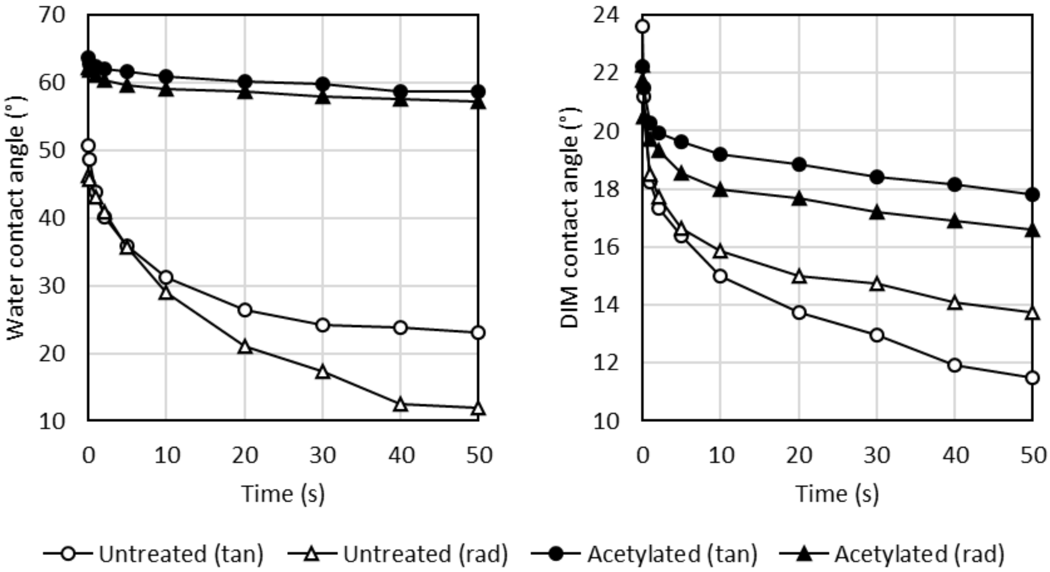


Figure A89. Change of water contact angle and diiodomethane contact angle as a function of time on untreated and acetylated hornbeam.

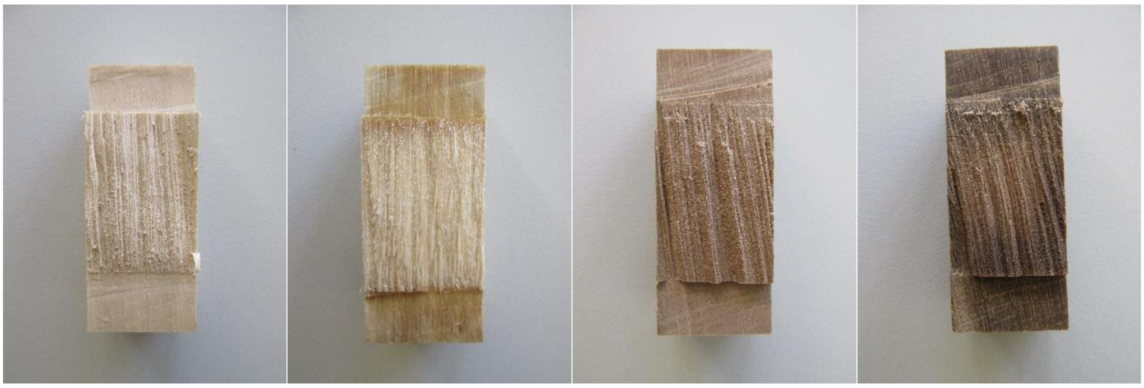


Figure A90. Fracture of shear strength samples. From left to right: hornbeam, wet hornbeam, acetylated hornbeam, wet acetylated hornbeam.

Table A35. Phenomena that occur during weathering of wood and coated wood (Sell and Feist, 1986; Williams, 2005).

Weathering factor	Impacts
Irradiation	- photo-oxidation of the polymers present in wood - destruction of lignin leading to delamination - generation of secondary chromophores leading to wood photo yellowing - thermal radiation, heating of surface
Water	- precipitation causes surface leaching of degradation products - dimensional changes, deformation - stress in the material leading to fractures, splits, checks, cracks
Fungi and insects	- wood discoloration - depth degradation - patterns of degradation differ in terms of species - bore holes, strippings
Atmosphere	- oxygen, pollutants
Wind	- wind-driven rain, hail, particle-like sand, dust - leads to erosion

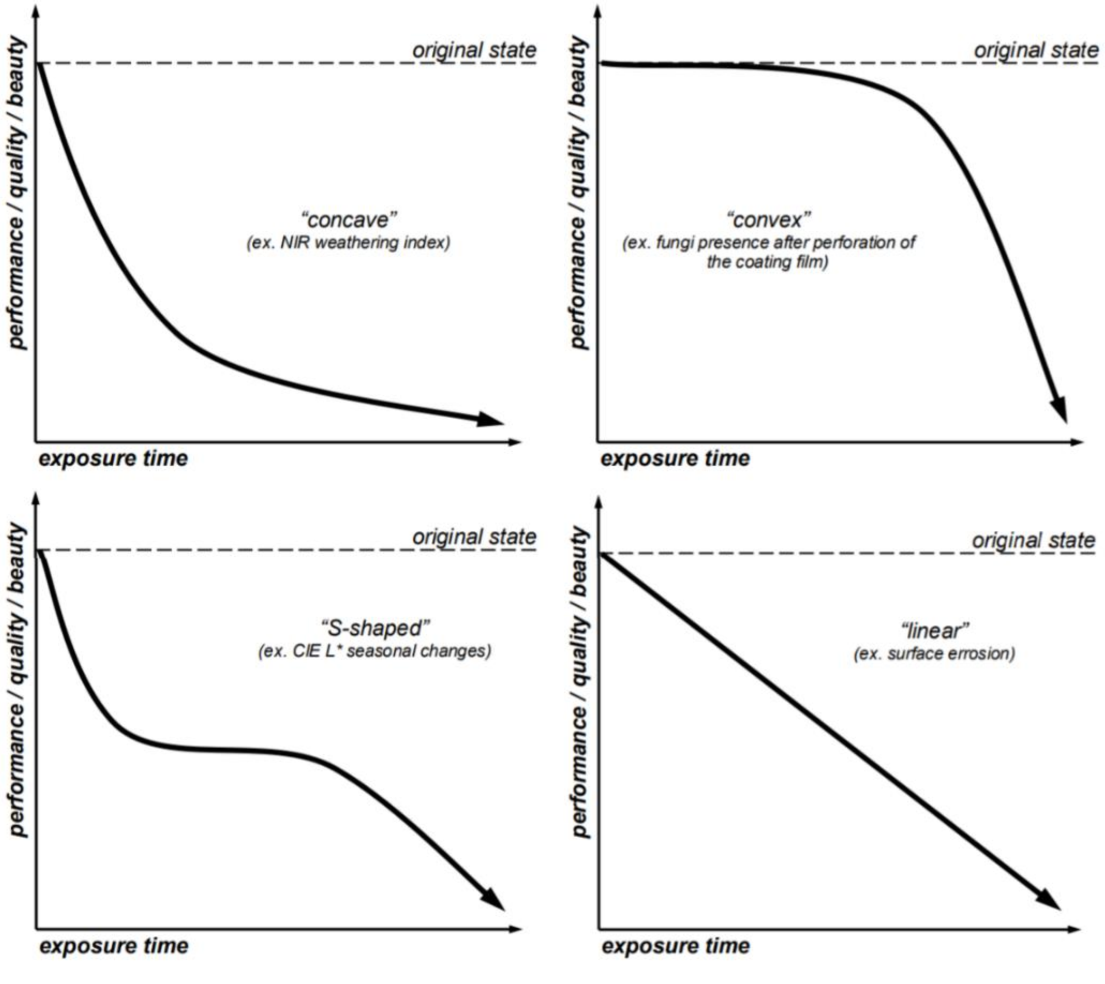


Figure A91. Various deterioration patterns observed in weathering of biomaterials (Sandak and Sandak, 2017).

Table A36. Average monthly breakdown of weather parameters during the test period (between July 2016 and January 2018). Months are marked with numbers (1-12), AVG denotes average values, SUM denotes sum of monthly values.

Monthly data	1	2	3	4	5	6	7	8	9	10	11	12
Mean temperature (°C) AVG: 11	0	3	9	10	16	22	22	21	17	11	5	2
Maximum temperature (°C) AVG: 24	12	16	22	25	32	34	35	34	29	23	17	14
Precipitation (mm) SUM: 541	21	36	24	33	31	57	88	49	67	56	48	26
Number of days with precipitation above 0.25mm SUM: 114	8	8	6	11	10	8	13	6	9	12	10	8
Sunshine duration (hours/month) SUM: 2,394	100	173	217	296	243	316	309	297	244	188	89	79
Relative humidity (%) AVG: 71	79	75	61	62	65	58	63	65	71	78	81	78
Solar irradiance (MJ/m^2) SUM: 4,750	13	172	403	446	663	721	686	608	425	245	136	111

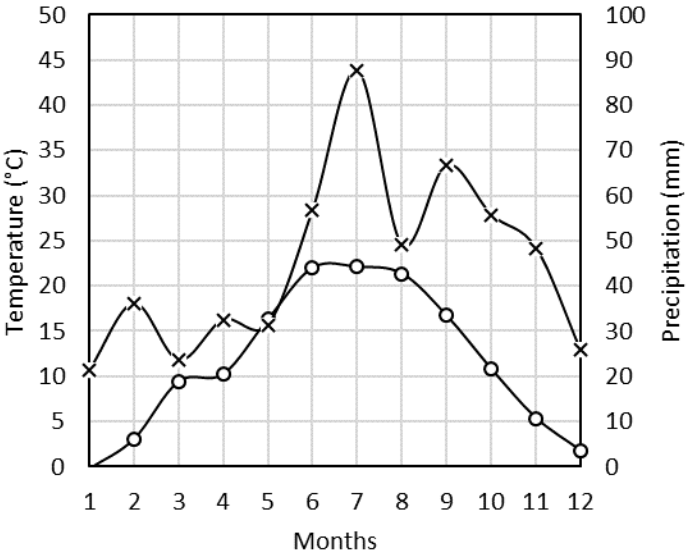


Figure A92. Ombrothermic diagram, which summarizes trends in temperature (O) and precipitation (X) of 18 months of exposure (July 2016 – January 2018). The wet period is more typical for the whole year.

Table A37. Composition of tested coatings and their markings.

Product Name, Type and Marking	Ingredients
Oli-Natura Yacht and Teak Oil - colorless (OO0)	Modified vegetable oils such as linseed oil; isoparaffinic hydrocarbon of pharmaceutical quality; lead-free drying agents, non-fading earth and mineral pigments, micronized titan oxide.
Auro Garden Furniture Oil No. 102 - teak (AOT)	Fatty acids, lecithin, linseed oil, mineral pigments, orange terpene, silica, tung oil, drying agents (cobalt-free)
Auro Wood stain No. 160 - colorless (AS0) - umbra (ASU)	Water, linseed oil*, colophonium glycerine ester with organic acids (as ammonium soaps), mineral fillers and pigments, surfactants made from rapeseed and Ricinus oil, silicic acid, dryers (cobalt-free), castor stand oil*, sunflower oil*, cellulose, fatty acids.
Biopin Weather Protection Stain - colorless (BS0) - palisander (BSP) - Swedish red (BSR)	Binding agents (polymer made from natural oils, fatty acids, and resins), solvent (water), pigments and fillers (earth and mineral pigments), additives (vegetable-based emulsifier, lead and barium-free stabilizers and drying agents, methyl cellulose, film treaters (3-iodine-2-propynyl butylcarbamate (max. 0.2%), and 2-octyl-2H-isothiazol-3-one (<0.01%)).
Biopin Terrace Oil - teak (BOT)	Binding agents (polymer made from natural oils, fatty acids, and resins), solvent (isoparaffin), pigments (mineral pigments), additives (silicic acid, lead-free drying agent).
Biopin Natural Impregnating Oil and 20 % K.O.S. Natural Pigment Paste - red (BOR)	Binding agents (polymer made from natural oils, fatty acids, and resins), solvent (isoaliphate), additives (lead and barium-free drying agents), and non-toxic natural mineral pigments prepared in vegetable oil.

Table A38. Important properties of tested coatings.

Marking	Volume Solids (%)	Density (g/cm^3)	Drying Time (hours)	Full Hardness (day)	Number of Layers	Application Amount (g/m^2)
OO0	68.39	0.875	1-2	2-3	2	40-80
AOT	90.53	0.95	24	28	2	38
AS0	12.78	1.065	24	28	3	75-96
ASU	31.96	1.065	24	21	3	75-96
BS0	58.59	0.98	24	14	3	69-83
BSP	50.97	0.98	24	14	3	69-83
BSR	59.15	0.98	24	14	3	69-83
BOT	72.94	0.84	4-6	14	3	55-105
BOR	50.26	0.86	6-8	14	3	60-69

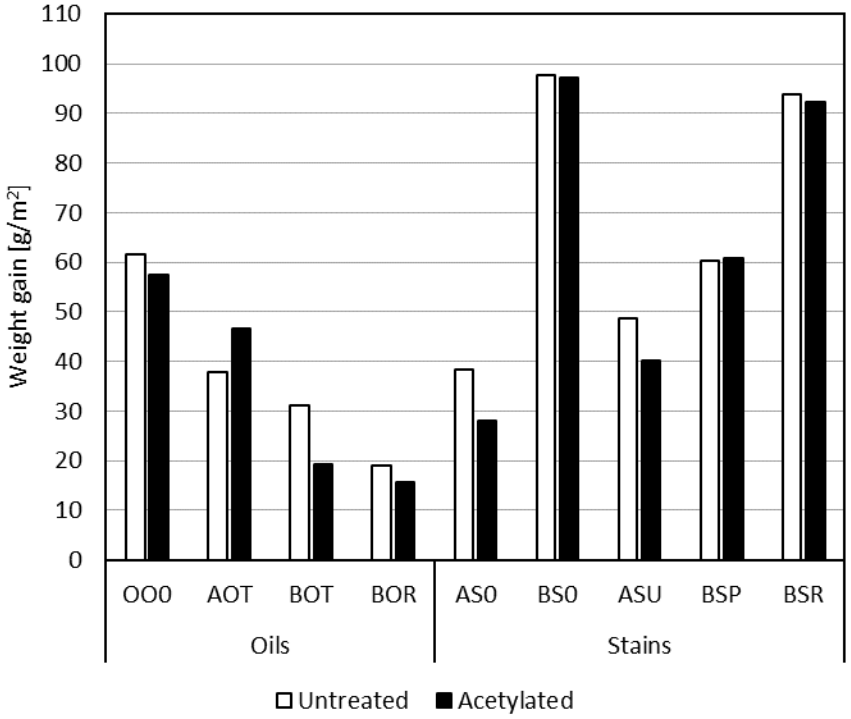


Figure A93. Weight gain of untreated and acetylated hornbeam after coating, at 20 °C temperature, 65 % relative humidity.

Table A39. Color variation of xenon-lamp-irradiated hornbeam (color difference compared to average color). Average values of 20 measurements are presented. A significant change after irradiation is marked by an asterisk if p < 0.05.

Marking	Untreated hornbeam		Acetylated Hornbeam	
	Before	After 200 h	Before	After 200 h
Uncoated	1.80	1.59	1.84	1.43
OO0	4.07	2.91*	3.96	2.40*
AS0	1.49	1.06	3.12	4.61*
AOT	2.66	1.71	3.09	4.63*
ASU	2.09	2.83	1.54	2.43
BS0	2.71	2.42	1.78	3.18*
BSP	1.23	3.04*	1.27	8.27*
BSR	1.57	3.19*	1.09	2.87*
BOT	3.87	2.55*	5.10	3.44*
BOR	3.07	3.23	1.94	3.22*

Table A40. Average monthly breakdown of weather parameters during the test period (between April 2018 and April 2020). Months are marked with numbers (1-12), AVG denotes average values, SUM denotes sum of monthly values.

Monthly data	1	2	3	4	5	6	7	8	9	10	11	12
Mean temperature (°C) AVG: 13	1	6	8	14	16	22	22	23	17	13	7	3
Maximum temperature (°C) AVG: 25	13	20	22	27	28	33	35	35	32	24	19	14
Precipitation (mm) SUM: 625	20	11	26	23	125	78	61	52	84	32	70	43
Number of days with precipitation above 0.25mm SUM: 83	1	6	8	14	16	22	22	23	17	13	7	3
Sunshine duration (hours/ month) SUM: 2,548	100	173	217	296	243	316	309	297	244	188	89	79
Relative humidity (%) AVG: 69	81	63	59	55	72	67	61	64	70	77	88	80
Solar irradiance (MJ/m^2) SUM: 4 895	123	241	390	584	585	710	699	618	443	281	123	99

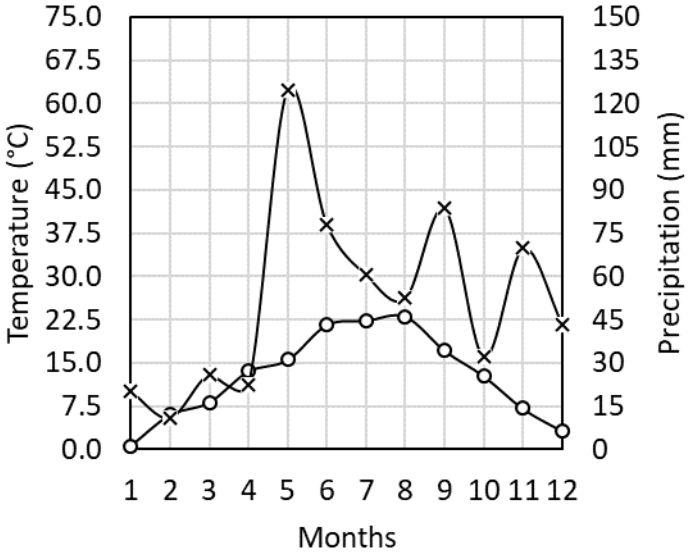


Figure A94. Ombrothermic diagram, which summarizes trends in temperature (O) and precipitation (X) of two years of exposure. The wet period is more typical for the whole year.

Table A41. Color variation of weather-exposed hornbeam (color difference compared to average color). Average values of 20 measurements are presented. A significant change after two years of weathering (April 2018 – April 2020) is marked by an asterisk if $p < 0.05$.

Marking	Untreated hornbeam 0 year	Untreated hornbeam 2 years	Acetylated hornbeam 0 year	Acetylated hornbeam 2 years
Uncoated	2.22	3.68	6.07	3.01*
OO0	3.59	2.67	5.94	2.67*
AS0	2.86	3.91	5.30	2.73*
AOT	3.05	6.20*	2.80	5.78*
ASU	2.08	2.13	2.70	2.15
BS0	2.47	5.37*	7.27	3.05*
BSP	9.93	13.06*	2.65	8.07*
BSR	2.39	6.82*	1.77	3.08
BOT	2.93	3.42	4.71	3.21
BOR	3.24	10.31*	3.00	6.30*

Table A42. Defining the length of weather exposure (from April 2018) needed to achieve similar color change of 200-hour-long xenon lamp irradiation. Samples are untreated and acetylated hornbeam, uncoated and coated with various oils and stains. Color parameters include lightness (L^*), redness (a^*), yellowness (b^*), and color difference between irradiated and weathered wood (ΔE^*).

Marking	After 200 h of xenon lamp irradiation L*	a*	b*	After Weather Exposure L*	a*	b*	Duration (month)	ΔE*
Untreated hornbeam								
Uncoated	67.59	10.64	34.27	73.98	5.46	25.20	1	12.24
OO0	55.14	16.91	48.41	71.96	9.53	39.01	1	20.63
AS0	58.92	15.52	49.36	69.52	9.47	38.05	1	16.64
AOT	53.41	18.82	50.86	63.45	14.64	44.32	1	12.70
ASU	31.93	15.14	31.48	31.66	15.18	32.12	1	0.69
BS0	55.45	17.91	68.43	61.43	14.11	53.22	5	16.77
BSP	6.76	25.07	11.50	6.41	20.53	10.90	1	4.59
BSR	21.42	43.76	36.78	22.19	44.33	38.11	3	1.64
BOT	54.12	17.98	49.27	67.41	12.61	38.63	1	17.86
BOR	39.60	38.57	50.08	45.44	37.75	46.33	1	6.99
Acetylated hornbeam								
Uncoated	77.32	2.20	15.51	77.15	2.01	15.35	1	0.30
OO0	72.74	4.12	25.71	72.76	3.91	25.07	1	0.68
AS0	66.39	5.29	32.76	70.19	3.83	25.97	1	7.92
AOT	60.41	11.12	36.13	63.76	11.36	37.21	1	3.53
ASU	32.21	14.09	31.19	31.69	13.72	31.54	1	0.73
BS0	59.15	9.97	52.19	65.87	5.42	37.03	1	17.20
BSP	4.81	17.72	8.13	5.62	20.85	9.53	1	3.53
BSR	21.28	43.05	36.54	21.29	43.13	36.55	1	0.09
BOT	67.30	7.42	26.20	68.91	7.33	25.77	1	1.67
BOR	45.75	32.43	38.06	48.00	31.05	36.86	1	2.91

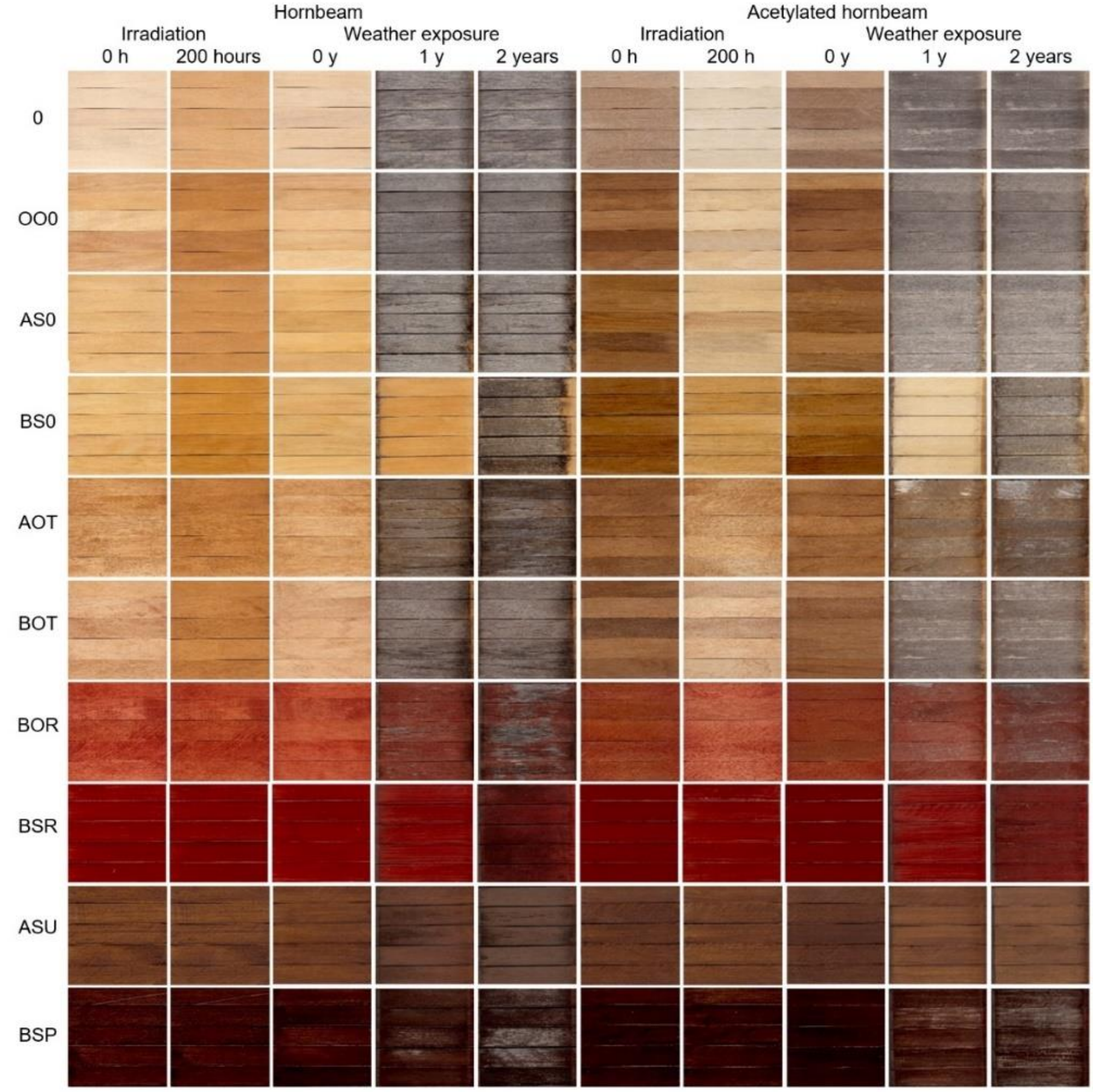


Figure A95. Scans of uncoated and coated, untreated and acetylated hornbeam samples before and after 200-hour-long irradiation, and before and after two-year-long weather exposure.

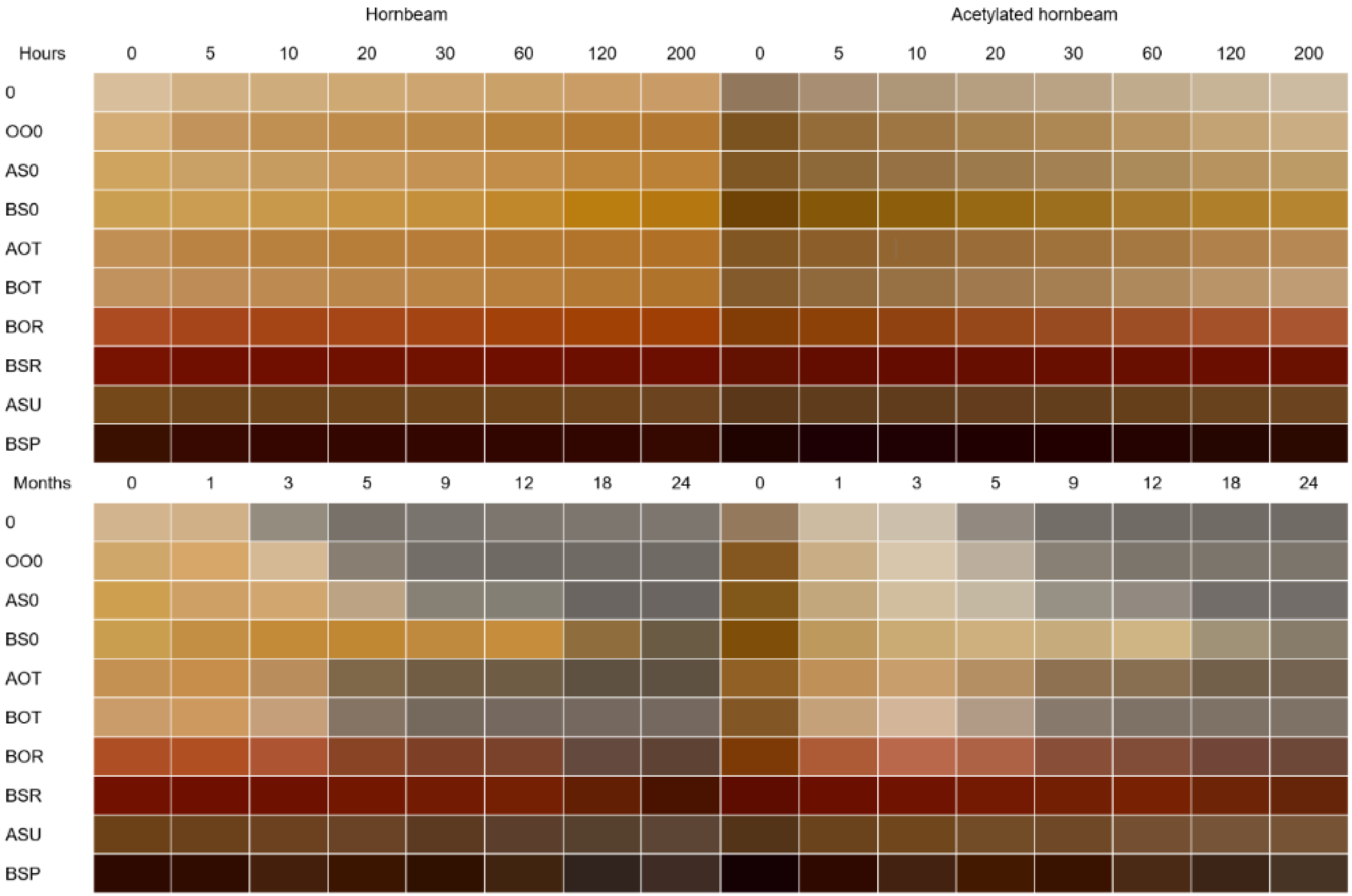


Figure A96. Color chart of uncoated and coated, untreated and acetylated hornbeam samples before and after 200-hour-long irradiation, and before and after two-year-long weather exposure.

Appendix 2. Product proposals and prototypes through collaborations

Figure A97. Knife handle made of acetylated hornbeam by Gergő Goszpodinov (2022)

Figure A98. Beach toys for sandpit and water play of acetylated hornbeam by Fanni Pozsgayné Fodor and Helga Nagy-Somlai (2022)

Figure A99. Small bench made of acetylated hornbeam by Fanni Pozsgayné Fodor and Imre Horváth. It was installed in the Botanical garden of Sopron (47°40'52.4"N 16°34'37.2"E) in 2022.

Appendix 3. List of related publications

Journal articles:

Fodor, F., Ábrahám, J., Németh, R., 2018a. Bonding acetylated hornbeam wood (Carpinus betulus L.). Pro Ligno 14, 31–38. https://www.proligno.ro/en/articles/2018/4/FODOR.pdf

Fodor, F., Bak, M., 2023. Studying the Wettability and Bonding Properties of Acetylated Hornbeam Wood Using PVAc and PUR Adhesives. Materials 16, 2046. https://doi.org/10.3390/ma16052046

Fodor, F., Bak, M., Bidló, A., Bolodár-Varga, B., Németh, R., 2022a. Biological Durability of Acetylated Hornbeam Wood with Soil Contact in Hungary. Forests 13, 1003. https://doi.org/10.3390/f13071003

Fodor, F., Bak, M., Németh, R., 2022c. Photostability of Oil-Coated and Stain-Coated Acetylated Hornbeam Wood against Natural Weather and Artificial Aging. Coatings 12, 817. https://doi.org/10.3390/coatings12060817

Fodor, F., Lankveld, C., Németh, R., 2017a. Testing common hornbeam (Carpinus betulus L.) acetylated with the Accoya method under industrial conditions. iForest - Biogeosciences and Forestry 10, 948. https://doi.org/10.3832/ifor2359-010

Fodor, F., Lankveld, C., Németh, R., 2017b. The influence of acetylation on the colour and photostability of common hornbeam wood (Carpinus betulus L.). Pro Ligno 13, 323–330. https://www.proligno.ro/en/articles/2017/4/FODOR.pdf

Fodor, F., Németh, R., 2017. Testing the Photostability of Acetylated and Boiled Linseed Oil-coated Common Hornbeam (Carpinus betulus L.) Wood. Acta Sylvatica et Lignaria Hungarica 13, 81–94. https://doi.org/10.1515/aslh-2017-0006

Fodor, F., Németh, R., Lankveld, C., Hofmann, T., 2018b. Effect of acetylation on the chemical composition of hornbeam (Carpinus betulus L.) in relation with the physical and mechanical properties. Wood Material Science & Engineering 13, 271–278. (published online in 2017) https://doi.org/10.1080/17480272.2017.1316773

Rousek, R., Fodor, F., Németh, R., 2022. Microscopic characterization of sound and decayed acetylated hornbeam (Carpinus betulus L.). Wood Material Science & Engineering. https://doi.org/10.1080/17480272.2022.2057817

Trade publications:

Pozsgayné Fodor, F., Ábrahám, J., Németh, R., 2018. Miben más acetilezett faanyagot ragasztani? Magyar Asztalos- és Faipar: Az Országos Asztalos- és Faipari Szövetség Hivatalos Fóruma 28, 108–109. https://faipar.hu/data/file/8026/8667,miben-mas-acetilezett-faanyagot-javitani

Pozsgayné Fodor, F., 2017. A faanyagok kémiai modifikációja – Acetilezés. Magyar Asztalos- és Faipar: Az Országos Asztalos- és Faipari Szövetség Hivatalos Fóruma 27, 62–65. https://faipar.hu/data/file/4465/8103,faanyagok-kemiai-modifikacioja

Pozsgayné Fodor, F., 2016. A famodifikálás. Magyar Asztalos- és Faipar: Az Országos Asztalos- és Faipari Szövetség Hivatalos Fóruma 25, 48–50.

Conference papers:

Fodor, F., Ábrahám, J., Németh, R., 2018b. Bonding acetylated hornbeam wood (Carpinus betulus L.), in: Proceedings of the 5th Processing Technologies for the Forest and Biobased Products Industries. Technische Universität München, Freising, Germany, pp. 132–139.

Fodor, F., Bak, M., Bidló, A., Bolodár-Varga, B., Németh, R., 2022b. Can acetylation make hornbeam wood last? Results of 6-year-long field stake test, in: 10th Hardwood Conference Proceedings. University of Sopron Press, Sopron, Hungary, pp. 194–202.

Fodor, F., Lankveld, C., Németh, R., 2017c. Improving the durability of common hornbeam wood (Carpinus betulus L.) acetylated with Accoya® method, in: Proceedings of the 11th Edition of the International Conference "Wood Science and Engineering in the Third Millenium." Transilvania University of Brasov, Brasov, Romania, pp. 811–815.

Fodor, F., Lankveld, C., Németh, R., 2017d. The influence of acetylation on the colour and photostability of common hornbeam wood (Carpinus betulus L.), in: Proceedings of the 11th Edition of the International Conference "Wood Science and Engineering in the Third Millenium." Transilvania University of Brasov, Brasov, Romania, pp. 436–443.

Fodor, F., Németh, R., 2018a. Examining the coating performance of finishes on acetylated hornbeam wood (Carpinus betulus L.), in: Book of Abstracts of the 9th Conference on Wood Modification. SHR B.V., Arnhem, the Netherlands, p. 37.

Fodor, F., Németh, R., 2018b. Photodegradation of acetylated wood irradiated by xenon lamp and mercury-vapour lamp, in: Proceedings of the 8th Hardwood Conference - With Special Focus on "New Aspects of Hardwood Utilization from Science to Technology." University of Sopron Press, Sopron, Hungary, pp. 129–130.

Fodor, F., Németh, R., 2016. Gyertyán (Carpinus betulus L.) faanyag acetilezése a szilárdság és tartósság javításának céljából, in: V. Interdiszciplináris Doktorandusz Konferencia Konferenciakötet. Pécsi Tudományegyetem Doktorandusz Önkormányzat, Pécs, Hungary, pp. 106–117.

Fodor, F., Németh, R., Hofmann, T., 2016. Chemical analysis of acetylated hornbeam (Carpinus betulus L.) wood, in: Proceedings of the 7th Hardwood Conference: Eco-Efficient Resource Wood with Special Focus on Hardwoods. University of West Hungary Press, Sopron, Hungary, pp. 47–48.

Rousek, R., Fodor, F., 2017. Microscopic investigation of acetylated hornbeam and densified beech, in: Proceedings of COST Action FP1407 - 3rd Conference : Wood Modification Research & Applications. Salzburg University of Applied Sciences, Salzburg, Austria, pp. 49–50.