Wood Modification for Under-Utilised Hardwood Species

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Abstract. The different wood modification processes give the opportunity to improve the applicability of such wood materials, which due to their lower biological resistance and/or weather resistance and/or dimension stability have a limited application field. Beside several plantation grown species (e.g. poplars or black locust), there are some species that are not plantation grown but available in considerable quantities, but with low added value during their utilization. These species are mainly used for energy recovery, but they have also the potential for the utilization with higher added value (e.g. furniture, claddings, etc.). These hardwood species are Turkey oak (Quercus cerris L.), hornbeam (Carpinus betulus L.) and tree-of-heaven (Ailanthus altissima Mill.). They have in general high density, strength values and surface hardness. By improving of the properties their application could be widened by substituting more valuable wood species. Different modification techniques were used for the improvement of the properties of these wood species, namely heat treatment and oil heat treatment. In this paper selected wood properties were investigated which are important by the specification of the application fields of the treated material.

1. Introduction

Wood is recognised as the most important of the renewable base materials with the added advantage of being recyclable and CO₂-neutral. It is a highly versatile material and as such has been utilized in building and construction for millennia. The demand for timber is continually increasing, especially in slower growing hardwood and tropical species. Such species offer a greater durability and mechanical properties and often higher aesthetic qualities than many of the faster growing soft- or hardwood species (e.g. radiata pine, poplars, eucalypt, etc.). [1] It is well known that there are grave ecological and environmental concerns over current ‘virgin timber’ demands, and various attempts are underway to prevent the demise of many of the biologically diverse regions where these timbers originate. A greater emphasis is now being placed in sustainable harvesting of timber species, though the slow growth of many species means a slow turnover in materials and profits. Thus, it is necessary to encourage the use of faster growing timbers, which may be readily gained from sustainable plantations, or to improve the utilization field of less used wood species. Whilst the timber sector recognizes these increasing requirements, it also realizes a lot of research and development will be required in overcoming the problems. Wood modification is a generic term describing the application of chemical, physical, or biological methods to alter the properties of the material [2]. The aim is to get better performance from the wood, resulting in improvements in dimensional stability, decay resistance, weathering resistance, etc. It is essential that the modified wood is non-toxic in service and the disposal at the end of life does not result in the generation of any toxic residues. The demand for modified wood material increased worldwide, due to the commercialisation of different wood modification processes in the last decades. Wood modification processes indicate continuously new challenges.
The literature about the modification of less utilized wood species like Turkey oak, hornbeam or tree-of-heaven is very poor. Effect of steaming in the temperature range of 80-120°C with different schedules was investigated by [3]. Results showed the reduction of equilibrium moisture content and the increased dimensional stability. Aesthetical value of Turkey oak was improved as well, by the darkening and red shift of the colour parameters. Improvement of the aesthetetical value of Turkey oak by colour homogenisation as a result of different steaming schedules was also reported by [4]. Effectiveness of colour homogenisation is depending on the steaming temperature. Effect of steaming on Turkey oak was investigated by [5] with different temperatures between 100-130°C, as well as combined treatments of steaming (100-130°C) and heat treatment (120 and 180°C). Results showed an increased ratio of lignin as a result of the different treatments. However, the amount of extractives decreased with the increasing temperature of the treatment. Turkey oak with its wide sapwood is less durable than grand oaks. Therefore, the effect of dry heat treatment on Turkey oak had a special importance in research works in Hungary [6].

Thermal modification of hornbeam was the subject of several studies in Turkey [7, 8] and Iran [9, 10] where the physical and mechanical properties were evaluated according to different temperatures (130 to 210 °C) and treatment times (3 to 12 hours). All papers identified a reduction of physical and mechanical properties while increasing the treatment temperature and duration. These results were confirmed by chemical analysis [11].

Tree-of-heaven veneers modified by urea-formaldehyde pre-polymer and compression drying can improve its properties, like dimensional stability, bending strength and tensile strength parallel to the grain. The hygroscopicity was reduced significantly and the thermal stability was enhanced as well [12]. There is a lot of potential in the utilization of tree of heaven, based on its favourable mechanical properties. In comparison to the appearance, physical and mechanical properties of the European ash (Fraxinus excelsior) a strong affinity was verified [13, 14].

Oil-Heat-Treatment (OHT) is a promising alternative among heat treatment methods. In the literature of [15] are detailed studies about the effects of different heat treatment methods on wood. However, investigations about OHT are remarkable limited for all its favourable properties. One of the advantages of the method is its high intensity, thus it is a fast treatment. Other, industrially established methods are using long warm up and cooling periods, whereas by OHT wood is directly placed into the hot oil bath and after the treatment it is placed on room temperature without a special cooling period in the chamber. Owing to the reasons mentioned, the treatment time can be significantly shortened. Additional advantage of the OHT method is, that the heating medium and its heat is recyclable [16].

The aim of this paper is to summarize the results available about the modification of the three underutilized wood species of Turkey oak, hornbeam and tree-of-heaven. With the improved properties by modification, the utilization field of these wood species can be widened. Investigated modification methods were dry heat treatment, oil-heat-treatment and acetylation.

2. Materials and methods

2.1. Dry heat treatment

During the complex research work in case of Turkey oak (Quercus cerris L.) logs were taken from one certain production site. The so-called juvenile wood was minimized by removing the first 5-10 annual rings (close to the pith). The native and to be treated sapwood and heartwood samples were cut out from the same board before the tests. The temperature of treatments was limited to 200°C and the heating medium was dry, normal atmospheric air, without adding steam. The schedules were based on the Finnish ThermoWood schedule combined with 5-, 10- and 15-hour-long treatment period after reaching the 180°C and 200°C reaction temperatures. In this part, we published only the result of fungal decay tests based on standard [17] and test fungi was oak mazegill (Daedalea quercina).

Another research work was focused on the selected properties of tree-of-heaven, and the variability of them according to the radial position of the specimen. The native specimens were cut out in radial direction from one log with wide annual rings (widths ranging from 7 to 14 mm). One specimen contained one annual ring. In this way, six series of samples were produced from the 3rd, 5th, 7th, 9th,
11th, 13th annual rings. The radial dimension of the samples was set to 7mm, so that their basic surfaces were directly cut out in the tangential direction along the early-late wood boundary. The tangential and the longitudinal dimensions of the samples were 20 and 30 mm respectively. The dry heat treatments were performed at 180 °C and 200 °C with a 10-hour-long treatment period after reaching these reaction temperatures. After the treatments, the airdry density (t=20°C and RH=65%), the anti-swelling efficiency (ASE) and the equilibrium moisture content (EMC) at normal climate (t=20°C and RH=65%) were determined. For the determination of the airdry density and EMC, the samples were stored at normal climate. After they reached constant mass they were weighed and dimensions were measured in the three anatomical directions. After that, the samples were dried at 103 °C until constant mass and weighed again to get the dry mass. The dimensions were measured again and from this data it was possible to determine the EMC and ASE.

2.2. Oil heat treatment (OHT)
Hornbeam (Carpinus betulus L.) and tree-of-heaven (Ailanthus altissima Mill.) wood was oil-heat-treated in linseed oil. The dimensions of the treated samples were 18×40×220 mm (T×R×L). The treatments were performed at the temperature of 200°C, with 2, 4 or 6 hours duration. The crack formation during the OHT was tested with scanning electron microscope (SEM) imaging technique, in correlation with the initial moisture content of the wood. Samples with different initial moisture contents were heat treated at 200°C with 6 hours duration. The investigated initial moisture contents were 0% (absolute dry state), ~12% (airdry state) and above fiber saturation point (green state). The presence and location of cracks were investigated with SEM imaging. After OHT the samples were cut to get clear anatomical surfaces (tangential, radial and cross section), and to make visible the internal cracks in the wood tissue.

2.3. Acetylation
Hornbeam boards were acetylated at Accsys Technologies (Arnhem, The Netherlands) under industrial conditions. Physical, mechanical and durability properties were evaluated. The equilibrium moisture content was determined according to the standard DIN 52183:1977. Swelling and shrinking rate was determined according to the standard DIN 52184:1979. The compression strength was determined according to the standard DIN 52185:1976, bending strength according to DIN 52186:1978, impact bending strength according to DIN 52189-1:1981, Janka hardness according to ISO 3350:1975 and Brinell hardness according to EN 1534:2010. The bending strength, modulus of elasticity, Janka hardness and Brinell hardness were determined after conditioning at normal climate and also after soaking in water (water saturated state). Durability tests were carried out according to the standards EN 113:1996 and EN 252:1994.

3. Results and discussion
3.1. Dry heat treatment
The primary aim of our complex research program called “Chemical free wood protection” was to clear up the effect of dry thermal treatment on wood properties of selected hardwoods in Hungary, and with special emphasis on wood resistance to fungal decay. According to our result we could establish that the dry heat treatment is able to decrease the mass loss caused by enzymatic attack of oak mazegill (Daedalea quercina) on Turkey oak (Table 1.). The schedule including a 10-hour-long period at 180°C was found suitable to reduce the mass loss of sapwood from 24.76 % to 12.1 %, although increasing of the treatment period to 15 hours showed not significant effect on mass loss. In case of the schedule with 15-hour-long period at 200°C the sapwood samples represented less than 3% average mass loss in opposite to the native’s high value. It was also established that the native heartwood has a significant resistance against the enzymatic decomposition caused by oak mazegill in comparison to native sapwood. The average mass loss of the untreated samples of heartwood was about the half of sapwood’s value. The schedule including 15-hour-long treatment period at 180°C reduced the mass loss of heartwood from 11.06 % to 4.98 %. In case of Turkey oak heartwood a treatment temperature of 200°C for a duration of 5 hours ensured mass losses below 3%.
Table 1. Results of fungal decay tests of Turkey oak based on EN 113 norm

| Mass loss | m (%) caused by *Daedalea quercina* |
|-----------|-----------------------------------|
| Turkey oak | 180°C | 200°C |
|           | x     | s     | x     | s     |
| Sapwood   |        |       |       |       |
| untreated | 24.76  | 5.35  | 26.72  | 5.28  |
| 5h        | 18.64  | 4.83  | 5.50  | 1.24  |
| 10h       | 12.10  | 3.69  | 3.49  | 1.73  |
| 15h       | 10.09  | 2.17  | 2.22  | 1.06  |
| Heartwood |        |       |       |       |
| untreated | 11.60  | 2.40  | 12.22  | 3.96  |
| 5h        | 9.95   | 2.64  | 2.19  | 0.52  |
| 10h       | 7.23   | 2.98  | 2.38  | 0.60  |
| 15h       | 4.98   | 2.15  | 1.01  | 0.65  |

After analysing the results of tree-of-heaven, we could prove, that the average equilibrium moisture content (T=20°C and RH=65%) of native samples was 13.6 %, while after treatment at 180°C it was significantly lower (7.2 %). In case of schedule at 200°C the samples showed 4.8 % moisture content in average at normal climate. The differences between the moisture content values of the selected annual rings were not significant in comparison to each other. The density showed also lower deviation along the measuring line from the 3rd to the 13th annual ring. The average airdry density of the native wood specimens was 641 kg/m3. After the treatments at 180°C and 200 °C the average densities of the treated tree-of-heaven samples varied between 604 kg/m3 and 591 kg/m3. It can be also stated, that the density increased from the pith to the bark up to the 9th annual ring of the untreated wood, which may be related to the juvenile wood’s boundary in the xylem between the 9th and 11th annual rings.

Figure 1. The improvement of ASE in tangential direction of tree-of-heaven wood

In case of the swelling values it could be proved, that the dry heat treatment has the same effect on all the native wood series independently from the annual ring’s position. Thus the moisture distribution in an equilibrated board can be considered as homogeneity, because no influence of the radial position of
samples on the moisture content could be found. According to the expectations, the native samples showed the highest swelling values. The radial swelling values decreased continuously starting from the 3rd annual ring towards the 3th. The tangential anti-swelling efficiency (ASE) achieved ca. 19-26% in cease of the treatment temperature at 180°C, and reached 32-44% in cease of the schedule at 200°C (Fig. 1). By studying the ASE values, similar to the density values, the 9th annual ring indicates the juvenile wood’s boundary.

3.2. Oil heat treatment (OHT)
According to earlier investigations [18], poplar and beech wood did not show cracks or deformations as a result of this treatment method, but Turkey oak or ash wood cracked severely. Anatomical structure, cell types present in the wood species and presence of tyloses have large effect on the crack formation during heat treatment. It is important to know the effect of initial moisture content on the crack formation, because micro-cracks influence the strength properties and the quality of the heat treated wood. As initial moisture content is a process parameter which can be influenced before heat treatment, it is important to know how it affects the wood quality during heat treatment.

In case of specimens heat treated with green state initial moisture content, the cracks could be seen well with the naked eye (Figure 2.) The reason for this is the intensive heat transfer to the wood. During the intensive heat treatment method the steam pressure increases quickly in the lumens of the wood. As parenchyma cells have the weakest cell wall in the structure of the wood, the cracks occur in the rays which are visible as radial cracks. Additionally, deformations of the cross sections occurred during heat treatment, as the edges of the cross sections were not straight after the treatment, but rather curved.

![Figure 2. Radial cracks and deformations on the cross section of tree-of-heaven (left) and hornbeam (right)](image)

In case of tree-of-heaven the cracks occurred almost only in radial direction. The most of the micro cracks could be observed next to the rays or in the rays between the single ray cells (Figure 3.). As the moisture/water leaves the wood in the form of steam during heat treatment, the steam pressure increases rapidly in the lumens. The reason for the high amount of the cracks in this region is the thin and weak cell wall of the ray parenchyma cells, which can collapse easier compared to the libriform fibers. Several cracks were continued from the rays into the base tissue (libriform fibers) of the wood as well. In the vessels, only a few and small cracks occurred as a result of the treatment. Tree-of-heaven has large and open vessels (without tyloses), thus the steam formed during heat treatment from the moisture in the cell walls and lumens can leave the wood tissue easily. Therefore the stresses induced by the increased steam pressure are lower in the vessels as well. On the other hand, the collapses occurred often between the cells along the middle lamellae, which is also a weak point in the wood structure.

Similar to tree-of-heaven, in case of hornbeam the cracks occurred almost only in radial direction as well. Large cracks could be observed, and the cracks were located mostly in the cumulative rays
between the single cells, along the middle lamellae (Figure 4). Damage of the vessels could not be found.

Figure 3. SEM images from cracks of tree-of-heaven tangential surface (left) and radial surface (right)

Figure 4. SEM images from cracks of hornbeam cross section (left) and tangential surface (right)

3.3. Acetylation

Hornbeam achieved a weight percentage gain (WPG) of 15%, which indicated good impregnability and treatability. The most favourable properties (like durability and strength) are achieved at a WPG of 15-20% according to various studies found in the book of Hill [2]. The OH groups were replaced by acetyl groups thus the wood material became less sensitive to moisture. This is confirmed by the results (Table 2).

The equilibrium moisture content decreased by 70% and the swelling and shrinking rate decreased by 24-82%. Hornbeam gained high anti-swelling efficiency of 81-88%. These properties have a high importance in the service life of wood products, which are exposed to frequently changing climate and moisture conditions. As the acetylated material is less sensitive to moisture it also has a lower tendency to crack than natural hornbeam.

The compression strength, bending strength, impact bending strength, Janka hardness, Brinell hardness increased by 43%, 20%, 88%, 55-56%, 49-68%, respectively. In water-saturated state, the bending strength, modulus of elasticity, Janka hardness, Brinell hardness increased by 93%, 36%, 111-154%, 124-163%, respectively. The increment of mechanical properties enable the use of acetylated hornbeam in applications where tough structure, high wet strength, bearing of heavy loads and resistance to deflection is essential. It also has similar or improved mechanical properties compared to Accoya® beech.
Durability tests were carried out where the weight loss of acetylated hornbeam was below 1% after being exposed to *Coniophora puteana*, *Poria placenta* and *Coriolus versicolor* for 16 weeks. In an ongoing research, acetylated hornbeam showed no sign of decay or degradation after 9 months of exposure in soil while natural hornbeam already had surface softening and insect damages. The improvement of fungi resistance ensures the use of acetylated hornbeam in outdoor applications like decking, terrace, furniture, docks, façade, etc.

Table 2. Effect of acetylation on the properties of hornbeam

| Properties                              | After acetylation |
|-----------------------------------------|-------------------|
| Equilibrium moisture content            | - 70%             |
| Swelling-shrinking rate                 |                   |
| - in tangential direction               | - 81%             |
| - in radial direction                   | - 82%             |
| - in longitudinal direction             | - 24%             |
| Compression strength                    |                   |
| - conditioned (20°C 65%)                | +43%              |
| Bending strength                        |                   |
| - conditioned (20°C 65%)                | +20%              |
| - water-saturated                       | +93%              |
| Modulus of elasticity                   |                   |
| - conditioned (20°C 65%)                | 0%                |
| - water-saturated                       | +36%              |
| Impact bending strength                 |                   |
| - conditioned (20°C 65%)                | +88%              |
| Janka hardness (20°C 65%)               |                   |
| - tangential surface                    | +55%              |
| - radial surface                        | +56%              |
| Janka hardness (water-saturated)        |                   |
| - tangential surface                    | +154%             |
| - radial surface                        | +111%             |
| Brinell hardness (20°C 65%)             |                   |
| - tangential surface                    | +68%              |
| - radial surface                        | +49%              |
| - end grain                             | +51%              |
| Brinell hardness (water-saturated)      |                   |
| - tangential surface                    | +163%             |
| - radial surface                        | +124%             |
| - end grain                             | +145%             |

4. Conclusions
The investigations were performed in order to clear up the behaviour of Turkey oak, hornbeam and Tree-of-heaven xylem in case of three different modification methods. Based on the quality of the treated samples the ThermoWood schedules at 180 and 200 °C were able to modify the chosen
hardwoods without cracks and other damages on the surface. The results of our preliminary investigations on the selected physical properties of tree-of-heaven showed that the dry heat treatments decrease significantly the equilibrium moisture content and swelling of the xylem. Correlation could be found between the anti-swelling-efficiency and the annual rings’ position. According to our further results the dry heat treatments are able to decrease the mass loss caused by enzymatic attack of oak mazegill (Daedalea quercina) on Turkey oak. Turkey oak with wide sapwood can be only used with added preservatives in outdoor constructions. The dry heat treatment has been proved, as an alternative method to reach higher resistance class against basidiomycetes, thus the service life of the wooden constructions and products can be prolonged in case of outdoor applications too.

The role of the initial moisture content during OHT was clear, as with the increase of it the number and dimensions of the cracks were increasing. In case of 0% initial moisture content only a few and very small damages were observed, and a little more and larger cracks in case of ~12% initial moisture content. In case of green state initial moisture content the cracks were large and very frequent. The cracks occurred mostly in case of all wood species and initial moisture contents next to the rays and along the middle lamellae.

With the acetylation method, mechanical properties, dimensional stability and equilibrium moisture content could be improved remarkably. These results mean that it is possible to significantly reduce the initially high shrinking and swelling tendency of hornbeam wood, which is one of its biggest lack. However, the mechanical properties of native hornbeam are high, with the treatment it is possible a further increase of them, thus, a production of a dimensionally stable material with outstanding mechanical properties is available.

These wood species have much more potential to be used for more applications than they are used now. If high-quality raw material is selected and proper process parameters are chosen during the modification treatment, these wood species can have a bigger share on the wood market. Other modification techniques could also be tested on these wood species.

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