Mendel University in Brno

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Wood impregnation

Doctoral Thesis

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Abstract

Pařil, P. (2016) Wood impregnation, Doctoral thesis, Mendel University in Brno, 131 p.

Wood impregnation is one of the oldest and the most frequently used techniques to protect the wood. This treatment offers a wide range of protection depending on used impregnants (preservatives). Impregnation can make the wood more resistant to decay, less flammable, more dimensionally stable, harder, stronger, more UV stable resistant and many more.

Generally, the aims of this thesis is to give a new and modern approaches to already known technologies.

The experimental part have been carried out using laboratory vacuum-pressure impregnation plant and many other devices. Almost all treatments and measurement have been done in laboratories of Research centre in Útěchov. The different wood species e.g. European beech (*Fagus sylvatica* L.) and hybrid poplar (*Populus hybrids*) have been studied.

The patented solution shows the method of the treatment and colouring of wood containing tannins, characterized by impregnation with a product containing iron oxide nanoparticles, in a concentration of 0.4 g/l to 42 g/l, an average particle size in the range of 1 to 100 nm, and a liquid medium. Impregnation can be performed as pressure impregnation, followed by soaking, or the product can be applied by brushing or spraying. This method is an alternative to wood ammonification. The tests (Paper I) shows following results. Both nanoiron and ammonia treatments tested induced darker colouring of oak wood, more intensive darkening was observed in case of the nano-iron treatment. The native oak showed a steep drop in lightness ca 25–50 hours of exposure followed by gradual re-increase during further exposure to the artificial sunlight. The darker surfaces generated by tannin reacting chemically with iron and ammonia evidently faded in the course of light exposure. In case of chromatic parameters a* and b*, the AT (ammonia treatment) oak more or less copied the colour change progress of native oak. On the contrary, the NIT (nanoiron treatment) wood showed a double increase in both parameters. The colour of NIT wood after light exposure was more or less equivalent to the original colour of the ammonium-treated. Distinct reddening of NIT oak may be caused by oxidation of non-precipitated iron particles.

The antifungal effects of copper and silver nanoparticles against two wood-rotting fungi were investigated with following results (Paper II). The highest value of retention was observed for pine sapwood (~ 2 $kg \cdot m^{-3}$) for both nanoparticle solutions. The amount of nanoparticles in the wood did not increase proportionally with an increasing concentration, but only 1.5–2 times increase was reached. An average leaching of 15% to 35% was observed for copper nanoparticles, depending on used wood species and concentration. Significantly lower leaching (max. 15 %) was observed for pine sapwood impregnated by silver nanoparticles with a concentration of 3 g/l. The highest antifungal effect (under 5 % of mass loss) against both tested fungi was found for nano-copper treatment at the concentration of 3 g/l. However, this effect of treatment seems to be almost negligible after the leaching test. Therefore, this study aims to present fundamental material properties of wood treated with copper and silver nanoparticles, and provide groundwork for further research (e.g. fixation of substances in the wood structure, etc.).

In this study (Paper III), selected physical and mechanical properties, i.e., density profile, bending strength, hardness and moisture absorption were investigated for Lignamon (i), which was obtained from the Czech industrial production. Selected properties were also investigated using steam-densified beech (ii) and native beech (iii) and compared with each other. Densitometry of Lignamon showed a large variability of the density profile compared to the density profile of only densified beech. It is affected by the degree of densification, temperature and moisture gradients, and their relationship to the glass transition of the wood cell wall. Modulus of elasticity, hardness, moisture exclusion and anti-swelling efficiency of Lignamon are enhanced compared to densified beech. The enhanced dimension stability and lower hygroscopicity of Lignamon are probably caused by heat treatment during the process. Further investigation will be carried out with self-produced Lignamon samples.

The paper IV deals with the effect of vacuum-pressure impregnation of poplar wood (*Populus alba* L.) by aqueous solutions of sucrose and sodium chloride on its physical properties. The most satisfying final properties were achieved in impregnation of sucrose with concentration of 6.25 g/100 ml H2O. The retention was 31 $kg \cdot m^{-3}$ (WPG around 8 %). The values of ASE (anti-swelling efficiency) reached to 36 % and MEE (moisture exclusion efficiency) was reduced by 33 %.

In Paper V, MW and conventional acetylation of wood was carried out to determine its efficacy on the material properties. Both MW and conventional heating positively affected the selected material properties. The results showed that no significant differences were found between MW and conventional heating; therefore, MW heating can be used as a valid replacement in the acetylation process. MW power of 2 kW and 0.1 m·min-1 conveyor speed were the optimum conditions for MW acetylation. These process parameters resulted in 39.4 % ASE (T) and 35.2 % ASE ® for beech and 38.0 % ASE (T) and 16.3 % ASE (R) for poplar samples. This work provides insight into the details of wood acetylation using MW heating.

The study (Paper VI) aims to evaluate the antifungal activity of extractive compounds obtained with fexIKA accelerate extraction process. Results showed that the extractive compounds obtained from black locust heartwood were able to increase the native durability of European beech from class 5 (i.e. not durable with an average mass loss of 43.6 %) to class 3 (i.e. moderately durable with an average mass loss of 12.7 %).

The final Paper VII shows following results. After impregnation with residual liquids and leaching, high amounts of TT (thermal treatment) and HTC (hydrothermal carbonisation) solution were washed out, whereas Pyrolysis liquids stayed with 25 % to 40 % remaining in the wood. Volumetric swelling in 65 % relative humidity at 20 °C was reduced from 6.5 % in untreated poplar to 5 % in impregnated samples with process residues of thermal treatment using 180 °C or 200 °C. The processes using HTC liquids from Miscanthus sp. (Misc.) or Sawdust showed reduction to 3-3.5 % and Pyrolysis liquid treatment to 2.5 %. After exposure to fungi, the mass loss of untreated Beech (30-35 %) and Poplar (40-50 %) was reduced to 2 % in case of Pyrolysis- and 4 % in case of TT-treatment.

Key words: impregnation; modification; pressure; vacuum; penetration; permeability; nanoparticles; copper; silver; iron oxide; acetylation; dimensional stability; temperature, preservation; extractives; residue; sucrose; sodium chloride

Abstrakt

Pařil, P. (2016) Impregnace dřeva, Disertační práce, Mendelova univerzita v Brně, 131 s.

Impregnace dřeva je jedním z nejstarších a nejčastěji používaných technik k ochraně dřeva. Toto ošetření nabízí širokou škálu ochrany v závislosti na použité impregnační látce (konzervační látce). Impregnace může dřevo učinit odolnější vůči hnilobě, méně hořlavé, rozměrově stabilnější, tvrdší, pevnější, UV stabilnější a další.

Obecně má práce za cíl poskytnout nové a moderní přístupy k již známým technologiím.

Experimentální část byla provedena za použití laboratorní vakuo-tlakové impregnační linky a mnoho dalších zařízení. Téměř všechny procesy a měření byli provedeny v laboratořích výzkumného centra v Útěchově. Pro výzkum byly použity různé dřeviny jako např. buk lesní (*Fagus sylvatica* L.) nebo topol (*Populus hybrids*).

Patentované řešení poskytuje způsob ošetření a barvení dřeva obsahujícího třísloviny, vyznačený tím, že dřevo se impregnuje přípravkem obsahujícím nanočástice oxidů železa v množství 0,4 až 42 g/l, o průměrné velikosti částic v rozmezí 1 až 100 nm, a kapalný nosič. Impregnace může být prováděna jako tlaková impregnace s následným máčením nebo nátěrem či postřikem. Tento způsob je alternativou k čpavkování dřeva. Testy (Článek I) ukazují následující výsledky. Úprava čpavkem i nanoželezem vykazuje tmavší zbarvení dubového dřeva, intenzivnější ztmavnutí bylo pozorováno v případě ošetření nanoželezem. U neošetřeného dubu došlo k prudkému pokles světlosti po cca 25-50 hodin expozice a dalšímu postupnému zvýšení během další expozici. Tmavší plochy vytvořené reakcí tříslovin s železem nebo amoniakem zmizely po světelné expozici. V případě parametrů a * a b *, AT (úprava čpavkem) dubu je shodná s průběhem změny barvy neošetřeného dubu. Naopak se ukázalo, že u NIT (úprava nanoželezem) dubu byl dvojnásobný nárůst u obou parametrů. Barva NIT dřeva, po světelné expozici, byla více či méně ekvivalentní původní barvě AT. Zřetelné zčervenání NIT dubu může být způsobeno oxidací nevysrážených částic železa.

Fungicidní účinek nanočástic mědi a stříbra proti dvěma dřevokazným houbám byly zkoumány s následujícími výsledky (Článek II). Nejvyšší hodnota příjmu látky byla pozorována u běli borovice (~ 2 $\mathrm{kg \cdot m^{-3}}$) pro obě formulace. Množství nanočástic ve dřevě se nezvyšovalo úměrně s rostoucí koncentrací, ale zvýšilo se pouze 1,5 až 2 krát.

Nanočástice mědi dosahovaly průměrné vyluhovatelnosti 15 % až 35 % v závislosti na dřevině a koncentraci. Výrazně nižší vyluhovatelnost (max. 15 %) byla u běli borovice impregnované nanočásticemi stříbra o koncentraci 3 g/l. Nejvyšší fungicidní účinky (pod 5% ztráty hmoty) proti oběma testovaným houbám byly zjištěny u vzorků ošetřených nanočásticemi mědi o koncentraci 3 g/l. Nicméně, tento účinek je po testu vyluhování téměř zanedbatelný. Další výzkum by měl být zaměřen na fixaci látek ve struktuře dřeva.

V této studii (Článek III) jsou zkoumány fyzikální a mechanické vlastnosti, tj., hustotní profil, pevnost v ohybu, tvrdost a navlhavost Lignamonu (i). Pro srovnání byly zkoumány vybrané vlastnosti lisovaného (pařeného) buku (ii) a neošetřeného buku (III). Lignamon vykazoval velkou variabilitu hustotního profilu ve srovnání s hustotním profilem pouze slisovaného buku. Toto je ovlivněno stupněm slisování, teplotou a vlhkostí. Modul pružnosti, tvrdost, odolnost proti navlhání a bobtnání se u Lignamonu zvyšuje ve srovnání se slisovaným bukem. Zvýšená rozměrová stabilita a nižší hygroskopicita Lignamonu jsou pravděpodobně způsobeny procesem tepelné úpravy. Další výzkum bude proveden s vlastně vyprodukovaným materiálem.

Článek IV se zabývá účinkem tlakové impregnace topolového dřeva (*Populus alba* L.) vodnými roztoky sacharózy a chloridu sodného na jeho fyzikální vlastnosti. Nejlepších vlastností bylo dosaženo u impregnace sacharózou o koncentraci 6,25 g / 100 ml H_2O. Příjem látky byl 31 kg·m^{-3} (WPG kolem 8%). Hodnoty ASE (odolnost vůči bobtnání) dosáhly 36 % a MEE (odolnost vůči navlhavosti) byla snížena o 33 %.

MW (mikrovlnná) a konvenční acetylace dřeva byla provedena s cílem určit účinnost na vlastnostech materiálu (Článek V). MW a konvenční ohřev pozitivně ovlivnily vybrané vlastnosti materiálu. Výsledky ukázaly, že nebyly zjištěny žádné významné rozdíly mezi MW a konvenčním ohřevem; Proto, MW ohřev může být použit jako náhrada v procesu acetylace. MW výkon 2 kW a rychlost dopravníku 0,1 m·min^{-1} byly optimální podmínky pro MW acetylaci. Tyto parametry procesu měli za následek 39,4 % ASE (T) a 35,2 % ASE (R) u buku a 38,0% ASE (T) a 16,3 % ASE (R) u topolových vzorků. Tato práce poskytuje detailní pohled na acetylaci dřeva za použití MW ohřevu.

Studie (Článek VI) si klade za cíl vyhodnotit fungicidní aktivitu extraktivních látek získaných z urychleného procesu extrakce (fexIKA). Výsledky ukázaly, že extraktivní látky získané z jádra akátu zvýšily trvanlivost buku z třídy 5 (netrvanlivý s průměrným hmotnostní úbytkem 43,6 %) do třídy 3 (středně odolný s průměrnou hmotnostní ztrátou 12,7 %).

Výsledky posledního Článku VII jsou následující. Po impregnaci odpadními látkami a následném luhování, velké množství TT (proces tepelné úpravy) a HTC (proces hydrotermální karbonizace) roztoku bylo vyluhováno, zatímco 25 % až 40 % pyrolýzních roztoků zůstaly ve dřevě. Objemové bobtnání (při 65% relativní vzdušné vlhkosti a 20 °C) bylo sníženo z 6,5 % u neošetřeného topolu na 5 % u impregnovaných vzorků odpady z tepelného procesu (180 °C nebo 200 °C). Procesy využívající HTC odpad z Miscanthus sp. (Misc.) snížily obj. bobtnání na 3-3,5 % a 2,5 % v případě ošetření pyrolýzními látkami. Hmotnostní úbytky (po testech odolnosti) neošetřeného buku (30-35 %) a topolu (40-50 %), byly sníženy na 2 % v případě pyrolýzních látek a 4 % v případě TT úpravy.

Klíčová slova: Impregnace; modifikace; tlak; vakuum; penetrace; propustnost; nanočástice; měď; stříbro; oxid železa; acetylace; rozměrová stabilita; teplota, konzervace; extraktiva; reziduum; sacharóza; chlorid sodný

Preface

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Brno, October 2016
Petr Pařil

List of Patent and Papers

This doctoral thesis includes the following patent and papers, which are referred in text by Roman numerals I-VII.:

Patent Pařil, P., Baar J., Dejmal, A., Foret, F., Křenková J. (2016) THE METHOD FOR THE TREATMENT AND COLOURING OF WOOD CONTAINING TANNINS. Patent number 306249, Industrial Property Office (CZ).

I. Baar, J., Pařil, P., Rozbořil, T., Kúdela, J. (2016) COLOUR STABILITY OF CHEMICALLY MODIFIED OAK WOOD – NANOIRON AND AMMONIA TREATMENT. Eco-efficient resource wood with special focus on hardwoods. University of West Hungary, p 35–36.

II. Pařil, P., Baar J., Rademacher, P., Prucek, R., Sivera M., Panáček, A. (2016) ANTIFUNGAL EFFECT OF COPPER AND SILVER NANOPARTICLES AGAINST WHITE-ROT AND BROWN-ROT FUNGI. J Mater Sci (under revision).

III. Pařil, P., Brabec, M., Maňák, O., Rousek, R., Rademacher, P., Čermák, P., Dejmal, A. (2014) COMPARISON OF SELECTED PHYSICAL AND MECHANICAL PROPERTIES OF DENSIFIED BEECH WOOD PLASTICIZED BY AMMONIA AND SATURATED STEAM. Eur. J. Wood Prod. 72(5): 583-591.

IV. Pařil, P., Dejmal, A. (2014) MOISTURE ABSORPTION AND DIMENSIONAL STABILITY OF POPLAR WOOD IMPREGNATED WITH SUCROSE AND SODIUM CHLORIDE. Maderas (16)3: 299–311.

V. Dömény, J., Čermák, P., Pařil, P., Fodor, F. P., Dejmal, A., Rademacher, P. (2015) APPLICATION OF MICROWAVE HEATING FOR

ACETYLATION OF BEECH (FAGUS SYLVATICA L.) AND POPLAR (POPULUS HYBRIDS) WOOD. BioResources 10(4): 8181–8193.

VI. Sablík, P., Kyriaki G., Pařil, P., Baar, J., Rademacher, P. (2015) IMPACT OF EXTRACTIVE CHEMICAL COMPOUNDS FROM DURABLE WOOD SPECIES ON FUNGAL DECAY AFTER IMPREGNATION OF NONDURABLE WOOD SPECIES. Eur. J. Wood Prod. 74(2): 231-236.

VII. Rademacher, P., Pařil, P., Baar, J., Čermák, P., Rousek, R., Meier, D., Koch, G., Schmitt U. (2015) IMPROVEMENT OF WOOD PROPERTIES DUE TO IMPREGNATION OF WOOD WITH RENEWABLE LIQUIDS FROM DIFFERENT PROCESS RESIDUES OF NATIVE ORIGIN. Conference paper (Cost action FP1407), Koper, Slovenia.

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List of Abbreviations

ACA	ammoniacal copper arsenate
ACQ	alkaline copper quat
ACZA	ammoniacal copper zinc arsenate
ANOVA	analysis of variance
ASE	anti-swelling efficiency
AT	ammonia treatment
AWPA	The American Wood Preservers' Association
CA	copper azole
CCA	chromated copper arsenate
CCB	copper-chromium-boron
CCP	copper-chromium-phosphate
DOT	disodium octaborate tetrahydrate
EMC	equilibrium moisture content
EU	European union
H_B	Brinell hardness
HSD	Tukey's honest significance test
HTC	hydrothermal carbonisation
IPBC	3-Iodo-2-propynyl butyl carbamate
IRGWP	The International Research Group on Wood Preservation
MC	moisture content
MEE	moisture exclusion efficiency
MOE	modulus of elasticity
MOR	modulus of rupture
MW	microwave
NIT	nanoiron treatment
PAH	polynuclear aromatic hydrocarbons
PCP	pentachlorphenol
R	retention
RH	relative humidity
S	swelling
SD	standard deviation

TT	thermal treatment
UV	Ultraviolet
WPG	weight percentage gain
ZB	zinc borate

1 INTRODUCTION

1.1 Background

Wood as a natural product is susceptible to biodegradation, weather conditions, chemical degradation, fire and mechanical wear. These processes changes its properties such as weight, dimensions, colour, etc. There are a lot of techniques to protect wood against these biotic and abiotic factors. However, wood impregnation is one of the oldest and the most frequently used techniques to protect the wood. This treatment offers a wide range of protection depending on used impregnants (preservatives). Impregnation can make the wood more resistant to decay, less flammable, more dimensionally stable, harder, stronger, more UV stable resistant and many more.

The natural resistance of wood to decay or other factors varies by species, position in the trunk, growth conditions, etc. There are some species with very high durability (e.g. tropical hardwoods), which can be used without any treatment. There are many limitation for their usage (demand exceeds supply, cost, etc.). This is the reason why the wood preservation is so important. Some of the preservatives are more or less toxic and progressively restricted. The future is in the utilization of non-toxic preservatives and “eco-friendly” processes, which is also the objective of this thesis.

1.2 Aims of the study

The presented doctoral thesis aims to give a new and modern approaches to already known technologies. The thesis pursues the following objectives:

I. Transform the known process of colour and UV stabilization (ammonia treatment) to the new enhanced process using nanoparticles (iron oxide).
II. Examine the antifungal effect of nanoparticles impregnation (copper and silver).
III. Examine the properties of modified wood so-called Lignamon for its possible future use.
IV. Evaluate the physical and mechanical properties of wood impregnated with natural compounds (sucrose and sodium chloride).
V. Accelerate the acetylation process using MW heating.
VI. Examine the effect of impregnation with extractives from durable wood species to non-durable wood species.
VII. Evaluate the properties of wood impregnated with renewable liquids from different process residues.

2 LITERATURE REVIEW

2.1 History of Wood Impregnation

Improving the wood properties by impregnation with various substances is known for millennia. One of the oldest example of wood preservation is impregnation of wooden sculpture called Diana of Ephesus (628 – 356 BC), which was reported by Plinius. The sculpture was drilled by small holes for better penetration of oil "Nard" (extract of plant Nardostychos from India). It was used also asphalt, olive and other oils. Leonardo da Vinci (1452–1519) coated the wood panels for his paintings with mercuric chloride and arsenic trioxide. The physician and chemist Homberg in 1705 also recommended mercuric chloride to control wood borers. Boric acid (sal sedativum Hombergi), which is one of the most important wood preservatives nowadays, is attributed to Homberg. In the 1832, Englishman named Kyan established industrial impregnation with mercury dichloride (The Kyan Process). Copper sulphate was also used for wood protection industry. Coal-tar oil (creosote) was patented by Moll (1836) and introduced into the impregnation industry by Bethell in 1838. The pressure impregnation process known as Bethel was developed by Breant and Englishman Bethel was responsible for its adaptation to creosote treatments. The process started with an initial vacuum followed by filling of the vessel with preservative and application of a pressure period to inject the preservative. Creosote was cheaper in England compared to European continent. Therefore, it was started to use zinc chloride, which was introduced to the practise by the Englishman Burnett. Treatment with zinc chloride has some negative properties, such as easy leachability and low efficiency. Due to this, zinc chloride was impregnated in combination with creosote. Copper naphthenate has been used as a wood preservative since 1889. In 1902 the Englishman Max Rüping commercially developed empty-cell process (Rueping Process) but the earliest empty-cell process was developed by Wassermann. The process is initiated with air pressure before filling the vessel and applying a higher pressure to inject the preservative. After release of pressure, the excess preservative in the cell lumen is "kicked back," resulting in a much lower retention than the conventional full-cell treatment (Bethel Process). It is one of the biggest milestones in pressure impregnation techniques. This process reduce the consumption of creosote and thus cost reduction and it is still used today (also for other preservatives). C.B. Lowry patented the second empty-cell treatment (Lowry Process), which utilizes atmospheric pressure as the initial air pressure. Basilius Malenkovič discovered an effective fungicide fluorides in 1901. K. Wollmann used sodium fluoride as the wood preservative and helped to expanded usage of fluorides. Insecticidal and fungicidal effects of arsenite discovered Falck. The American Wood Preservers' Association (AWPA) was formed in 1904. K. Bubla started the first impregnation production in Březnice (Czechoslovakia) in 1934 and the company exists with the same name (Sublima) until now. Bubla patented and developed pressure impregnation process with the preservative so-called "Sublimate". This preservative has low leachability, sufficient protection efficiency but causes strong corrosion of the steel. The company Osmose (Leipzig, Germany) patented a preservative process using sodium fluoride, potassium dichromate, sodium arsenate and dinitrophenol. Penetration was achieved through the process of diffusion into green wood or wood of high moisture content. CCA (chromated copper arsenate) was patented by S. Kamesam in 1938. The other major arsenical preservative, ammoniacal copper arsenate (ACA), was standardized in 1950. The International Research Group on Wood Preservation (IRGWP), formed in 1969, now plays a major international role in dissemination of information on the destructive agents of wood and stimulation of research on wood preservation (Ille 1959, Richardson 1978, Zabel and Morrell 1992, Unger et al. 2001, Freeman et al. 2003). The preservatives and processes used in the last decades will be described in chapter 2.3.

2.2 Impregnation Techniques, Methods and Processes

There are many of application techniques that ensure transport of active ingredient into the treated wood in required quantity and well distribution. Selection of impregnation techniques depends on the wood properties (species, permeability, moisture content, temperature, etc.), preservative characteristics (crystallising point, etc.), end use (use class, health risk, etc.), and others (customer requirements, technology available, etc.). The key indicators of the quality of impregnation are: retention of preservatives (or retention in an assay zone) expressed in [$kg \cdot m^{-3}$] (at pressure impregnation) or [$g \cdot m^{-2}$] (at non-pressure impregnation) and depth of penetration indicated in [mm].

The impregnation treatments can be divided into non-pressure (see chapter 2.2.2) and pressure (see chapter 2.2.3). This usually requires to carry out pre-treatments (see chapter 2.2.1).

2.2.1 Pre-treatments

The ideal time range between felling and milling is a week at most. For longer periods can be used biocide such as copper-8 quinolinolate for brushing or spraying the exposed end-grain of logs. The poles are usually debarked before drying.

With few exceptions, wood should be dried to its fibre saturation point (~ 25-30 %) or below before impregnation treatment. Kiln-drying is limited by the dimensions of treated wood and is more common for lumber. Air-drying is used for large timbers (railway sleepers, poles, etc.) as seen in Figure 1. This method is more time consuming (e.g. spruce poles requires about 3 months of air-drying depending on the season). Drying increases preservative penetration and retention. It has also great significance for cracking, which much of them occurs before impregnation treatment. If the timber is not adequately dried the cracks may occur in the service of timber. These cracks can expose untreated locations in the wood and enable the way for wood-destroying insects or fungi (Walker 2006).

Figure 1 The storage of air-drying poles (left) and railway sleepers (right) (unpublished, photo was taken in the company Impregnace Soběslav).

Hardwood sleepers are susceptible to end cracking. Anticracking irons are often used in the end-grains of the sleepers when they are stacked for air-seasoning (see Figure 2). The use of anticracking irons does not always prevent serious end cracking, and there is some disagreement regarding their value. Their continued use by various railroads, however, indicates that some still consider them an important help in reducing the danger of injury from end cracking (Maclean 1953).

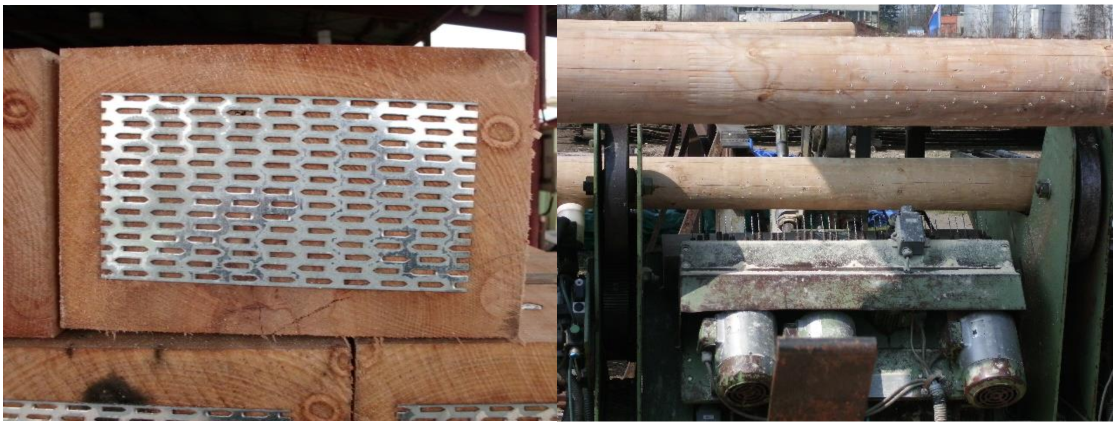


Figure 2 Anticracking irons in the end-grains of the sleeper (left) and drilling machine for perforation of poles (right) (unpublished, photo was taken in the company Impregnace Soběslav).

Incising, drilling (see Figure 2) and other machining are mainly used for spruce poles or other impermeable species (Douglas fir, larch, etc.). Drilling can be also used for railway sleepers (Tsoumis 1991).

2.2.2 Non-pressure Impregnation

Brushing and spraying are simple and low-cost treatment method but the depth of penetration and retention are very limited. Penetration across the grain is minimal and some penetration along the grain is possible.

Dipping for a seconds can increase end-grain penetration compared to brushing or spraying. The end-grain of pine sapwood is able to get penetration depth in range of 25 to 75 mm.

Soaking is the same process like dipping with a difference of the immersion time, which could be hours, days or weeks. This process is often applied in sawmills for small poles and lumbers. The sapwood of pine after 24 to 48 hours of soaking in preservative solution was well penetrated and retention levels ranged from 32 to 96 kg·m^{-3}.

Diffusion method is applied to freshly sawn green wood with a moisture content in excess of 50 % (e.g. poles or construction timber). A water-borne preservative (boron salts, fluorine compounds) in paste form is brushed on the surface of the wood, where diffuses mainly to sapwood. The substances flow during diffusion is ensured by concentration gradient across the material, which cause the movement of solution from a place with higher concentration to place with lower concentration. The method is mainly used for impermeable species.

Boucherie process (sap displacement) is applied to freshly cut green logs with bark. The tank containing preservatives is placed on scaffolding (height of 10-15 m) and the logs on the ground (butt a little higher than top). A tight metallic cap attached to clean surface of butt is connected by piping to the tank.

Hot and cold bath is the physical methods of impregnation, when the wood is soaked in the hot preservative bath and then in the cold preservative bath. The air in cell cavities of wood placed to the hot bath expands. The preservatives are penetrated to wood due to partial vacuum, which is created by the air contraction after immersion in cold baths (Richardson 1978, Tsoumis 1991, Walker 2006).

2.2.3 Pressure Impregnation

Impregnation, which combine vacuum and pressure, is the most common and effective methods. The process requires specially equipped plants (see Figure 3) with pressure vessels, air compressors, vacuum pumps, measuring and storage tanks, etc. The pressure impregnation methods can be divided into two methods: full-cell and empty-cell. There are many variations of treatment cycles, which will be described in the following text. Figure 4 shows diagrams of mentioned and described processes conventionally used nowadays.

Figure 3 Charging the timber to the vessel of vacuum pressure impregnation plant (http://www.wtt.dk/products/impregnation/impregnation-plant/pictures)

Bethell process (full-cell) is started with an initial vacuum (-85 kPa at least) for 15 minutes or more depending upon permeability and cross-section dimensions of treated wood. Then the preservatives solution is filled into the impregnation vessel and the starts to penetrate into the wood porous system. Subsequently, the pressure (usually about 800 to 1400 kPa, above atmospheric pressure) is typically applied for 1-5 hours but occasionally many hours according to permeability and cross-section. The pressure is held until the timber is fully impregnated or the rate of preservative absorption by the timber becomes negligible. After that, the pressure is released while the preservative solution is drained from the vessel. The last step is to use final vacuum (typically about -50 kPa for 5-10 minutes) to avoid kickback effect and bleeding of preservatives from the surface of treated wood (commonly used for water-based preservatives). Water-borne preservatives are usually used at room temperature but e.g. creosote is heated at 60-120 °C to reduce the viscosity and thus increase penetration. The preservative retention of permeable timber (e.g. beech or pine sapwood) may reach up to 600-700 kg·m^{-3}. Using this method the retention of creosote varies from 80 to 250 kg·m^{-3}.

Vacuum process (full-cell) is used for permeable wood species or small dimensions of treated wood. The process begins with vacuuming followed by impregnation under atmospheric pressure and it ends with the final vacuum.

Rueping process (empty-cell) was originally developed for creosote treatment and is usually used for this treatment up to now. The process is initiated by the air pressure, commonly in the range of 150 to 400 kPa for a period of 10 to 60 minutes depending on the permeability and sizes of the treated wood. Setting the air pressure value and its duration at the beginning of the process is the most suitable and practically the only way to affect the retention. The preservative is pumped into the impregnation vessel without releasing the pressure which increase to 800-1400 kPa. After the pressure is released the preservatives can be removed from the vessel. A final vacuum (about -75 kPa) is also applied with time period about 10 minutes to minimize weeping. The creosote can be used only at high temperatures (100-120 °C). After Rueping treatment permeable timber may have 40-50 % of maximal retention. For example, the creosote retention of approximately 250 kg·m-3 can be achieved with Bethel method, but with a Rueping method the retention will be only about 110 kg·m-3 with the same depth of penetration.

Double Rueping process (empty-cell) is two single Rueping methods (cycles) in consecutive with shorter time period of impregnation pressure phase. Second cycle has higher pressure with longer duration. The process is mainly used for the treatment of beech railway sleepers with creosote.

Lowry process (empty-cell) ensures maximum penetration with a low retention of preservative. This process is not initiated by either vacuum or pressure but simply by atmospheric pressure. The next steps are already similar to the Rueping method, which includes pressurizing and final vacuum. The method is useful mainly for the permeable timbers such as pine. It is also used for impregnation of oak sleepers. Benefits of this method is the lower costs for technological equipment of the plant.

Oscillating pressure process utilizes repeated applications of high pressure and vacuum to penetrate preservative into green wood. The cycles increase progressively in length from about 1 to 7 minutes. The number of cycles varies about from 40 cycles to 400 cycles depending on permeability and dimensions of treated wood.

There are many other processes which are less known and used as e.g. *cascade process*, *Nordheim process*, *Cellon or Drilon process*, *pressure-stroke process*, *Boulton process*, *Poulain process*, etc. (Ille 1959, Richardson 1978, Tsoumis 1991, Walker 2006).

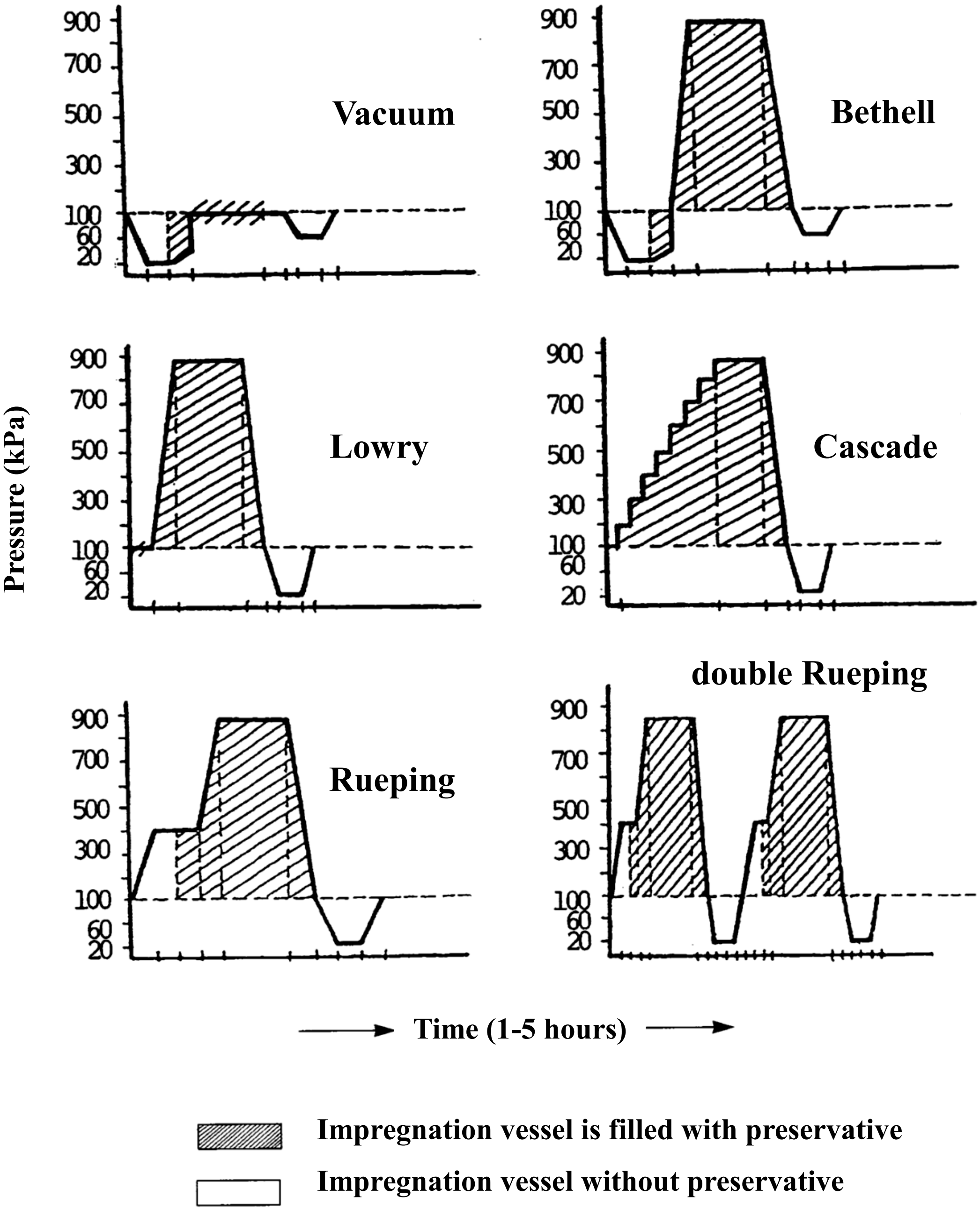


Figure 4 Diagrams of common used pressure impregnation methods

2.3 Wood Preservatives

Wood preservatives are intended to protect wood against biological factors, weathering, fire, chemicals and mechanical wear. According to Walker (2006), chemical preservative systems (against biological attack) can be divided in two main groups so called water-borne and oil-borne. These chemicals, natural preservatives (protection from biological attack), fire retardants and other preservatives will be described in the text below.

Active biocidal substances, approved by EU Directive for wood preservation (25.02.2014), are following:
4, 5-Dichloro- 2-octyl-2H- isothiazol-3-one (DCOIT), Alkyl (C12-16) dimethylbenzyl ammonium chloride, – C12-16 ADBAC, Basic copper carbonate, Bifenthrin, Boric acid, Boric oxide, Chlorfenapyr, Clothianidin, Copper (II) oxide, Copper hydroxide, Creosote, Cypermethrin, Dazomet, DDACarbonate, Dichlofluanid, Didecyldimethylammonium Chloride (DDAC), Disodium octaborate tetrahydrate, Disodium tetraborate, Etofenprox, Fenoxycarb, Fenpropimorph, Flufenoxuron, Hydrogen cyanide, IPBC, Propiconazole, Sulfuryl fluoride, Tebuconazole, Thiabendazole, Thiacloprid, Thiamethoxam and Tolylfluanid (Salminen et al. 2014).

2.3.1 Water-borne preservatives

Water-borne preservatives consist various inorganic chemicals (copper, chromium, arsenic, fluorine, mercury, and others) which are dissolved in water. They are available in powder form or liquid concentrates (Tsoumis 1991). Zabel and Morrell (1992) state that water-borne preservatives leaves wood surface clean and paintable. Another advantage is the reduction in release of volatile hydrocarbons as atmospheric pollutants during the treatment process. However, these preservatives do not offer protection against mechanical wear or improved dimensional stability of wood. Some water-based preservatives can leach out when the wood is exposed to liquid water and increase corrosion of steel fasteners (Tsoumis 1991, Walker 2006).

Chromated copper arsenate (CCA), developed in 1930s, was the most commonly used water-borne wood preservative. Nowadays, the usage of this preservatives is restricted in many countries, because arsenic and hexavalent chromium are recognized as potential human carcinogens. It exists many formulations with different ratios of copper, chromium and arsenic. The most common, type C, is 47.5% chromium trioxide, 18.5% copper oxide and 34% arsenic pentoxide dissolved in water (Walker 2006). CCA preservative is strongly fixed to the lignin components by the reduction of Cr^{6+} to Cr^{3+}. The fixation is influenced by pH and temperature of wood (Zabel and Morrell 1992).

Ammoniacal copper zinc arsenate (ACZA) is a refinement of an earlier formulation ACA (Ammoniacal copper arsenate). ACZA or Chemonite® contains copper oxide (50 %), zinc oxide (25 %) and arsenic pentoxide (25 %). It is also prohibited in many countries due to the presence of arsenic.

Acid copper chromate (ACC) is composed of copper oxide (31.8 %) and chromium trioxide (68.2 %). *Copper-chromium-boron (CCB)* and *Copper-chromium-phosphate (CCP)* is similar in many respects to CCA and arsenic is replaced by boron or phosphate. All of these preservatives are prohibited by the Biocidal Products Directive in Europe.

Alkaline copper quat (ACQ) was developed as a replacement of CCA due to restrictions on the use of chromium and arsenic. Copper provides the primary fungicide and insecticide activity in ACQ formulation, while the quaternary ammonium compounds ('quats') provide additional protection against copper tolerant fungi and insects. ACQ are a combination of copper oxide (66 %) and quaternary ammonium compounds (34 %). Various formulations of ACQ were developed and marketed but the most common are type B and D. The copper solubilizing agent may be ammonia (type B) or ethanolamine (type D). *Copper azole (CA)* is another water-borne preservative based on copper (96 %) and tebuconazole (4 %). *Copper HDO* is composed of three active ingredients as copper oxide, boric acid and Bis-N-cyclohexyldiazeniumdioxy copper (Walker 2006, Coudert et al. 2013).

Borates include formulations prepared from sodium tetraborate, sodium pentaborate, boric acid, zinc borate (ZB) and disodium octaborate tetrahydrate (DOT). The advantages of borates are low mammalian toxicity, activity against fungi and insects, and low cost. The biggest disadvantage is poor resistance against leaching from the treated wood (Walker 2016). This issue has been subject of many studies. For example, authors Jebrane and Heinmaa (2015) demonstrated satisfactory results with vinyl ester of carboxyphenylboronic acid for improving leach resistance of boron. Boron is fixed onto the wood by covalent bond as a result of transesterification between wood hydroxyl groups and the vinyl ester.

There are many others water-borne preservatives like *zinc naphthenate, triazoles, IPBC (3-Iodo-2-propynyl butyl carbamate)*, etc.

2.3.2 Oil-borne preservatives

Creosote is a complex mixture of over 200 polynuclear aromatic hydrocarbons (PAH) produced as a by-product of the high-temperature carbonization (Zabel and Morrell 1992). It is the main representative in oil-borne category. This preservative is very effective and often used for treatment of railway sleepers, poles, etc. It has high toxicity against fungi, insects and marine borers, low volatility, electrical resistance. Creosote does not oxidize metals and protects wood against weathering. The disadvantages are increased flammability of the treated wood, and impaired or impossible paintability. Also, creosote may bleed, has a disagreeable odour and present health hazard (Tsoumis 1991). EU directive has classified creosote as a dangerous waste (Polcaro 2008). There are restrictions to its application and the future of creosote as a wood preservative is uncertain.

Pentachlorphenol (PCP) is developed as a substitute for creosote but today, PCP has curtailed or severely restricted use in many countries (Walker 2006). It is easily synthesized by successive chlorination of phenol (Zabel and Morrell 1992).

Copper naphthenate, Tributyltinoxide, Copper-8-quinolinolate etc. are next less used oil-borne preservatives.

2.3.3 Natural Preservatives

A review of T. Singh and A.P. Singh (2011) shows plenty of studies targeted to natural products (Table 1), with little or no toxicity, used as wood preservatives. Some of these products can be alternative for traditional chemical preservatives that are considered toxic and can adversely affect human health and the environment. Implementation of the technologies has been countered because of certain limitations, including discrepancies between laboratory and field performance of natural products, variability in their efficacy related to exposure/environmental conditions, and legislation difficulties due to disagreements globally on setting standards defining the quality of their performance and use.

Table 1 Summary of natural compounds and their reported uses (T. Singh and A.P. Singh 2011)

Natural Product and sources	**Uses**
Essential oils	
Essential oil from cinnamon leaves	Wood decay fungi (nutrient medium)
Essential oils from Japanese cedar (Cryptomeria japonica) heartwood	Wood decay fungi (nutrient medium)
Anise oil, lime oil and tangerine oil	Moulds on rubberwood (dip treatment on wood)
Essential oils from lemongrass, rosemary, tea tree and thyme	Mould growth on yellow pine (dip and vapour treatment on wood)
Cinnamon oil	Ponderosa pine (dip treatment on wood)
Essential oil compounds and plant extracts; cinnamaldehyde, cinnamic acid, cassia oil, wood tar oil	Brown, white rot decay fungi and termites (pressure treatment on wood)
Essential oil from fruit peel of citrus	Fungi and termite (nutrient medium)
Essential oils from Japanese cedar (Cryptomeria japonica) heartwood	Wood decay and tree pathogenic fungi (nutrient medium)
Cinnamon (Cinnamomum osmophoeum)	Wood decay fungi (nutrient medium)
Cinnamon and clove oils	Mould fungi on rubberwood (nutrient medium and dip treatment)
Hinau (Elaeocarpus dentatus) leaf extract	Brown rot fungi (nutrient medium)
Cinnamaldehyde in combination with antioxidants propyl gallate, octyl gallate, quercetin, eugenol, catechin	White rot and brown rot fungi (nutrient medium)
Cinnamaldehyde, eugenol	White rot and brown rot fungi (nutrient medium)
Twelve essential oils screened, including eugenol and oil from cinnamon leaf and germanium	Mould, sapstain and decay fungi (nutrient medium and radiata pine pressure treatment)
Plant-derived oils (almond bitter, anise, basil, bay, caraway, cardamom, cedar, celery, chamomile, cinnamon, citronella, clove, coriander, cumin, dill, eucalyptus, fennel, ginger, grapefruit, lemon, lime, mint, parsley, peppermint, pepper, rose, spearmint, sweet orange, thyme, turmeric, juniper, winter green, tall, pine oils in combination with silicone based polymer	Mildew, termites and insects on wood (the method of treatment not disclosed)
Oxygenated aromatic essential oil compounds—22 essential oil phenols, phenol ethers and aromatic aldehydes	White rot and brown rot (nutrient medium)
Boron-linseed oil combination treatment	Japanese cedar, beech and pine against termites (pressure treatment)
Waxes, resins and tannins from bark	
Tannins from the bark of Southern pine	Brown and white rot fungi (pressure treatment)
Aleppo pine leaves and bark	Dip treatment
Bark from six species of wood	Mould, stain, brown and white rot fungi (nutrient medium)
Guayule (Parthenium argentatum Gray)	Decay fungi, termites and marine borers (pressure treatment)
Pinus bruita bark extracts	Brown and white rot (pressure treatment)
Extractives	
Extractives of Milicia excelsa and Chlorophora excelsa	Fungi, insects and marine borers (pressure treatment)
Heartwood extract of Milicia excelsa and Erythrophleum suaveolens	Brown and white rot fungi (pressure treatment)
Extract from Taiwania (Taiwania cryptomerioides)	White and brown rot fungi (nutrient medium), Termite

Lignans and glycorides from Gmelina arborea heartwood	White rot (nutrient medium)
Heartwood extractive of Thuja plicata and Chamaecyparis nootkatensis	Termite and brown rot (pressure treatment)
Valonia extract, sumac leaf extract and pine bark extract	White and brown rot fungi (pressure treatment on wood)
Extract of herbaceous plant, Inula viscose in combination with cinnamon oil, carvacol or thymol	White and brown rot fungi (pressure treatment on pine wood)
Heartwood extractive of Prosopis juliflora	White rot, brown rot, mould and termite (durability test without pressure treatment)
Australian native tree (Eremophila mitchelli)	Termites
Extract from white cypress pine	Termites
Miscellaneous	
Chitosan	Sapstain, mould and wood decay fungi (nutrient medium and dip and pressure treatment on wood)
Silicon compounds	Decay fungi
Trichoderma extracts	Sapstain and basidiomycetes
Lactobacillus extracts	Sapstain

2.3.4 Fire retardants

Fire retardants are applied to reduce the flammability of wood and act by creating a barrier to the spread of flame and/or generating non-combustible gases. Chemicals of the first type speed the formation of a charred wood layer or form a massive layer of foam. The second type provide fire-retardant action by melting, evaporation, or thermal decomposition. Usually, they contain silicas, ammonium phosphate, ammonium sulphate, zinc chloride, boric acid, or other borates (Tsoumis 1991, Richardson 1993).

2.3.5 Chemical modification

The chemical modification changes the chemical nature of wood. Some chemicals can react with the cell wall polymer hydroxyl groups. This can result in the formation of a single chemical bond with one OH group or cross-linking between two or more OH groups. The cell wall polymers is modified and the properties of treated wood is changed (Hill 2006).

Acetylation is the most common and successful marketed (Accoya® and Tricoya®) process in the area of chemical modifications. This marks guarantee modified wood free of toxic substances, durability class 1 (with more than 20 % WPG), and improved dimensional stability of 75 % or more. Moreover, the treatment does not influence the strength properties (except for a slightly increased hardness), and the material exhibits increased UV - stability (Kattenbroek 2007). Hydroxyl groups play the main role in many chemical modifications. In the reaction of OH groups with carboxylic acids anhydrides the esters are formed (Figure 5). The acetylation process is usually initiated by the pressure impregnation, whereby the temperature is applied (about 70 °C), when the exothermic reaction starts. Finally, the residual acetic acid is removed. In Sweden, researchers focus on the use of microwave technology for rapid heating during the modification process. Paper V deals with the same issue (Homan et al. 2004).

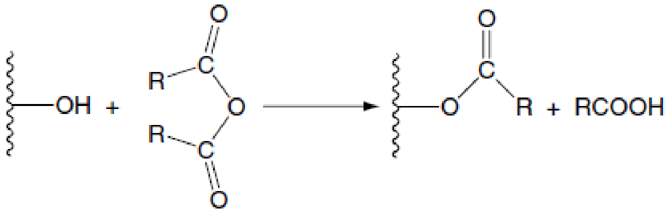


Figure 5 The reaction of an anhydride with wood, for acetic anhydride (R = CH3): propionic (R= C2H5), butyric (R= C3H7), valeric (R= C4H9), hexanoic (R= C5H10) and heptanoic (R= C6H11) (Hill 2006).

Furfurylation is chemical modification (impregnation) using furfuryl alcohol (2-furylmethanol), which forms highly branched and cross-linked furan polymer grafted to wood cell wall polymers. It can also forms covalent bonds with the lignin. The wood is first impregnated with the treating solution by a full cell process. Then an intermediate drying step is needed and after that the reaction curing-step is carried out. During the curing step the wood is brought to temperatures of 80-140 °C by injection of steam. The curing period is 6-8 h. Finally the wood is dried in a kiln to minimize emissions and to ship dry timber. The furfurylated products has high dimensional stability, high durability and resistance towards alkalis and acids (Homan et al. 2004, Hill 2006). Kebony®, which is homogeneously treated sapwood of various wood. Kebony® is marketed as an alternative to tropical hardwoods, and is well suited for floors, interior panels and other applications where an exclusive, tropical appearance, hardness and dimensional stability are important criteria. (Brynildsen 2007).

DMDHEU (1, 3-dimethylol-4, 5-dihydroxyethylenurea), *Resins (PF, MF, MMF and UF)*, *Silicates*, *Silicones*, *Citric acid polymates*, *polycarboxylic acids*, *Ketene gas*, *Isocyanate*, etc. are another substances used in the chemical modification (impregnation) of wood (Hill 2006, Jones 2007).

2.4 Effect of wood structure on the impregnation treatment

Wood varies greatly in its structure. Hardwoods (Figure 7) differ from softwoods (Figure 6), and in each of these groups there are differences among individual species. In fact, there are differences even in the same tree, since the heartwood, although its gross structure is the same, commonly contains certain substances not abundant in the sapwood. All these differences have their influence upon the penetrability of the wood by preservatives (impregnants) (Maclean 1953).

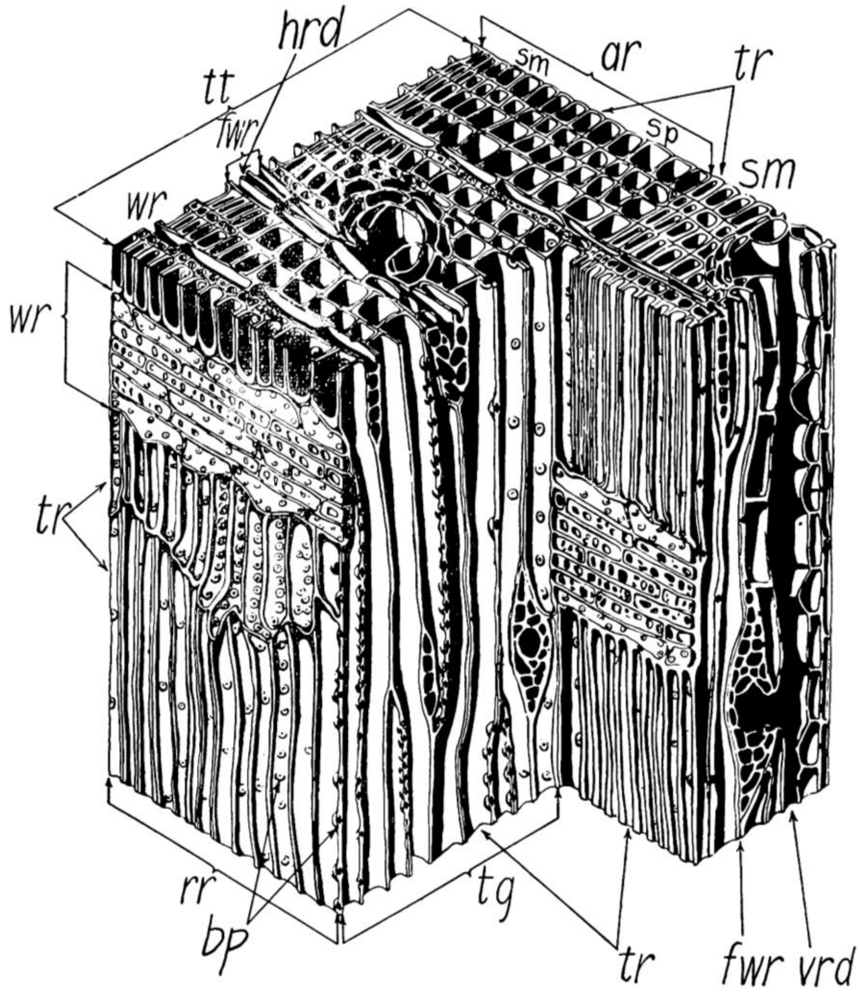


Figure 6 Drawing of a highly magnified block of softwood measuring about 0,635 mm vertically: tt, cross-section surface; rr, radial surface; tg, tangential surface; ar, annual ring; sm, latewood; sp, earlywood; tr, tracheids, or fibres; hrd, radial resin canal; vrd, axial resin canal; fwr, fusiform wood ray or ray having radial resin canal; wr, wood rays; bp, bordered pits (Maclean 1953).

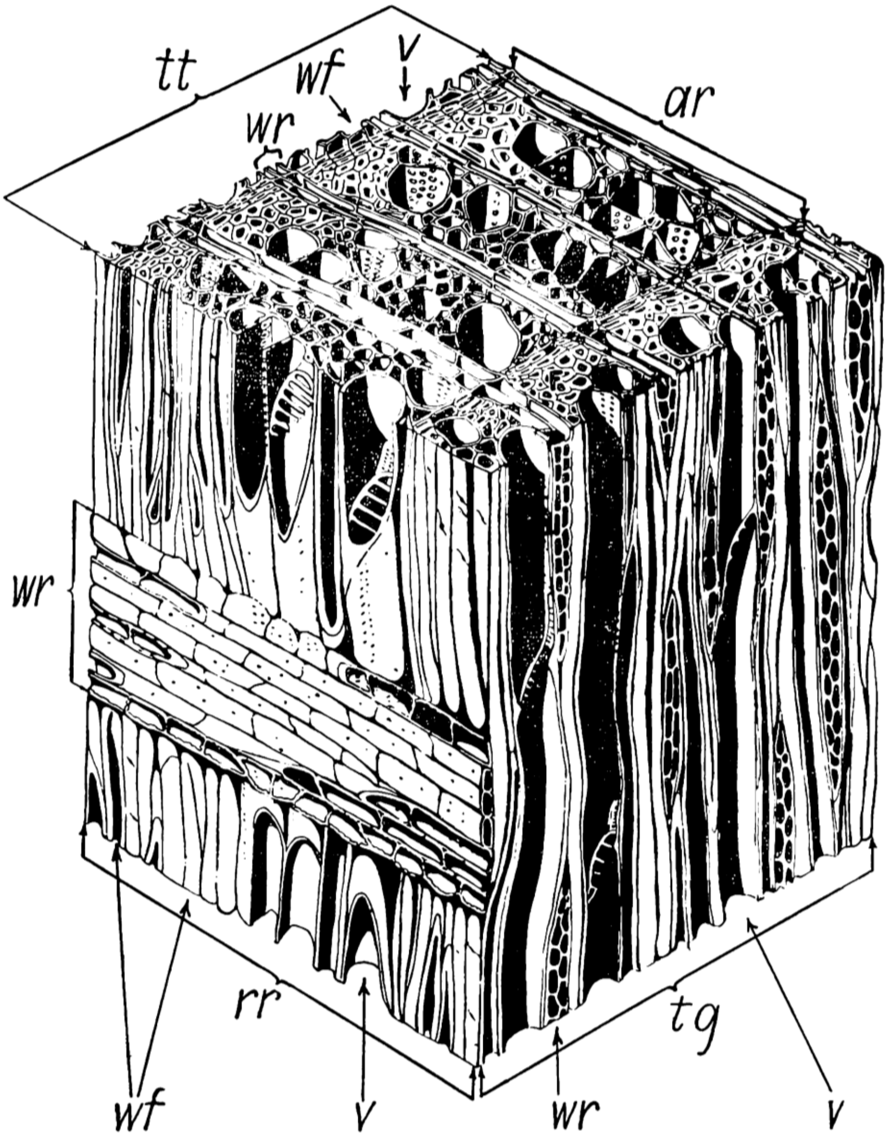


Figure 7 Drawing of a highly magnified block of hardwood measuring about 0,635 mm vertically: tt, cross-section surface; rr, radial surface; tg, tangential surface; v, vessel or pore; wf, wood libriform fibres; wr wood rays; ar, annual ring (Maclean 1953).

2.4.1 Heartwood and sapwood

The biggest difference in the permeability is between heartwood and sapwood. The sapwood of the tree is physiologically active composed of lived xylem cells. Therefore, almost all of the sapwood (both hardwoods and softwoods) is well permeable (impregnable). The heartwood is formed by physiologically dead part of xylem contained various organic substances, known collectively as extractives. The tyloses may occur in the vessels of hardwoods and cause their impermeability (Panshin and Zeeuw 1980). The softwoods are permeable because the tracheid lumens are connected by pit pairs with openings in the membranes. If these membranes are occluded or encrusted, or if the pits are aspirated, the wood becomes impermeable (Figure 8). These processes take place commonly in the heartwood, or in sapwood due to drying (Siau 1984).

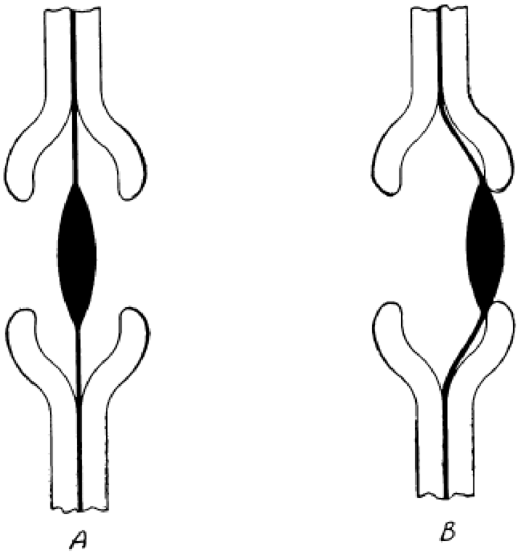


Figure 8 Cross-sectional sketch of a bordered pit: A, pit membrane centrally located; B, pit membrane permanently displaced (Maclean 1953).

2.4.2 Resin canals

The species, as white spruce or larch, has very small resin canals. These species are usually less permeable in the heartwood (Maclean 1953).

2.4.3 Earlywood and latewood

The latewood of softwoods contains more centrally located pits compared to early wood. Thus, the latewood of most of the softwoods species is more permeable than the earlywood. Latewood cells with thicker walls mean the pit membranes are less likely to aspirate and permeability can remain high (Walker 2006).

2.4.4 Direction of penetration

Practically all species are most easily penetrated longitudinally, since liquids can follow in the direction of the vessels in the hardwoods and through the full length of the cellular space of the tracheids. Liquids passing in a transverse direction, radial or tangential, must generally pass through many cell walls (Maclean 1953). Longitudinal/tangential permeability ratios of softwoods, measured by several investigators, are between 500 and 80,000 to one. Longitudinal/radial ratios extended from 15 to 50,000 to one. In hardwoods, there is a little difference between tangential and radial permeability. Longitudinal/tangential ratios measured by several authors are in range between 3×10^4 and 4×10^8 to one with the highest ratio for the ring-porous red oaks. These high ratios in hardwoods may be explained by: (a) the generally poorer penetrability of rays in hardwoods than in softwoods and (b) the very high longitudinal permeability of ring-porous hardwoods with open vessels (Siau 1984).

2.5 Permeability and Retention

Table 2 shows the categories of permeability of some selected species.

Table 2 Categories of permeability: 1, permeable; 2, moderately permeable; 3, little permeable; 4, non-permeable; s = sapwood, h = heartwood (Tsoumis 1991)

Softwoods	**Permeability s/h**	**Hardwoods**	**Permeability s/h**
Larch	2/3	Beech	1/3
Pine, Scots	1/3	Black locust	-/4
Spruce	-/3	Elm	1/3
Douglas-fir	2/3	Maple, field	1/1
		Oak, white	2/4
		Poplar, hybrid	1/2

2.5.1 Permeability

According to Siau (1984), permeability is a measure of the ease with which fluids are transported through a porous solid under the influence of a pressure gradient. The steady-state flow of fluids through wood and other porous solid sis described by Darcy's law, which may be written as

$$k = \frac{\mathrm{Flux}}{\mathrm{Gradient}} = \frac{Q/A}{\Delta P/L} = \frac{QL}{A\Delta P} \tag{1}$$

where k = coefficient of permeability ($m^2 \cdot Pa^{-1} \cdot s^{-1}$), Q = volumetric flow rate ($m^3 \cdot s^{-1}$), L = length of specimen in the flow direction (m), A = cross-sectional area of specimen perpendicular to flow direction (m^2), ΔP = pressure differential (Pa)

Darcy's law for liquid flow in an annulus:

$$Q = \frac{2\pi k h \Delta P}{\ln r/r_i} \quad (2)$$

where h = axial length of annulus, r = outside radius, r_i = inside radius.

Poiseuille's law of viscous flow for liquids:

$$Q = \frac{N\pi r^4 \Delta P}{8\eta L} \quad (3)$$

where N = number of uniform circular capillaries in parallel, η = viscosity of fluid (Pa·s)

.

Turbulent flow of liquids:

$$Q = \frac{14.79 r^{19/7} \Delta P^{4/7}}{\eta^{1/7} L^{4/7} \varrho^{3/7}} \quad (4)$$

where ϱ = density at P (kg·m^{-3}).

2.5.2 Retention

According to standards, the retention (pressure method) of preservative is calculated as

$$X = \frac{(G_2 - G_1)c}{100V} \quad (5)$$

where X = retention (kg·m^{-3}), G_1 = weight of wood before impregnation (kg), G_2 = weight of wood after impregnation (kg), c = concentration of preservative solution (%), V = volume of impregnated wood (m^3).

Or

$$X = \frac{V_2 c h}{100000 V_1} \quad (6)$$

where h = density of preservative (kg·m^{-3}), V_1 = volume of impregnated wood (m^3), V_2 = volume of consumed preservative (l).

The retention (non-pressure method) of preservative is calculated as

$$X = \frac{\text{V}ch}{100P} K \quad (7)$$

where X = retention (g·m^{-2}), V = volume of consumed preservative (l), c = concentration of preservative solution (%), h = density of preservative (kg·m^{-3}), P = surface of impregnated wood (m^2), K = dissipable coefficient; brushing: K = 0,8 – 0,9, spraying: K = 0,5 – 0,7).

Other formulas and calculations like WPG, ASE, etc. are listed in Papers I –VII.

2.6 Wood deterioration

2.6.1 Abiotic factors

Weathering – photodegradation (short-wave and long-wave UV) and oxidation is the major associated events with weathering. The colour change to brown is the results of lignin and extractive photo-chemical decomposition, forming free radicals, which lead to further decomposition of the structural carbohydrates and oxidation of phenolic moieties. Coatings or films that absorb or reflect UV portion of light are conventional preventing methods. Patent and Paper I, listed in this thesis, deal with increasing of UV-resistance of wood.

Wood thermal decomposition is slowly initiated at a temperature around 100 °C. There are colour changes, serious strength losses, a reduction in hygroscopicity, weight losses, and the evolution of gases such as CO, CO_2, CH_4, and water vapour.

Chemical decomposition may be caused by strong acids, bases, oxidizing agents or some organic solvents (Zabel and Morrell 1992).

2.6.2 Biotic factors

Insects are major biodeterioration agents. They damage wood by chewing it with their mandibles, although in many cases they derive no direct nourishment form it. The most important wood destroying insects are termites (order *Isoptera*) and beetles (order *Coleoptera*). All termites feed on cellulosic materials. The most destructive beetles, which attack wood in service, are *Anobium punctatum*, *Hylotrupes bajulus*, *and Lyctus brunneus.* Marine borers damage wood structures in salt or brackish water. The most damaging marine boring organism are shipworms, pholads and gribbles (Walker 2006).

Sapstain and Moulds fungi grow on the surface of extremely wet wood (freshly felled). They are saprophytic organism that utilize simple sugars and other carbohydrates derived from cell lumens. They do not attack the wood cell wall components and affect only the aesthetic appearance of the wood. *Bacteria* grow primarily on wood surface. They can destroy parenchyma cells and pit membranes, causing substantial increases in wood permeability.

Wood inhabiting fungi need air (oxygen), moisture and nutrients in order to invade and colonize wood. The optimal moisture content of wood for decay is above fibre saturation point. The lowest moisture content for growing of fungi is 20–22 %. However, some fungi can persist for years under dry conditions and when the moisture content rises the fungi are reactivated. The optimal temperature for the growth of most fungi is 25-30 °C. Few fungi are active above 40 °C and decay is very slow below 12 °C. The range of pH from 3 to 6 is favourable for growth of most fungi.

Soft rot is caused by *Ascomycotina* and many *Deuteromycotina* and usually attack surface of wood in wetter or aquatic environments. Typically they produce chains of cavities with conical ends within the S2 cell wall layers. Soft rot may progress in ground contact conditions, despite very high retentions of preservatives such as creosote. *Phialophora* spp. is tolerant against some wood preservatives. *Scytalidium lignicola* are antagonistic to other fungi and occurs on utility poles.

Brown rot is more associated with softwoods and characterized by their rapid depolymerization of cellulose. They change the lignin very slightly and the decayed wood develops a brown colour that could exhibit extensive cubical cracking as it dries. Brown rot fungi colonize wood tissue via the rays, from where the hyphae ramify out into the axial wood structure. *Serpula lacrymans* is able to transport adequate water for decay through the mycelium (masses of hyphae) and thus can wet wood. This fungi is the best known for its destructive effects in buildings. *Gloeophyllum trabeum* produces a diamond decay pattern reminiscent of soft rot erosion. *Coniophora puteana* destroy the cellulose by the enzymes and leave the lignin largely unaltered so that wood acquires a distinct brown colour and the structural strength is lost.

White rot affects both softwoods and hardwoods. Cellulose, hemicelluloses and lignin are degraded. Fungal hyphae are typically localized in the wood cell lumen during the decay process. *Poria Placenta* requires higher moisture content and the growth or decay process is generally similar to *Serpula lacrymans*. *Trametes versicolor*, *Phanerochaete chrysosporium*, *Phlebia radiata* are other representatives of white rot (Zabel an Morrell 1992, Richardson 1993, Goodell 2003, Walker 2006).

2.6.3 Natural durability

The sapwood is rarely durable and heartwood of many species exhibits resistance to attack by decay fungi or insects. Table 3 shows natural durability of some selected species (heartwood) against fungi.

Table 3 Natural durability: 1, very durable; 2, durable; 3, moderate durable; 4, little durable; 5, non-durable (Tsoumis 1991)

Softwoods	Durability	Hardwoods	Durability
Fir, white	5	Beech	5
Larch	2	Black locust	2
Pine, Scots	4	Elm	4
Spruce	5	Maple, field	5
Douglas-fir	3	Oak, white	2
		Poplar, hybrid	5

2.7 Industry and Market

Wood impregnation industry and market are huge around the world. Wood impregnation takes place in specialized companies or as a production step in sawmills or other wood processing industries. The European preserving industry produces around 6.5 million m^3 of pressure-treated wood per year. Figure 9 shows market share categorized by impregnants and products.

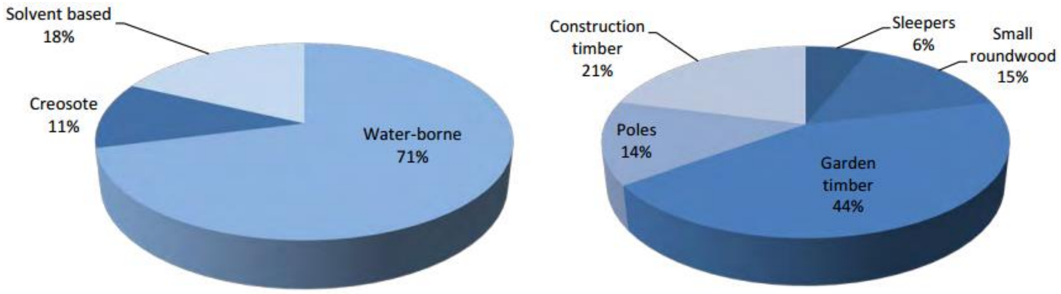


Figure 9 European wood preserving industry production categorized by impregnant type (left) and by type of product (right) (Salminen 2004).

One of the famous and successful European company, which deals with wood impregnation, is WTT. The company dispose of the technologies for pressure impregnation (creosote, water-borne, etc.), hot-oil treatment, ammonia treatment, vacuum-drying and thermo-treatment. The biggest Czech companies, dealing with pressure wood impregnation, are Impregnace Soběslav and Sublima CZ, which produce mainly railway sleepers, poles and palisades.

3 MATERIAL AND METHODS

3.1 Experimental samples

The most commonly utilized European hardwood and softwood species (except African padauk) were used in this thesis. The white oak (*Quercus* sp.) in Patent and Paper I; the European beech *(Fagus sylvatica* L.) in Papers II, III, V, VI and VII; Scots pine (*Pinus sylvestris* L.) in Paper II; hybrid poplar (*Populus hybrids*) in Papers V and VII; white poplar (*Populus alba* L.) in Paper IV; the Black locust (*Robinia pseudoacacia* L.) in Paper VI and African padauk *(Pterocarpus soyauxii* Taub.*)* in Paper VI.

3.2 Treatment methods

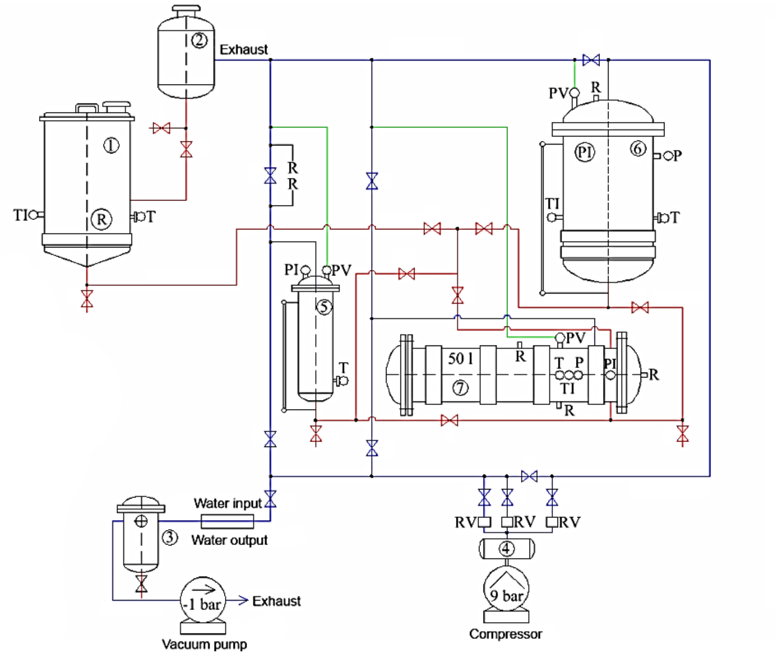
The experimental investigations have been carried out using laboratory vacuum-pressure impregnation plant (Figure 10). Detailed information about the treatment is presented in Papers II and IV-VII. There are also listed and described other devices and equipments, which was used during research.

Figure 10 Laboratory vacuum-pressure impregnation plant

Table 4 Technical specification of laboratory impregnation plant

Technical specification	
Power supply	TN-C-S 3 x 400/230V 50 Hz
Type (date of manufacture)	JHP 1-0072 (2010)
Length×width×height	2000×1010×2350 mm^3
Weight	560 kg

Laboratory vacuum-pressure plant for wood treatment were designed and manufactured according to the investor (Mendel University in Brno) by company J.Hradecký. The stainless steel was used for manufacturing of this plant. The assembly (plant) includes a pressure vessels, electric heating, electrical equipment (see Figure 11). It can be applied the maximum pressure 900 kPa, vacuum about -95 kPa and temperature up to 160 °C.



Description:

1. Storage tank
2. Exhaust collector
3. Collector
4. Air eliminator
5. Measuring tank
6. Preheater
7. Impregnation vessel

PV - Safety valve
TI – Thermal sensor
T - Thermometer
PI - Pressure sensor
P - Manometer
R - Reserve
RV - Reducer

Figure 11 Scheme of laboratory vacuum pressure impregnation plant (Dejmal et al. 2012)

Figure 12 Laboratory vacuum - pressure plant, basic view (upper); vessel with untreated and treated sample (middle); preheater and tubes with valves (bottom)

3.3 Testing methods

The testing methods, devices and equipments are listed and described in Papers I-VII.

PATENT

THE METHOD FOR THE TREATMENT AND COLORING OF WOOD CONTAINING TANNINS

Pařil, P., Baar J., Dejmal, A., Foret, F., Křenková J. (2016)

Patent number 306249, Industrial Property Office (CZ).

The method for the treatment and colouring of wood containing tannins

Petr Pařil [a,]*, Jan Baar [a], Aleš Dejmal [a], František Foret [b], Jana Křenková [b]

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THE FIELD OF TECHNOLOGY

The invention falls within the modification of the properties of wood, specifically the change of wood colour.

THE CURRENT STATE OF THE ART

The industrial practice currently uses ammonia treatment to colour wood without the need to use pigments. This method uses the reaction of tannins with ammonia vapours and the subsequent colour change - darkening. The disadvantage is that it can only be applied to new products and cannot be used to wood that is already integrated.

The reaction of wood, especially wood with a high content of tannins, with metal ions and the subsequent colour change is well known. As was known in the history, longer contact of an iron material with oak heartwood, especially under the influence of water, leads to darkening of the given spot. However, this is considered a flaw because it is local. That is why, for example, oak timber is stacked with plastic bands instead of iron. Many authors have described the reaction of phenols contained in tannins with metal ions. Phenols are a component essential for chelation of metal ions. Iron, depending on its concentration and the pH of the modified material, changes the colour of the phenols contained in oak to dark blue, dark green even black blue. The reaction is accelerated by the presence of oxygen.

THE PRINCIPLE OF THE TECHNICAL SOLUTION

The above mentioned disadvantage of wood ammonia treatment is to a significant extent removed by the iron oxide nanoparticles impregnation according to the present invention. The method is based on the modification of wood colour using the reaction between wood tannins and iron oxide nanoparticles. The impregnation of wood can be done by pressure, brushing or spraying.

The products treated with iron oxide nanoparticles can replace ammonia treated products. The advantage is the use of a non-toxic substance friendly to both the environment and humans, and also its very cheap and available production. Another important advantage is the possible brushing or spraying of older, already built-in wood (e.g. flooring, cladding). Additionally, wood gets a darker shade while its natural texture is preserved so it aesthetically resembles the desired exotic species.

The presented solution consists in the method used for the treatment and colouring of wood containing tannins by impregnation with a product containing iron oxide nanoparticles, with a concentration of 0.4 g/l to 42 g/l, an average particle size in the range of 1 to 100 nm – better 1 to 50 nm or 5 to 20 nm.

The product does not contain iron chlorides. The presence of iron chlorides in the product is undesirable, because they can cause increase in moisture absorption and corrode the wood more.

With the advantage, the product does not contain ammonia because ammonia causes other discoloration.

The desired colour change is achieved with very small concentrations (from 0.4 g/l). Considering the average size of the nanoparticles of 1 to 100 nm, 1 to 50 nm is very good, 5 to 20 nm even better, but at best 10 nm, the penetration into the wood cell wall, where the largest quantity of phenolic compounds are located, is well achieved. The UV resistance of the treated wood is increased, which is another advantage, and contributes to improved usability of the product.

The product also contains a liquid medium. This liquid medium can be polar or nonpolar. A polar medium may be for example water; a nonpolar liquid medium is e.g. oil. The use of oil is beneficial as it more increases the value in use of the treated wood, especially for outdoor applications.

The colouring is a result of the reaction of iron oxide nanoparticles with wood tannins; i.e. the principle is not applying pigments containing iron oxide particles, where the colouring would be caused by iron oxides as a pigment. Therefore, the colouring is more natural and similar to the result of ammonia treatment. The content of tannins in wood markedly affects the resultant colour change. Therefore, heartwood (oak or Acacia) with high content of tannins darkens considerably. However, the colour changes can also be observed in the sapwood and other tree species. Wood from which the tannins have been extracted cannot be coloured using this invention. The cause of the colour change must be the reaction of iron oxide nanoparticles with tannins.

To increase the penetration and reach its maximum depth, impregnation is carried out as pressure impregnation, followed by soaking. Pressure impregnation can be done, for example, so that the wood is inserted in a closed chamber. First, negative pressure is induced (i.e. pressure lower than atmospheric pressure), then impregnation agent is filled and the pressure is increased above the atmospheric. Subsequently, negative pressure can be used to remove the product remnants from the surface and lumina of the wood cells. Finally, the wood is soaked in the impregnation substance.

In the case of integrated wood, where pressure impregnation and soaking are not feasible, or easily impregnated wood, impregnation is carried out by brushing or spraying.

If required, the final surface treatment, such as varnish, wax, etc. can be added after impregnation.

EXAMPLES OF INVENTION APPLICATION

Example 1

Iron oxide nanoparticles were prepared by condensation of ferrous and ferric ions in an alkaline environment at laboratory temperature. 54.08 g of ferric chloride hexahydrate, 19.87 g of ferrous chloride tetrahydrate, 37.50 g of sodium citrate dihydrate, and 130 µL of hydrochloric acid were dissolved in 250 mL of deionized water. While stirring continuously (1400 RPM), 50 mL of the ammonium hydroxide solution (25% w/w) was added to the reaction mixture and stirred for 1 hour. The prepared nanoparticles were purified with a repeated precipitation in acetone (3 x) and then dissolved in deionised water. The size of the nanoparticles was measured using the DLS (dynamic light scattering) and was about 10 nm.

Example 2

Products containing nanoparticles prepared by example 1 in several different concentrations in the range from 0.4 up to 40 g/l were used for the treatment of wood of different species. The colour change of wood is caused by the reaction of tannins (mainly phenols) and iron. The content of tannins in wood markedly affects the resultant colour change. Therefore, heartwood (oak or Acacia) with high content of tannins darkens considerably. However, the colour changes can also be observed in the sapwood and other tree species. The effect of the concentration of the solution of iron oxide nanoparticles (0.4 to 40 g/l) on the colour change of oak heartwood is negligible; however, the differences in colour of oak sapwood are noticeable (see Table 1). Another advantage of wood treated in this way is the reduced moisture absorption of wood and increased UV resistance. In tests of lightfastness, the values after 500 hours of radiation reached almost the results of ammonified oak (see Table 2). Wood manifested deeper darkening after the treatment by nano-iron than after ammonia treatment. The solution of iron oxide nanoparticles can be prepared both in polar (e.g. water) and nonpolar (e.g. oil) solvents. Oil more increases the value in use of the treated wood, especially for outdoor applications.

The heartwood of oak and Acacia is hardly impregnable due to the large amount of tyloses in the wood conductive tissues. To increase the penetration and its maximum depth, a specific way of impregnation was selected. It consisted in pressure impregnation (Bethel) and subsequent soaking. The procedure for oak with a moisture content of 20 to 30% is the following: First, negative pressure of 10 kPa is created in the chamber with wood and it is kept for one hour. Then impregnation agent is filled and a pressure of 800 kPa is used for two hours. Then, negative pressure of 25 kPa can be used to remove the substance remnants from the surface and lumina of the wood cells. Finally, wood is soaked for one week. Specific parameters of the impregnation can be modified based on the input parameters of the wood (tree species, temperature, moisture content, and dimensions). Brushing or spraying with a final surface finish (lacquer, wax, etc.) can be used for the application to integrated wood (where pressure impregnation is not feasible).

Table 5 The effect of the concentration of the solution of iron oxide nanoparticles on the colour change in oak heartwood and sapwood; lightness L is a unitless quantity that can be measured with a mobile spectrophotometer (measurement geometry 45/0, standard light d65)

	Lightness L	
concentration of iron nanoparticles in the product	**heartwood**	**sapwood**
untreated wood	65.24	77.27
0.4 g/l	30.1	48.18
4 g/l	27.31	47.45
40 g/l	27.25	39.86

Table 6 Lightfastness of treated wood; lightness L is a unitless quantity that can be measured with a mobile spectrophotometer (measurement geometry 45/0, standard light d65)

	Lightness L		
Time of dry mode	**Without treatment**	**Ammonia**	**Nano-iron**
0 h	62.84	41	36.21
500 h	60.64	47.04	43.72

INDUSTRIAL APPLICATION

The way of wood colouring by this solution is suitable for wood located in the interior and exterior; use for interior wood is preferred. It is applicable for colouring directly in the production; application to integrated wood is also possible. It can therefore be used for flooring, cladding, furniture, etc.

PATENT CLAIMS

1. The method of the treatment and colouring of wood containing tannins, characterized by impregnation with a product containing iron oxide nanoparticles, in a concentration of 0.4 g/l to 42 g/l, an average particle size in the range of 1 to 100 nm, and a liquid medium.

2. The method according to claim 1, characterized by the fact that the product does not contain iron chlorides and/or ammonia.

3. The method according to claim 1 or 2, characterized by the fact that the liquid medium is water or oil.

4. The method according to any of claims 1 to 3, characterized by impregnation carried out as pressure impregnation with the given product with subsequent soaking in the product.

5. The method according to any of claims 1 to 3, characterized by impregnation carried out by brushing or spraying with the given product.

ANNOTATION

Name of the invention: The method for the treatment and colouring of wood containing tannins

The presented solution shows the method of the treatment and colouring of wood containing tannins, characterized by impregnation with a product containing iron oxide nanoparticles, in a concentration of 0.4 g/l to 42 g/l, an average particle size in the range of 1 to 100 nm, and a liquid medium. Impregnation can be performed as pressure impregnation, followed by soaking, or the product can be applied by brushing or spraying. This method is an alternative to wood ammonification.

PAPER I.

COLOUR STABILITY OF CHEMICALLY MODIFIED OAK WOOD – NANOIRON AND AMMONIA TREATMENT

Baar, J., Pařil, P., Rozbořil, T., Kúdela, J. (2016)

Eco-efficient resource wood with special focus on hardwoods.

University of West Hungary, p 35–36.

Colour stability of chemically modified oak wood – nanoiron and ammonia treatment

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Key words: *Quercus sp.,* colour change, artificial sunlight, nanoiron, ammonia gas

ABSTRACT

Wood colour and its stability are very important aesthetic aspects of interior-used wood products such as furniture or flooring. Most temperate wood species are characterized by pale inconspicuous colour patterns. These, however can be modified by processes like steaming, heating or ammonia treatment to mimic appearance of tropical wood species (Miklečić *et al*. 2012, Tolvaj *et al.* 2012, Fehér *et al.* 2014).

Particularly disposed to discolouration in contact with iron and moisture are wood species rich in tannin-like compounds. In these conditions, strongly coloured tannin-iron complexes are produced. Same extractives cause wood darkening if this is exposed to ammonia (Farmer 1967). The current demanded dark surfaces typical for subfossil oak obtaining its colour by contamination with soil iron can be met by targeted impregnation of oak wood with water solutions containing iron particles.

The tests were carried out on three test sets, each containing ten specimens, prepared from oak wood. The first consisted of native specimens, the specimens of the second one were treated by ammonia gas (AT) for 3 days, and the specimens of the last were vacuum impregnated with nano-iron (NIT) water solution (4 g/l) for one hour. After the conditioning (20 °C, 65%). the specimens were exposed to a 500-hour treatment with a xenon-arc lamp light (Q-SUN XE-3) simulating outdoor sunlight. The colour changes in particular parameters, caused by individual treatments and the following light exposure were monitored by means of a spectrophotometer (BYK-Gardner spectre-guide 45/0 gloss) working in the CIEL*a*b* colour system. The colour of the samples surface was measured at 0, 25, 50, 100, 200, 300 and 500 hours from the beginning.

Both treatments tested induced darker colouring of oak wood, more intensive darkening was observed in case of the nano-iron treatment (Figure 1, Table 1).

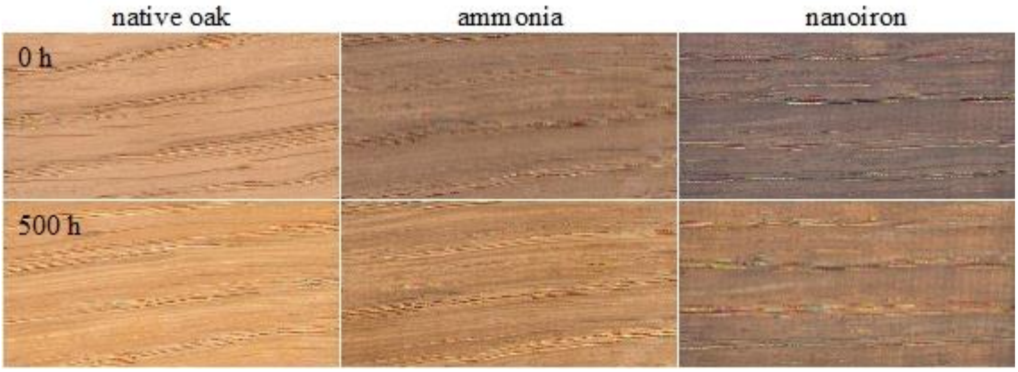

Figure I. 1 The colour of native and treated oak wood before and after artificial sunlight exposure for 500 hours.

Table I. 1 The colour parameters of native and treated oak wood before and after artificial sunlight exposure

	native oak			ammonia			nano-iron		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
0 h	62.8	8.0	22.0	41.0	4.9	12.7	36.2	2.9	6.0
500 h	60.5	10.1	27.4	47.0	7.0	18.8	43.7	6.9	17.3

The native oak showed a steep drop in lightness ca 25–50 hours of exposure followed by gradual re-increase during further exposure to the artificial sunlight (Figure 2). The darker surfaces generated by tannin reacting chemically with iron and ammonia evidently faded in the course of light exposure. In case of chromatic parameters a* and b*, the AT oak more or less copied the colour change progress of native oak. On the contrary, the NIT wood showed a double increase in both parameters. The colour of NIT wood after light exposure was more or less equivalent to the original colour of the ammonium-treated oak (Figure 1). Distinct reddening (Figures 1, 2) of NIT oak may be caused by oxidation of non-precipitated iron particles.

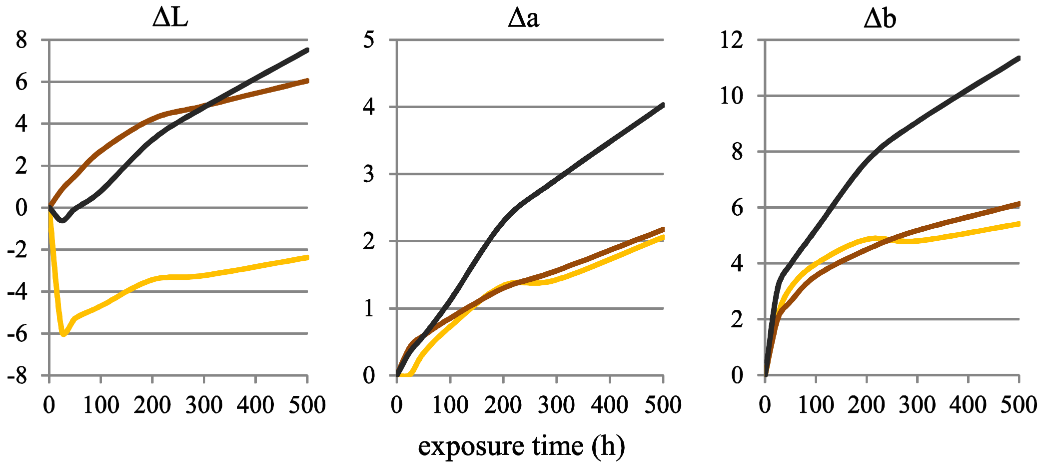

Figure I. 2 Colour parameters variation during exposure to artificial sunlight (yellow – native oak, brown – ammonia treatment, black – nano-iron treatment).

PAPER II.

ANTIFUNGAL EFFECT OF COPPER AND SILVER NANOPARTICLES AGAINST WHITE-ROT AND BROWN-ROT FUNGI

Pařil, P., Baar J., Rademacher, P., Prucek, R., Sivera M., Panáček, A. (2016)

J Mater Sci (under revision).

Antifungal effects of copper and silver nano-particles against white and brown-rot fungi

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ABSTRACT

In this study, the antifungal effects of copper and silver nanoparticles against two wood-rotting fungi were investigated. European beech (Fagus sylvatica L.) and Scots pine (Pinus sylvestris L.) sapwood specimens of dimensions 50 × 25 × 15 mm^3 were vacuum impregnated using dispersions of copper and silver nanoparticles within two concentrations, i.e. 1 and 3 g/l. Beech wood specimens were tested against white-rot fungus (Trametes versicolor) and pine wood against brown-rot fungus (Poria placenta) according to EN113. Furthermore, leachability, retention and protection efficiency (mass loss due to decay) were analysed afterwards. The highest value of retention was observed for pine sapwood (~ 2 $kg\cdot m^{-3}$) for both nanoparticle solutions. The amount of nanoparticles in the wood did not increase proportionally with an increasing concentration, but only 1.5–2 times increase was reached. An average leaching of 15% to 35% was observed for copper nanoparticles, depending on used wood species and concentration. Significantly lower leaching (max. 15 %) was observed for pine sapwood impregnated by silver nanoparticles with a concentration of 3 g/l. The highest antifungal effect (under 5 % of mass loss) against both tested fungi was found for nano-copper treatment at the concentration of 3 g/l. However, this effect of treatment seems to be almost negligible after the leaching test. Therefore, this study aims to present fundamental material properties of wood treated with copper and silver nanoparticles, and provide groundwork for further research (e.g. fixation of substances in the wood structure, etc.).

Key words: wood protection; nanoparticles; nano-metals; bio-durability; decay resistance; wood-rotting fungi; wood modification

INTRODUCTION

The interaction of nanoparticles with biomolecules and microorganisms is an expanding field of research. It has been suggested that nanometer-sized metal particles have different physical and chemical properties from their macroscale counterparts that alter their interaction with biological structures and physiological processes (Nel et al. 2003). Civardi et al. (2015) evaluated the new generation of preservatives with Cu-based nanoparticles to be more efficient against wood-rotting fungi than conventional formulations. There are also some other applications like prevention of leaching in otherwise soluble metal oxides (Kartal et al. 2009) or altering treatability properties such as penetration and biocide distribution (Stirling et al. 2008, Matsunaga et al. 2009). Nevertheless, potential environmental and health risks and the risk governance recommendations has to be taken into account (Clausen 2007). Cu-based nanoparticles and/or their derivatives may during decomposition of treated wood accumulate in the mycelia of Cu-tolerant fungi and end up in their spores, which are dispersed into the environment. Choi and Hu (2013) reported the toxicity of silver nanoparticles against nitrifying bacteria through the generation of oxygen radicals. The production of lignocellulose degrading enzymes was decreased by iron and copper aggregated nanoparticles in the white-rot fungus Trametes versicolor (Shah et al. 2010). Such unknown and unpredictable influences on decomposition processes in the environment should be considered especially concerning treated wood with the ground contact.

Copper remains the primary biocide component used to protect wood. There are several brown-rot fungi species which are copper tolerant (Young 1961) and brown-rot fungi metabolite oxalic acid is a major factor leading to copper tolerance (Clausen et al. 2000, Green and Clausen 2005, Köse and Kartal 2010). Oxalic acid is accumulated at greater concentrations in liquid or semisolid culture, whereas white-rot fungi decompose metabolized oxalic acid by oxalate-decomposing enzyme systems (Takao 1965, Espejo and Agosin 1991, Mäkelä et al. 2002). The high affinity with heavy metals and ability of their accumulation is known for white-rot fungi (Baldrian 2003, Bayramoglu et al. 2003). The preservative formulation affects copper tolerance of fungi (Köse and Kartal 2010) and inhibition often depends upon the co-biocidal components (Illman et al. 2000). The different properties of nanoparticles as higher surface area or reactivity could positively influence the resistance of brown-rot fungi.

Kartal et al. (2009) reported that treatment with nano-copper (leached and unleached) significantly improved decay resistance (mass loss less than 10 %) to Gloeophyllum trabeum (brown-rot fungus) and Trametes versicolor (white-rot fungus) but failed after exposure to Antrodia spp. Chang et al. (2012) published that Cu nano-particles are more toxic than micro ones with the same composition. Results confirmed that size and surface characteristics of Cu nano-particles influenced its toxicity. Matsunaga et al. (2009) stated that nano-Cu preservatives are able to deliver bioactive components into wood cell walls and thus improve leach resistance as well as bio-durability. Mass loss of Paulownia treated with nano-copper aqueous dispersion (400 ppm) was less than 3 % and accompanied by the structural changes observed using SEM images of the undecayed and decayed treated wood (Akhtari and Arefkhani 2013).

Recent studies have reported the effectiveness of nano-sized silver particles as an antimicrobial agent (Rai et al. 2009, Morones et al. 2005) and several mechanisms have been proposed to explain the inhibitory effect of silver nanoparticles on bacteria, such as high affinity with sulphur and phosphorus (Ravishankar and Jamuna 2011, Dorau et al. 2004). The antifungal properties of silver are less known, because most of the studies have been focused on bacterial and viral pathogens in animals. According to Kim et al. (2009), silver nano-particles exhibited excellent antifungal activity on Candida albicans by disrupting the cell membranes and inhibiting the normal budding process due to the destruction of the membrane integrity. Authors also demonstrated the damage of fungal hyphae by silver nanoparticles but also the inhibition of conidial germination in phytopathogenic fungi Raffaelea spp. Furthermore, Pulit et al. (2013) showed growth inhibition of Cladosporium cladosporioides and Aspergillus niger strains even at low concentrations. Dorau et al. (2004) explained the theoretical mechanism of fungi-silver relation and reported the low to moderate wood resistance against brown-rot fungi when treated by silver salts. Unsuitable preservation efficiency against white-rot fungus Trametes versicolor was observed for wood treated by silver nano-particles at different concentrations, i.e. 200 and 400 ppm (Rezaei et al. 2011). However, Akhtari and Arefkhani (2013) stated that the micronized metals including silver were very effective in weight loss after 4 months and prevention of decay by Trametes versicolor.

In the present study, the biological durability and leachability of European beech (Fagus sylvatica L.) and Scots pine (Pinus sylvestris L.) wood treated with dispersions of copper and silver nanoparticles were investigated in order to understand performance of such material and its potential application/utilization.

MATERIAL AND METHODS

Test materials

European beech (*Fagus sylvatica* L.) and Scots pine (*Pinus sylvestris* L.) sapwood non-defects specimens of dimensions 50 × 25 × 15 mm^3 were used according to EN 113 standard. Specimens were sorted into 9 groups and each group consists 10 specimens. All together there was 90 specimens.

Chemical preparation of nano-particles

The dispersion of copper nano-particles with a concentration of 1 g/l of Cu was prepared by reduction of copper sulphate pentahydrate (Sigma-Aldrich, p.a.) solution by sodium borohydride (Sigma-Aldrich, p.a.) in a presence of sodium salt of polyacrylic acid with molecular weight ~ 1200 (Sigma-Aldrich, 45% aqueous solution). The 3.929 g of copper sulphate pentahydrate was dissolved in 895 ml of deionized water followed by addition of 5 ml of 45% sodium salt polyacrylic acid solution. Afterwards, 100 ml of sodium borohydride solution (100 mg in 100 ml of deionized water) was added to the reaction mixture.

The dispersion of silver nano-particles with a concentration of 1 g/l of Ag was prepared by reduction of silver nitrate (Sigma-Aldrich, p.a) solution by sodium borohydride in a presence of sodium salt of polyacrylic acid with molecular weight ~ 1200. The 1.574 g of silver nitrate was dissolved in 890 ml of deionized water followed by addition of 5 ml of ammonia solution and 5 ml of 45% sodium salt polyacrylic acid solution. Afterwards, 100 ml of sodium borohydride solution (100 mg in 100 ml of deionized water) was added to the reaction mixture. Immediately after addition of sodium borohydride, the dispersion turned dark-brown colour indicating formation of silver nanoparticles.

The prepared nanoparticles were characterized by dynamic light scattering measurements (ZetaSizer NanoZS, Malvern, UK) and transmission electron microscopy

(Jeol 2010, Japan). An average diameters of copper and silver nanoparticles were 15.6 nm and 7.8 nm, respectively (Fig. 1).

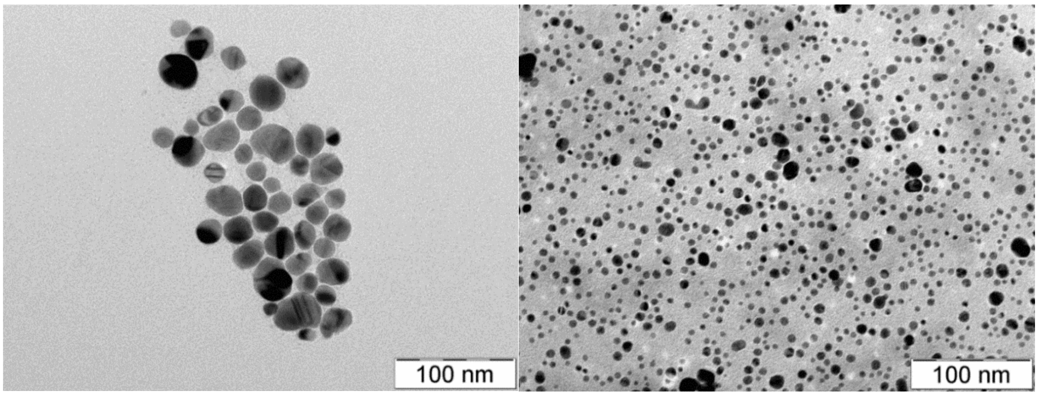

Figure II. 1 Transmission electron microscope image of copper (left) and silver (right) nanoparticles.

Preservative treatment

The impregnation was carried out using the laboratory vacuum-pressure impregnation plant (JHP-1-0072). Specimens were impregnated by copper and silver nano-particles solution with 1 and 3 g/l concentrations. Concentrations of nano-particles were chosen according to preliminary tests. All specimens were impregnated within single batch at vacuum of 80 kPa for 120 min.

Leaching test (EN 84)

Treated specimens were conditioned at 20°C and 65 % of RH for 4 weeks until the equilibrium moisture content was reached. Subsequently, specimens were submerged in deionized water, impregnated by vacuum at 80 kPa for 20 min and kept in water for 2 hours after impregnation. During following 14 days of leaching, the water was nine times changed. The leached water for the chemical analysis of the active ingredient amount was collected in certain periods, i.e. after the vacuum impregnation, after the 1st day of leaching and subsequently as a mixture of water collected during the period from 2nd to 4th and from 5th to 14th days.

Leachate and retention analysis

The amount of leached elements was analysed from the collected leaching water. Additionally, two impregnated specimens for each treatment group were split and ground to wood powder for retention analysis. Concentrations of copper and silver were determined by the AAS technique using flame ionization employing ContrAA 300 (Analytik Jena AG, Germany), equipped with a high-resolution Echelle double monochromator (spectral bandwidth of 2 pm at 200 nm) and a continuum radiation source (xenon lamp). The absorption lines used for the analyses were 324.754 for copper and 328.068 for silver.

Decay test

Decay test was performed according to EN 113 standard. Two fungi were used for the determination of nano-particles protection efficiency – white-rot fungus (*Trametes versicolor*) for treated beech and brown-rot fungus (*Poria placenta*) for treated pine sapwood specimens. Two nanoparticle solutions (Cu, Ag) and two concentrations (1 and 3 g/l) with ten replicates were tested. Treated and untreated specimens were steam sterilized and placed in Kolle flask on the sterile culture medium (Malt extract agar) previously exposed to fungi for 2 weeks. Kolle flasks were incubated for 16 weeks at 22°C and 75 % of RH. At the end of the exposure time, the mycelium was carefully removed from the surface of specimens. . Specimens were then oven-dried at 103±2°C to constant weight and weighed afterwards. The fungicidal efficiency of the treatment was determined by the mass loss (ML) due to fungi degradation.

RESULTS AND DISCUSSION

Retention of nano-particles

An average values of chemical retention based on water solution retention and active component concentration for the studied wood species are shown in Table 1. Slightly higher retention was observed for Scots pine sapwood, which is in agreement with other authors (Tascioglu et al. 2012, Sen et al. 2009). Humar et al. (2007) stated that the influence of species on the retention is less significant for vacuum impregnation, however pine sapwood showed the highest retention level when compared to beech or spruce wood. This can be explained by the difference in the anatomical structure and porosity of mentioned species. A higher concentration of the active component did not influence the water solution retention, but increased the biocide amount in wood. The results showed that the amount of nano-particles within wood did not increase proportionally with an increasing concentration, but only 1.5–2 times increase was reached. Unfortunately, the lower number of used specimens might influence the value, which is obviously too low for beech wood impregnated with a higher (3 g/l) concentration of Cu nanoparticles.

Absorption of preservatives and colour changes within the whole specimen's volume was confirmed by its splitting. Specimen's surfaces were intensively coloured to brown with the exception of pine treated by copper nano-particles, which got a green tone (Fig. 2). Matsunaga et al. (2009) found that copper nano-particles can pass through Southern pine pores in bordered pit membranes (an average diameter of 300–4000 nm) and even penetrate the cell walls, but most of them are too large to enter the cell wall's nano-capillary network. The partial conversion of copper from nano-particles to Cu^{2+} ions, which subsequently diffuse in the cell walls of tracheids, is another alternative (Matsunaga et al. 2010). Hardwood species are penetrated mainly through vessels, whose length as flow paths is much longer than the length of softwood tracheids (Cooper and Churma, 1990). However, the pore size in hardwood homogenous membranes are smaller than those in the margo area of softwood pits and varies from 5 to 420 nm, depending on species (Choat et al. 2007). This can cause a higher conducting of nano-particles on vessel pit membranes and therefore a reduced protection of other tissue elements, e.g. libriform fibres. For instance, Cronshow (1960) found that colloidal gold and carbon particles (diameters of 64 nm) are not able to pass through the pit membranes of *Eucalyptus regnans* wood. Dimensions of nano-particles used in the present study should be small enough to spread homogenously in wood conductive elements (tracheids or vessels) and pass through their pit membrane pores.

Table II. 1 Results of retention for analysed treatments

Species	Concentration		Retention (kg.m-3)			
			Copper nano-particles		Silver nano-particles	
Beech	1 g/l	3 g/l	0.667 (0.004)	1.970 (0.053)	0.657 (0.018)	1.967 (0.051)
Pine	1 g/l	3 g/l	0.709 (0.019)	2.083 (0.098)	0.698 (0.031)	2.092 (0.097)

* Standard deviation in parentheses

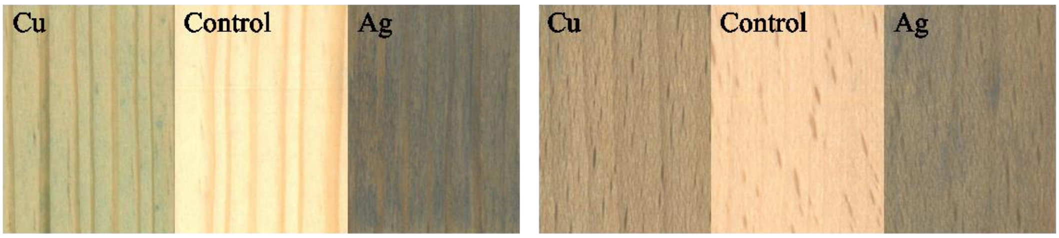

Figure II. 2 Colour of treated and untreated specimens - left pine sapwood, right beech wood (concentration 3 g/l, sanded surface)

Leachability of nano-particles

Leaching rates for all analysed groups at different stages of the process are shown in Fig. 3. The highest leaching rate was noticed after initial leaching periods, i.e. vacuum and first day of leaching. The amount of leached substances gradually decreased with time. Similar leaching progress was presented by Thaler and Humar (2014) for copper-based preservatives. The accessibility of copper deposited in a higher concentration in the wood surface layer is considered as the main reason.

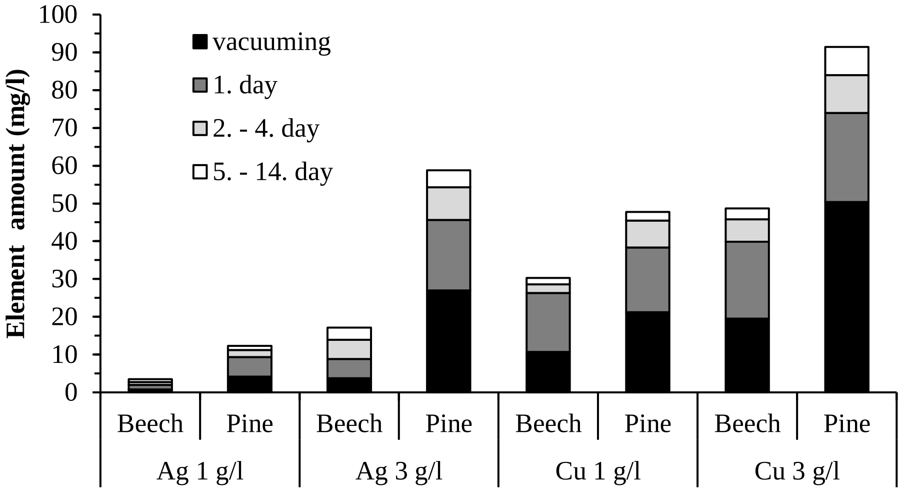

Figure II. 3 Amount of elements leached out from beech and pine wood specimens after vacuuming, 1st day, 2nd-4th day and 5th-14th day

The percentage loss of nano-particles impregnated within wood during leaching is depicted in Fig. 4. Nano-metals were leached more intensively from specimens impregnated with higher concentration (3 g/l) and from pine sapwood, when wood species are compared. Copper nano-particles leaching ranged 15 % to 35 % of its original retention, and depends on species and concentration. Furthermore, silver leaching was significantly lower and reached maximally 15 % for pine sapwood with a concentration of 3 g/l. Available literature sources about nano-particle leaching is very limited and presented results are rather contradictory. Copper compounds without proper fixation are very easily leached from wood (Richardson 1978, Thaler and Humar 2014). Regarding nano-particles, some authors anticipated its higher fixation rather than soluble forms of wood preservatives, for instance due to changes in charge properties and Van der Waals forces (Clausen 2007, Kartal et al. 2009). Moreover, Dorau et al. (2004) stated that size of silver nano-particles is too large to interact with a functional group in wood constituents unlike silver ions, which, in addition, penetrate wood more rapidly and effectively. Lesar et al. (2008) showed 29% and 57% leaching of copper sulphate impregnated in spruce wood at Cu concentrations of 0.1 % and 0.5 %, respectively (EN 84). Leaching of copper sulphate (1%) from southern yellow pine was 24 % after 14 days, compared to nano-particles, where leaching was almost negligible (Kartal et al. 2008). Ding et al. (2013) determined a higher rate of leaching for smaller nano-particles (10 nm vs. 50 nm), which ranged between 12 % and 16 % depends on usage and type of polymer stabilizers. The results indicated that nano-particles should be less susceptible to leaching, but a lot of factors, including size, type of stabilizers or treated species, could influence final behaviour.

Lower leachability of silver nano-particles could be explained by their smaller diameter when compared to copper particles (see Fig. 1). Smaller nano-particles better penetrate deeper into wood structure and they are not deposited and aggregated on pit membranes passing from one cell to another. Ding et al. (2013) showed by contrast that smaller nano-particles are more susceptible to be leached because of their higher mobility in the liquid phase. However, the particle size differences are not so obvious in present study.

A higher amount of copper and silver in leachates was found for pine wood, which can be explained by its higher retention level (Tab. 1). The differences within pit pore size may influence the mobility of particles, which are not driven by vacuum during leaching process and thus can be easily retained by the homogenous membrane of beech rather than more porous margo of pine wood. Various leaching rates for both species might be explained by the diverse chemical structure together with a related amount of reaction sites (Radivojevi and Cooper 2010, Temiz et al. 2014).

Specimens treated with copper (3 g/l), unlike silver, showed lower leaching of the active ingredient compared to the lower concentration. It can be explained by a distinctively higher retention determined from the water solution uptake than the actual nano-particle retention in wood (Fig. 5). The higher concentration of preservatives is usually associated with higher leaching, because of the limited amount of functional groups in wood, which could react with impregnated chemical compounds (Humar et al. 2007).

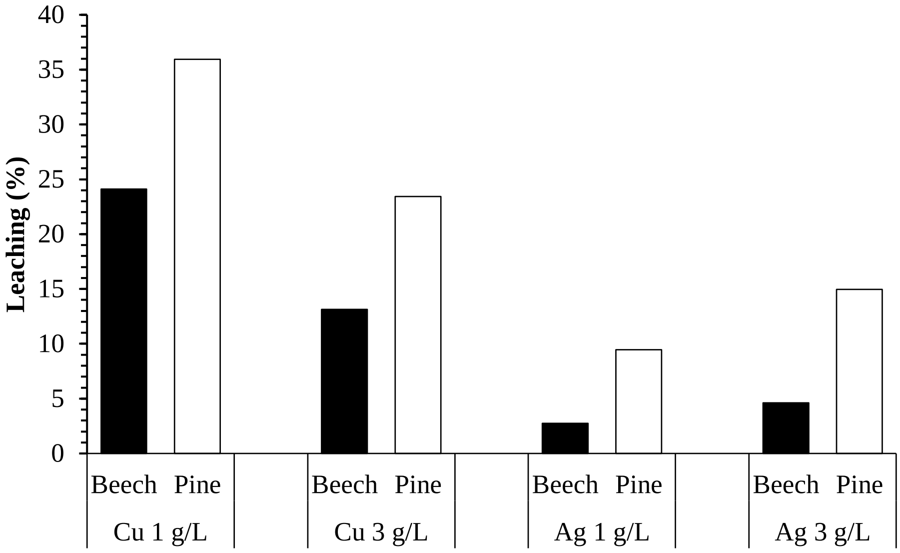

Figure II. 4 Leaching expressed as a quotient of element leachate to retention level

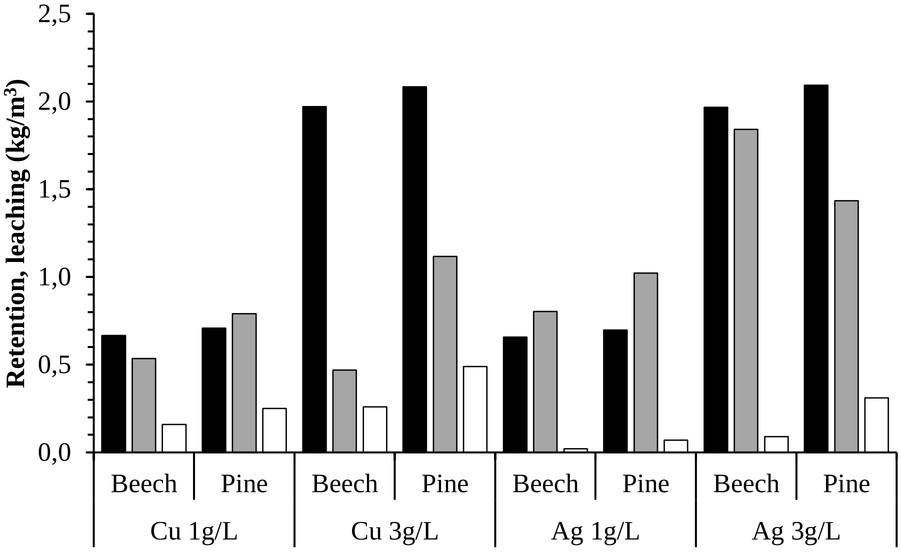

Figure II. 5 Retention and leaching of Cu and Ag nano-particles in impregnated pine and beech specimens – black bar: retention counted from nano-particle concentration in water solution, grey bar: actual retention by AAS, white bar: leaching of nano-particles

Treatment efficiency

Sixteen weeks of exposition to white-rot fungus *Trametes versicolor* and brown-rot fungus *Poria placenta* resulted in sufficient mass loss (ML) of control (untreated) specimens (beech and pine sapwood), which indicates both fungi activity according to EN 113 standard (Fig. 6).

ML due to the exposure of leached and unleached specimens to white-rot fungus (*T. versicolor*) and brown-rot fungus (*P. placenta*) are presented in Fig. 4. The ML caused by fungi degradation was significantly reduced for treated unleached wood, independently of concentration or fungus. The adequate performance (ML < 3 %) of nano-particles impregnated specimens against brown-rot fungi was achieved only when copper with concentration of 3g/l was used, while all applied treatments provide equal protection of wood against white-rot fungus. The silver nano-particles showed the lowest protection effect with the highest variability when the treated wood was exposed to *P. placenta*.

Copper is biocidally inactive in low quantities, even acts as an essential micronutrient. However, at higher levels it is toxic heavy metal for most of living cells. Copper tolerance is usually associated with brown-rot fungi, which was showed in many reports also for *P. placenta* (Young 1961, Green and Clausen 2005); besides that *P. placenta* is also known to be tolerant to zinc compounds (Clausen et al. 2009). Pohleven et al. (2011) determined the minimum inhibitory level for related *Antrodia vaillantii* on 1600 ppm in nutrient medium, whereas for *T. versicolor* it was found to be ten times lower (Humar and Lesar 2008). The effect of copper on growth of different fungi was evaluated for instance by Guillén and Machuca (2008). The increase of copper concentration to 3 mM led to complete growth inhibition in the majority of the WRF (white rot fungi) and *T. versicolor* was strongly suppressed. In contrast, two of three BRF (brown rot fungi) presented a higher growth rate. Presented results are in agreement with previous findings of other authors and the copper concentration of 3 g/l was found to protect wood even against brown-rot fungus *P. placenta*. A reduction of toxicity of copper or other metals is explained by the production of intracellular and extracellular chelating compounds such as oxalic acid. These compounds reacts with copper to form insoluble, and therefore bio-unavailable, inert forms of oxalate (Hastrup et al. 2005, Gadd 1999) or by increased acidity of substrate reducing the toxicity of copper (Humar et al. 2005). Guillén and Machuca (2008) showed only minor acidification of MEA (malt extract agar) medium by *T. versicolor* after copper adding unlike copper tolerant brown-rot fungi. The white-rot fungi capability of adsorption and accumulation of metals together with low concentration of metabolized oxalic acid leads to high efficiency of used treatments.

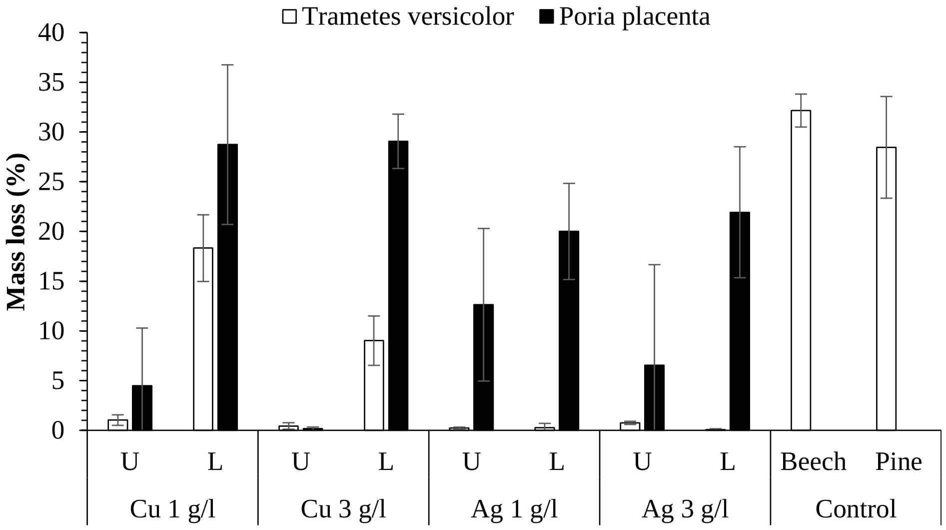

Figure II. 6 Mass losses of unleached (U) and leached (L) nanoparticle treated beech and pine wood after exposure to Trametes versicolor and Poria placenta (n = 10)

Silver is well known for its great antimicrobial and antifungal properties. Moreover, it is element with the highest toxicity for microorganisms followed by others heavy metals like copper, lead or tin, and lowest toxicity for animal cells at the same time (Golubovich and Rabotnov 1974, Rai et al. 2009, Pulit et al. 2013). Rezaei et al. (2011) stated that nano-silver in low concentration (400 ppm) is not able to inhibit *T. versicolor* activity within poplar wood. However, *Paulownia fortunei* wood impregnated by 400 ppm aqueous suspension of silver, copper and zinc oxide nano-particles resisted to decay caused by *T. versicolor* (Akhtari and Arefkhani 2013). Silver and copper nano-particles suspension used in the particleboard increased resistance against *T. versicolor* with higher efficiency of copper (Taghiyari et al. 2014). The ionic silver-based biocides (1% Ag solution) were tested by Dorau et al. (2004) and did not provide sufficient resistance of southern yellow pine wood to brown-rot fungi. In present study, silver nano-particles inhibited tested white rot fungus, whereas brown rot fungi was only suppressed which resulted in lower ML in comparison to control specimens. Highley (1975) tested different compounds that inhibit the action of extracellular celluloses. It showed that enzymes responsible for insoluble cellulose degradation, typical for white rot fungi, was inhibited by the metals mercury, silver, copper, and manganese. Only mercury and silver were able inhibit enzymes decomposing soluble cellulose, which are produced by brown rot fungi as well. Possible mechanisms by which microorganisms avoid the toxical effect of silver ions are summarized by Guggenbichler et al. (1999), i.e. biomethylation; complex formation with metal ions; development of efflux pumps; binding of metal ions to cell surfaces or the removal of metal ions by precipitating. Analogous mechanisms as immobilizing copper by precipitating copper oxalate is anticipated in case of brown rot fungi, which eliminates silver higher efficiency in celluloses inhibition.

As expected, higher ML usually occurred in leached wood specimens when compared to unleached (Fig. 4). Whereas in unleached copper treated specimens both concentration sufficiently blocked decay activity of fungi (ML < 5 %), after leaching the efficiency of treatment was significantly reduced. Especially the ML caused by brown rot fungus were as high as those in the control specimens. Low fixation of copper nano-particles led to remove of their substantial part from wood. Therefore, remain amount is lower than required minimum inhibitory level. Copper acts as an essential trace mineral – e.g. is a cofactor in the catalytic centre of laccase – one of ligninolytic enzyme (Vršanská et al. 2015). In low concentration is biocidally inactive (Baldrian 2003, Hrastnik et al. 2013) or even more, it can stimulate the growth of fungi (Wazny and Thornton 1986). When the efficacy of copper and silver nano-particles is compared, it can be seen that the latter is more effective than copper, when the wood is subjected to leaching. Higher retention of silver nano-particles together with better fixation in the wood enables to leave sufficient level of active substances for reduction of fungi activity (brown rot fungi) or even inhibition (white rot fungus).

CONCLUSIONS

This work deals with the antifungal effects of copper and silver nanoparticles against two wood-rotting fungi. Pine sapwood showed the highest retention for both concentrations. An average leaching of copper nanoparticles (15 % to 35 %) was higher compared to leaching of silver (up to 15 %). This research has shown that copper nano-particles at the concentration of 3 g/l are effective against both tested fungi (under 5 % of mass loss) but it seems to be ineffective after leaching. Nano-silver treatment shows very low ML (under 1 %) and high efficiency against *Trametes versicolor* fungi for leached and unleached specimens, but very low efficiency against *Poria placenta* decaying. Further steps for research in this area should be to improve fixation and determinate the influence of nanoparticles form (preparation method/technique).

PAPER III.

COMPARISON OF SELECTED PHYSICAL AND MECHANICAL PROPERTIES OF DENSIFIED BEECH WOOD PLASTICIZED BY AMMONIA AND SATURATED STEAM

Pařil, P., Brabec, M., Maňák, O., Rousek, R., Rademacher, P.,

Čermák, P., Dejmal, A. (2014)

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Comparison of selected physical and mechanical properties of densified beech wood plasticized by ammonia and saturated steam

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ABSTRACT

Gaseous ammonia treatment in combination with densification of wood has been known for several decades, but nowadays there is no industrial production of material modified in this way; also, little research is published in this area of wood science. In this study, selected physical and mechanical properties, i.e., density profile, bending strength, hardness and moisture absorption were investigated for Lignamon (i), which was obtained from the Czech industrial production. Selected properties were also investigated using steam-densified beech (ii) and native beech (iii) and compared with each other. Densitometry of Lignamon showed a large variability of the density profile compared to the density profile of only densified beech. It is affected by the degree of densification, temperature and moisture gradients, and their relationship to the glass transition of the wood cell wall. Modulus of elasticity, hardness, moisture exclusion and anti-swelling efficiency of Lignamon are enhanced compared to densified beech. The enhanced dimension stability and lower hygroscopicity of Lignamon are probably caused by heat treatment during the process. Further investigation will be carried out with self-produced Lignamon samples.

Key words: ammonia treatment; densified wood; Fagus sylvatica *L.*; plasticization; density; hardness; modulus of rupture; modulus of elasticity; Lignamon

INTRODUCTION

In this study three different materials were investigated. Ammonia-densified beech (Lignamon), only steam-densified beech (in following text called densified beech) and native beech were compared.

Wood densification is a well-known technique which improves the mechanical properties of wood, such as hardness and shear strength. Most of these improved properties are directly related to density and its profile. The density profile of wood varies with the degree of densification and determines bending properties. Different density profiles are affected by the temperature, moisture gradients and their relationship to the glass transition of the wood cell wall. Hardness of densified wood is strongly affected by the process parameters, such as temperature and the press closing speed (Laine et al. 2013a; Laine et al. 2013b; Kutnar et al. 2009).

A major disadvantage of densified wood is the recovery of the original dimensions due to moisture or water absorption. Dimensional stability of densified wood can be improved by post heat treatment or microwaving (Abe et al. 2001; Boonstra and Bloomberg 2007).

Scheuerch (1963) started a series of experimental work focused on the plasticizing effect of ammonia on wood. It was shown that this process is suitable to facilitate the creation of extreme shapes or complicated structures without decreasing the strength (Berzins 1972, Davidson and Baumgardt 1970, Kalnins et al. 1967, Pandey et al. 1991). Plasticization by ammonia has lower energy consumption than conventional steaming and does not require long time for the process settings (Strauss 1995, Wienhaus et al. 1978). Wood is a natural heterogeneous material consisting of three main constituents: cellulose, hemicellulose and lignin. These constituents are responsible for most of the physical and mechanical properties of materials (Banks and Gibson 1988).

Ammonia has a relatively high affinity to the main constituents of wood. Ammonia can penetrate into the crystal structure of cellulose. It leads to the disruption of the lignin-carbohydrate complex. An increase of the nitrogen content and the number of amide bonds can occur with a decrease in ester bonds (Rosca et al. 2002). Ammonia treatment of wood has no significant influence on the content of cellulose, hemicellulose and lignin; the plasticizing effect is temporary, the wood returns to its origin condition even with a more compressed / compact structure after evaporation of ammonia (Berzings and Rocens 1970).

Furthermore ammonia treatment may significantly upgrade the decorative value of wood (Weigl et al. 2012; Čermák and Dejmal 2013) and improve colour stabilization (constant colour of wood over time) and – under heat treatment due to Lignamon process parameters - dimensional stability (Weigl et al. 2009).

Rosca et al. (2002) studied the effect of ammonia treatment on physical and mechanical properties of wood. The authors confirmed that the deformability of ammonia plasticized wood increased when the initial moisture content of the material is higher than 20% (Rocens 1976). The results showed a decrease of modulus of elasticity and modulus of rupture in the direction of compression which led to an increase in deformability.

The changes are effective in the whole structure or only in the surface layers of wood with respect to the processing time, the dimensions of the material and the concentration of ammonia. Tannins are perceived as wood extracts that are responsible for reacting with ammonia that leads to the required colour changes of wood (Tinkler 1921; Bariska 1969). The content of extractives in native beech is about 2% (Wagenführ 1966).

A commercially applied process of wood plasticized by ammonia is called Lignamon. This technology uses mainly beech wood which is plasticized by ammonia gas and then densified in the perpendicular direction to wood fibres (up to 60%). Some tropical or subtropical wood species can be replaced by this modified material (improved hardness, colour, etc.).

This technology was developed in the sixties. The research was carried out by the Institute of Wood Chemistry on Scientific Academy in Latvia (Riga), led by I. Y. Kalninsha (Czerny and Valasek 1974). The methodology for process industrialization was developed in cooperation with A. Stojčev (Stojčev 1979). Unique semi industrial line for ammonia modified wood was produced in cooperation with the Czechoslovak Institute (VVÚD - Timber Research Institute in Prague) in 1974. Analyses have shown that processes designed by these authors are much more effective than the processes developed in the USA, Austria and other countries. The patent for wood modified in this way is owned by Soviet and Czechoslovak researchers.

OBJECTIVES

The aim of this paper is to investigate Lignamon from an old industrial production which was stopped because of low demand. The motivation is to revise properties of Lignamon and find a way to reactivate production in a new plant for interested companies. First negotiations with different national and international companies have already been started. Selected physical and mechanical properties of Lignamon were investigated to find new applications for this material. For comparison, steam-densified beech and native beech were tested. This study is the first step to further research, which will be the development of an ammonification unit and the determination of the optimal parameters for plasticization, compression and thermal modification. Also first results of improved durability, actual only with a wide variability, will be worthwhile to develop the process.

MATERIAL AND METHODS

Material called Lignamon was obtained from industrial production (closed in 2010) in the Czech Republic. The material for samples came from one process. Lignamon is the trade name for thermally, chemically and mechanically modified wood. The modification process is initiated by chemical modification of gaseous ammonia using vacuum and pressure. The transversal compression of wood is carried out in the radial or tangential direction. The modification process is completed by the thermal stabilization of ammonia in the compressed structure of wood. The whole process is carried out in a single device with built-in compressing plates. The total duration of the process is up to 30 hours depending on the material and the parameters of the modification. The modification process was optimized for wood of European beech (*Fagus sylvatica* L.). The moisture content of the wood entering this process is 18%. Finally, material with modified physical, mechanical and chemical properties of wood with various degree of densification (15%, 30% and 50%) is produced.

15 prisms with dimensions of 740 × 80 × 35 mm^3 were available from an old production process. Different directions of compression were found for each sample. The most of the samples were made from side boards so the direction of compression was not purely tangential or radial. Only a few of them were compressed strictly in the tangential direction. The density range was from 885 kg/m^3 to 1185 kg/m^3 (conditioned in 65 % rH and 20 °C).

The size of specimens for densified beech entering the process was 350 × 50 × 50 mm^3. The plasticization was carried out in a steam oven under the action of saturated steam. The plasticization proceeded for 4 hours at 100 °C and standard atmospheric pressure. The compression was carried out in the laboratory hydraulic press with heated pressing plates. The compacting pressure was 0.57 MPa with a final degree of densification about 40%. The temperature of pressing plates was 90 °C and conditioning proceeded for 10 days.

The specimen size for densitometry and hardness was 50 × 50 × thickness mm^3. Transverse dimensions of bending specimens were 14 × 14 mm^2 and the length was 210 mm. The ratio of these dimensions followed the British Standard BS 373-1957. The material was cut on a circular saw and machined using a cylindrical grinder. Sanding used a p150 grit size. Each sample was weighed and sorted by weight, then marked with a code defining the order position in the original block and the direction of compression in the production. 147 quality bending specimens of Lignamon, 30 densified beech specimens and 30 native beech specimens were obtained.

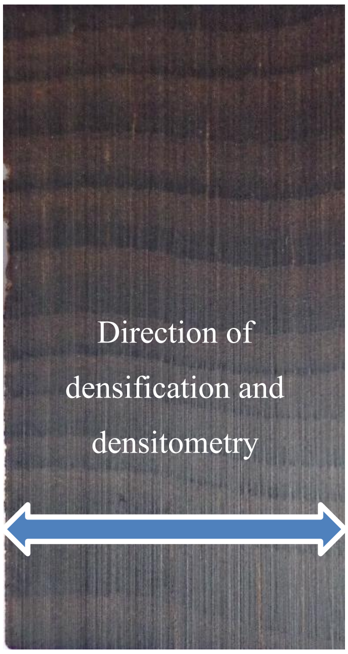


Figure III. 1 Cross-section of Lignamon sample

The aim of the x-ray densitometry measurement was to obtain the density profile of the available Lignamon blocks and densified beech samples. This gave us the information in which direction the Lignamon blocks had been pressed, and if the blocks had been cut after. The measurement was performed on X – RAY DENSE – LAB densitometer. The principle of measurement is sending an x-ray beam through the sample and intensity measurement on the other side. This scan is carried out in a single line in the direction of thickness, with steps of 0.01 mm. The direction of x-ray beam is perpendicular to the grain and parallel to the sample width. Computational software analyses the outputs and matches the average intensity with the average density, so the intensity of each measured position can be converted to a density.

The static bending test was carried out in compliance with the British Standards BS 373-1957. The bending test specimens were conditioned in a conditioning chamber (SANYO MTH 2400) at 20 ± 3 °C and a relative humidity of 65 ± 2 %. The process of conditioning was controlled by weighing 40 pieces of representative samples at regular intervals. Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined during the static bending test by the central loading method (three-point bend). The span of supports was 196 mm. For the calculation of MOE a linear part of stress-strain curve was used; limit values were $0.1 \times F_{max}$ and $0.4 \times F_{max}$ with the corresponding deflections. The input data for the TestXpert application were obtained by weighing and measuring each sample dimension. Each sample was placed between bending grips of the universal testing device (ZWICK Z 050) and the loading was launched. The samples marked with odd numbers were loaded parallel to the direction of compression. The other 50 % of samples were loaded perpendicular to the direction of compression. The density of each sample was calculated using its weight and dimensions. Small samples were prepared for the determination of moisture content (MC) of wood immediately after testing. They were dried to constant mass in a laboratory drying kiln (SANYO MOV 112) at a temperature of 103 ± 2 °C. Afterwards, each sample was weighed and measured. The obtained data were used to calculate the density of each sample.

Janka hardness method in combination with Brinell hardness method was used to determine the hardness. Hardness test specimens were conditioned in a conditioning chamber (SANYO MTH 2400) at 20 ± 3 °C and relative humidity of 65 ± 2 %. The testing of hardness was carried out on a universal testing device (ZWICK Z 050) in compliance with Czech Standard ČSN 49 0136. The impress depth was reduced to 2.82 mm because of small dimensions of the sample in the case of Janka method. The force was 1000 N for Brinell method. Hardness of Lignamon was measured on the side surface in the direction of compression and perpendicular to it.

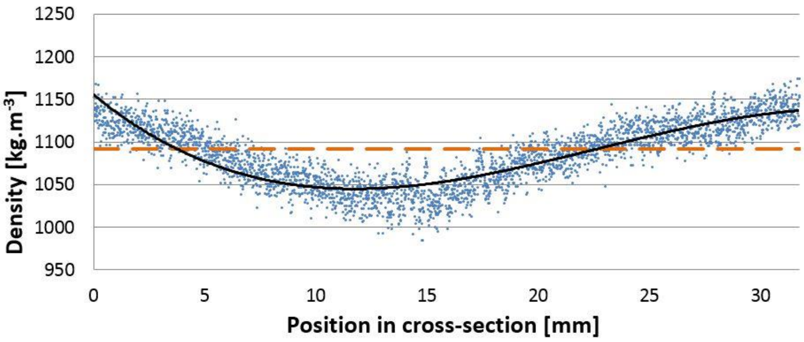
The moisture absorption test was done by placing the specimens into the conditioning chamber (99 % rH and 20 °C). The EMC and swelling in all directions were measured.

RESULTS AND DISCUSSION

Density

Densitometry results gave an image of a density profile and a range for 15 available samples. Three types of the density profiles were observed. Different density distributions are caused and influenced by the degree of densification, temperature and moisture gradients, and their relationship to the glass transition of the wood cell wall (Kutnar et al. 2009). The idea that samples had been cut after compressing and the original manufactured dimensions had been different was partially confirmed. Most likely the sample in Fig 2b represents edge part (a half) of the original compressed block, while Fig 2a shows typical density profile of Lignamon (for higher average density samples). But there is still the question of original conditions. Further look at the results suggests that the samples with a lower average density have a more uniform density profile (Fig. 2c), and the samples with a higher average density have higher density zones on the edges (Fig. 2a, b). This could lead to the conclusion that a lower degree of densification means a more uniform density profile as confirmed in the study of Kutnar et al. 2009 also for viscoelastic thermally compressed wood.

Average density ranged from 885 to 1185 kg/m^3. The differences between minimal and maximal density for each sample varied from 100 to 200 kg/m^3, coefficients of variation from 1.4 to 3.7 %, while higher values attribute with higher average density. Further investigation has to be carried out with self-produced samples.



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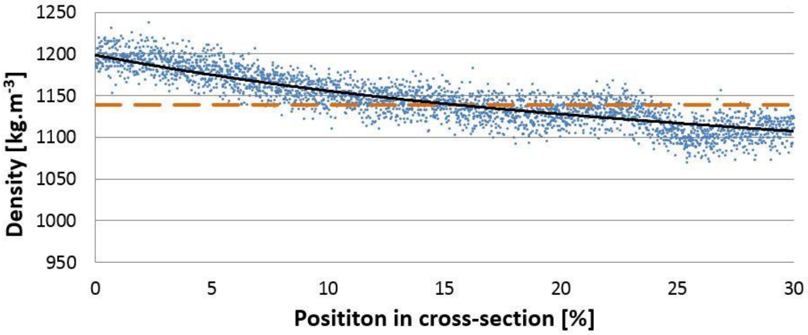

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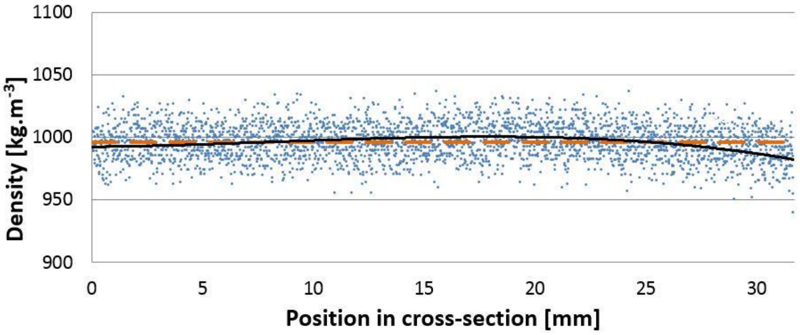

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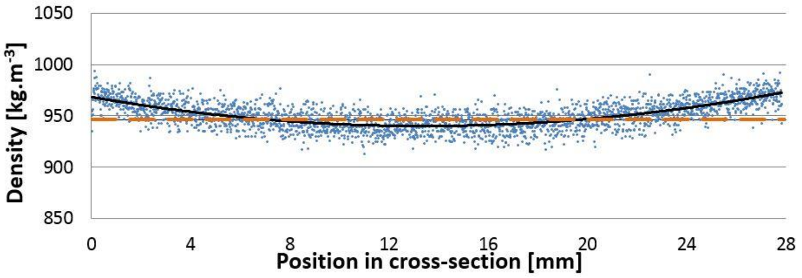
Figure III. 2 The density profile of Lignamon (65% rH, 20 °C); a- a profile with a higher density on the surfaces than in the core of sample; b- a profile with a higher density on the one surface than on the other; c- a profile with almost uniform density in whole cross section; dashed line in all figures represents mean value of density

Two types of density profile of steam-densified beech are shown in Fig. 3. The first has a higher density on the surface than in the middle (Fig. 3a). The second type of profile has almost uniform density in the whole cross-section (Fig. 3b). Process parameters were the same for all samples and differences in density are caused by the different quantity of void areas in the thickness direction (Kutnar et al. 2009). The density profile of densified beech shows a better uniformity compared to the density profile of Lignamon. The lower uniformity of Lignamon is probably caused by the above-mentioned process parameters.



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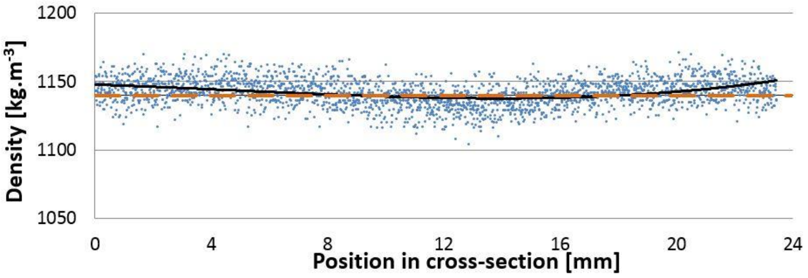

b

Figure III. 3 The density profile of densified beech (65 % rH, 20 °C); a- a profile with a higher density on the surfaces than in the core ; b – a profile with almost uniform density in the whole cross-section; dashed line in all figures represents mean value of density

Modulus of rupture (MOR) and modulus of elasticity (MOE)

The MOR and MOE of Lignamon, measured perpendicular to the direction of compression of the samples were higher by around 7 % and 18 %, respectively, compared to the MOR and MOE measured parallel to the direction of compression (Fig. 4a and 4b). These deviations were assessed by the T-test for independent samples as statistically significant at a level of significance $\alpha = 0.05$. The MOR of steam-densified beech measured perpendicular to the direction of compression of samples was lower by around 2 % compared to the MOR measured parallel to the direction of compression. This difference was not found as a significant deviation at a level of significance $\alpha = 0.05$ (Fig. 4a). A significantly higher MOE of densified beech (around 15 %) measured perpendicular to the direction of compression was observed (Fig. 4b). These significant differences can be caused by the different longitudinal shear strength of samples during loading perpendicular and parallel to the direction of compression. If a sample is loaded parallel to the direction of compression, the longitudinal shear strength will be affected by the uneven density profile (see Fig. 2). The differences in density dependent on the position of a sample probably cause a lower longitudinal shear strength and lower MOR and MOE.

Generally, the differences between p-values for Lignamon and densified beech are caused by the combination of ammonia and heat treatment with pressing in case of Lignamon which results in the lower variability of the bending properties compared to the densified beech. The lower variability of bending properties of Lignamon is reflected in lower p-values (more reliable) than p-values for densified beech. The difference between p-values for MOR ⊥ and ∥ (Lignamon and densified beech) can be affected by the different angle of wood fibre on the cross section of the samples. The old production of Lignamon, which was subjected to our investigation, had a mixture of fibre angles on the cross section. Therefore, we produced densified beech with various fibre angles on the cross section as well. The variability of fibre angles on the cross section could cause the reported various p-values.

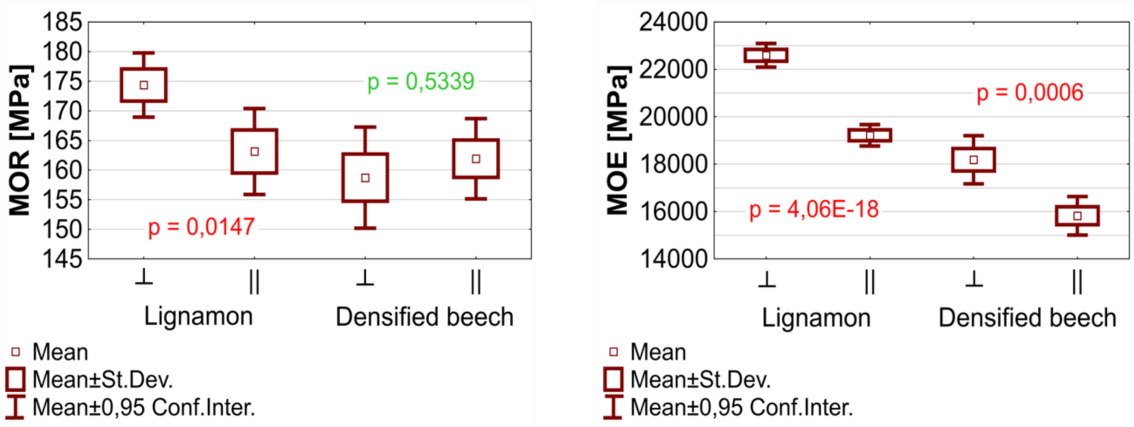

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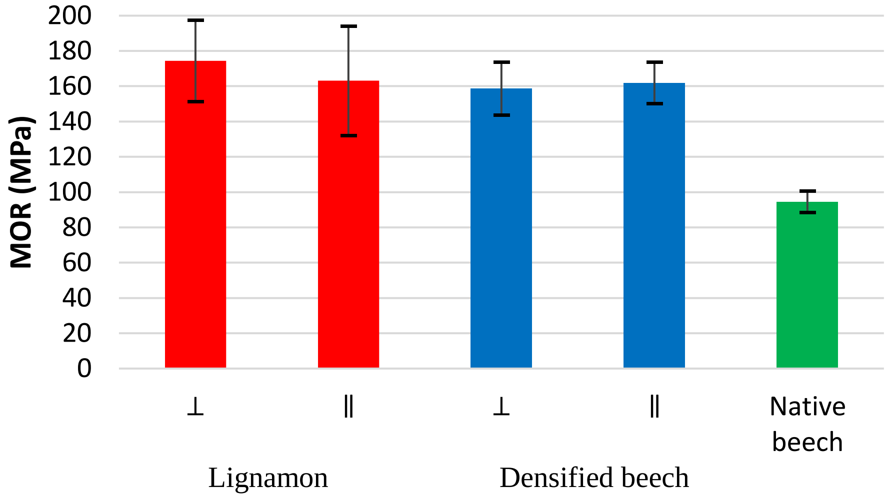
Figure III. 4 T-test perpendicular vs. parallel (Lignamon and Densified beech); a- Modulus of rupture; b- Modulus of elasticity

Fig. 5 shows an improvement of MOR and MOE in both cases of plasticization. Also the impact bending strength can be improved by ammonia treatment in combination with densification as shown by Kalnins et al. (1967). In the case of Lignamon, the MOR and the MOE increased by about 78 % and 86 %, respectively, compared to native beech (reference). The steam-densified beech MOR and MOE increased by about 69 % and 51 %, respectively, compared to native beech (reference) which is in agreement with observations of other authors (Kamke 2006, Blomberg et al. 2005). The MOR and MOE improvement of Lignamon and densified beech material can be seen in Fig. 5. Lignamon shows higher values of the MOE compared to densified beech (23 %) in spite of the fact density increased by only 4 %; results of the MOR are almost similar. Bach and Hastrup (1973) also observed the higher mechanical properties of the ammonia plasticized and compressed wood than proportional to the density. They suggested it is attributable to a mechanism involving no-fracture buckling of the cell walls and forming of the new secondary bonds. This assumption was confirmed by Bariska (1975). The increase in the MOR due to the ammonia treatment of wood was found by Mahdalík et al. (1971). The modulus of rupture and the modulus of elasticity are higher in the perpendicular direction of compression; in the case of densified beech, similar results can be only shown for the MOR. In addition, the temporary character of ammonia plasticization effect is also confirmed. This effect disappears due to the exhaustion of ammonia after compression during production. The increased MOR and MOE allow using modified wood in applications where natural wood would fail.



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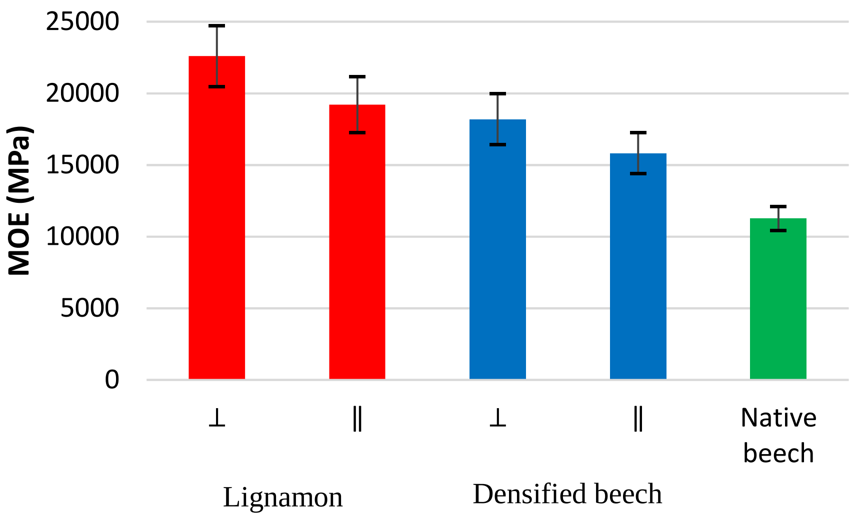
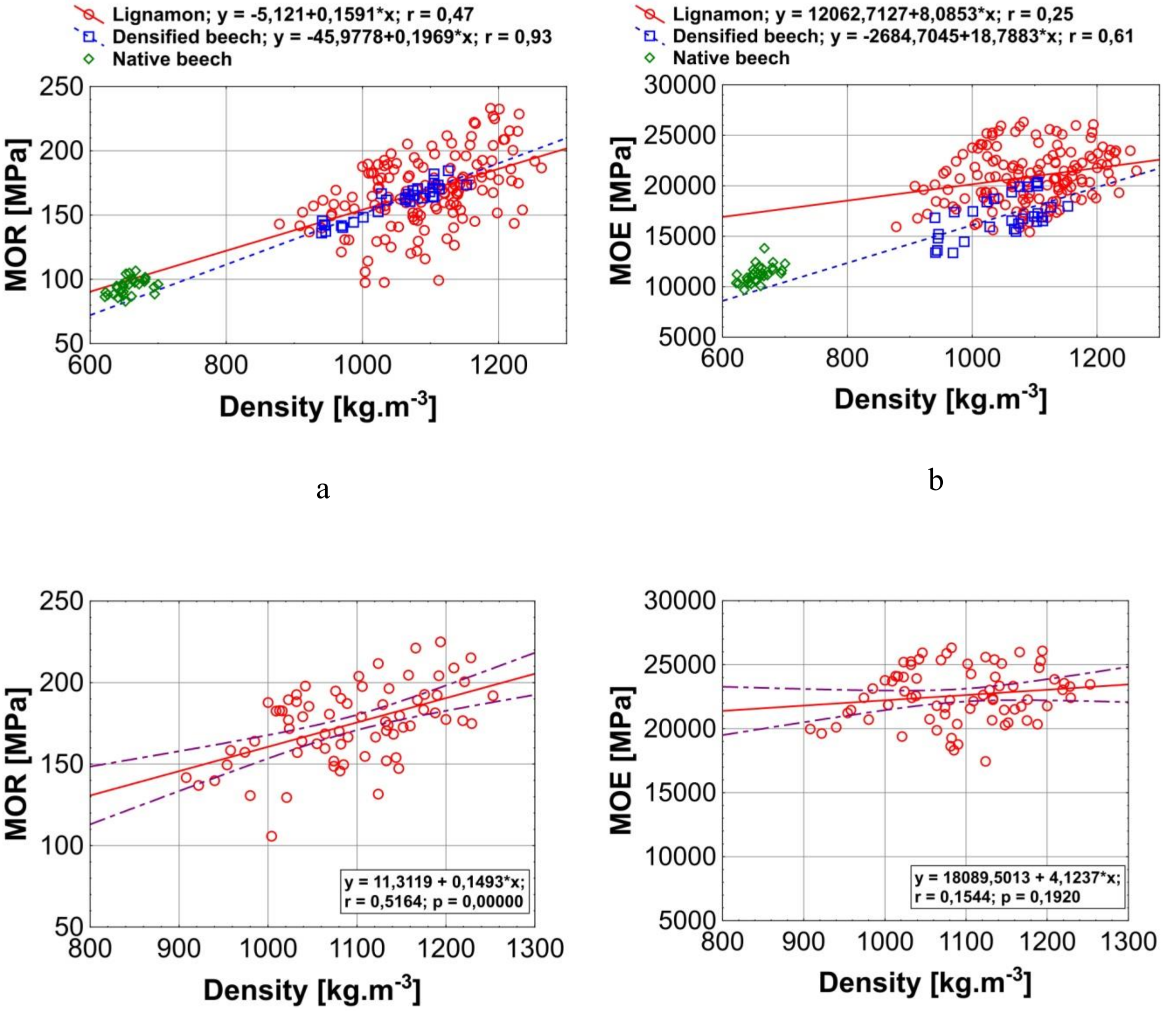


b

Figure III. 5 Comparison of MOR (a) and MOE (b); MOR (a) and MOE (b) of Lignamon samples with an average density of 1092 kg·m^{-3}, of densified wood (plasticized by saturated steam) with an average density of 1048 kg·m^{-3} and of native beech specimens (reference) with an average density of 657 kg·m^{-3}; ⊥ = perpendicular to the direction of compression, ‖ = parallel to the direction of compression

The relationships between the density and the MOR and the MOE of Lignamon, densified beech and native beech (reference) are shown in Fig. 6. A linear regression analysis was used to evaluate the influence of density on the MOR and MOE. As follows from Figs. 6a and 6b, influence of density on the MOR and MOE after the densification was quite well. Conversely, the modification process used in production of Lignamon caused a decrease in the correlation between the bending properties and the density compared to the densified beech. As mentioned by Miklečić (2012), the ammonia reacts especially with extractives of wood independently of the wood density. If the MOR and the MOE are proportional to the density (Bodig and Jayne 1993) and the MOR and the MOE of densified wood can be affected by ammonia within the plasticization process (Bach and Hastrup 1973), the relationship between bending properties and the density might be changed. Coffin and Copeland (2003) reported that the narrower range of an independent variable (in this case the density of native beech) can induce a lower dependency of a dependent variable (in this case the bending properties of native beech). Therefore there is not performed and presented the regression analysis of the relationship between the bending properties and the density of the native beech. In the case of the

MOR measured perpendicular and parallel to the direction of compression of samples, the values of the correlation coefficients were similar (Figs. 6c and 6e). Contrary, in the case of the MOE (Figs. 6d and 6f) there was a difference in correlation with density between mentioned directions of measurement. It can be potentially caused by the different influences of modification processes which were performed during Lignamon production. The new lateral bonds in wood cell wall responsible for increasing the stiffness can be created, but it is only a speculation and should be verified by other studies. The results from the linear regression analysis confirmed that the density affects strength and stiffness of the described modified wood not similarly to natural wood.



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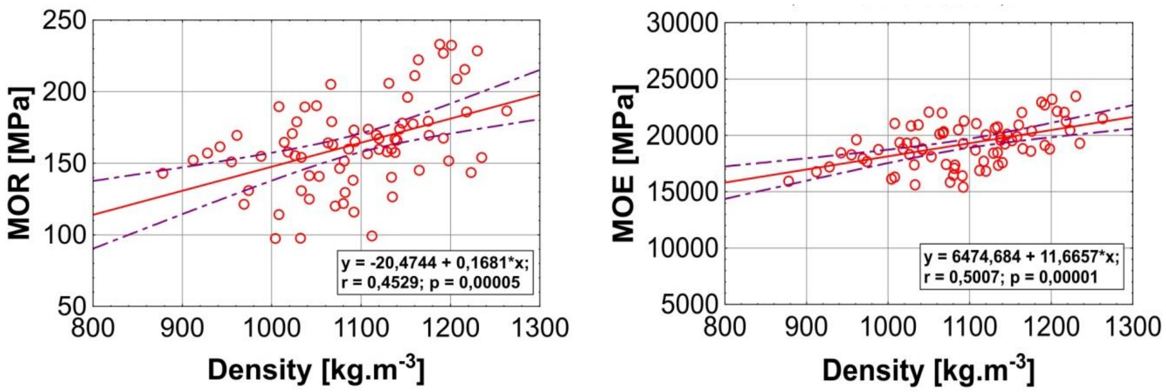

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Figure III. 6 Relationships of density and MOR and MOE; a,b- Influence of density on MOR and MOE for all sample series (Lignamon, densified beech and native beech); c, d- Influence of density on MOR and MOE perpendicular to the direction of compression (Lignamon); e,f- Influence of density on MOR and MOE in the direction of compression (Lignamon)

Hardness

The influence of the density on hardness is shown in Fig. 7. The correlation coefficient in the case of Janka hardness is very high (0.84); Brinell hardness has a lower value, but it is still above 0.5. Janka and Brinell hardness are significantly influenced by the density - with a higher density the hardness increases. Not only the average density but also the surface density affect hardness as confirmed for viscoelastic thermal compressed wood composite by Rautkari et al. (2011).

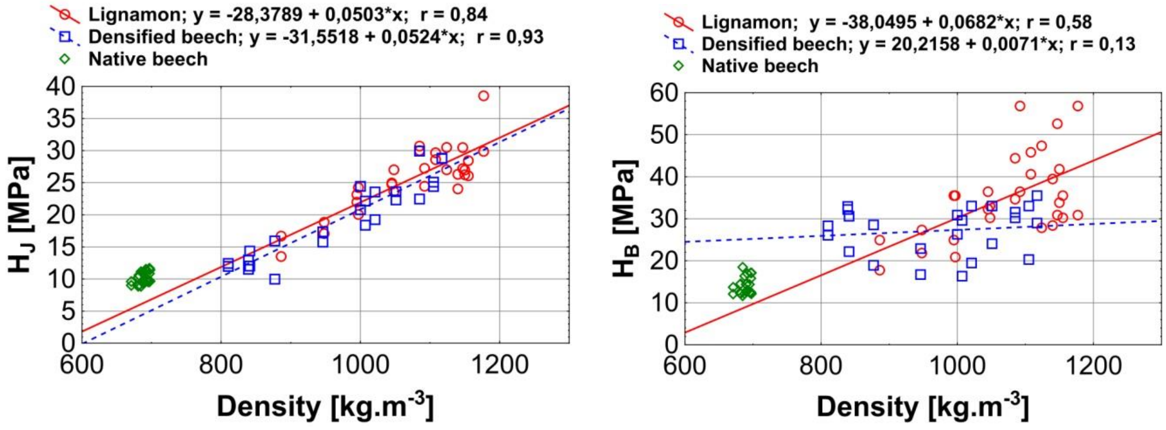

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Figure III. 7 Influence of density of Lignamon, densified and native beech on Janka (a) and Brinell (b) hardness (65 % rH, 20 °C)

The hardness of Lignamon increased by about 150 % compared to native beech (reference) and by about 30% compared to densified beech (see fig. 8) in spite of the same density. This might be caused by different densities on the surfaces which can be the reason for different compression parameters like the press closing time or temperatures (Laine et al. 2013b). There is a big difference between hardness in the parallel or perpendicular direction of compression. The biggest hardness is in the perpendicular direction of compression in the case of Lignamon and densified beech.

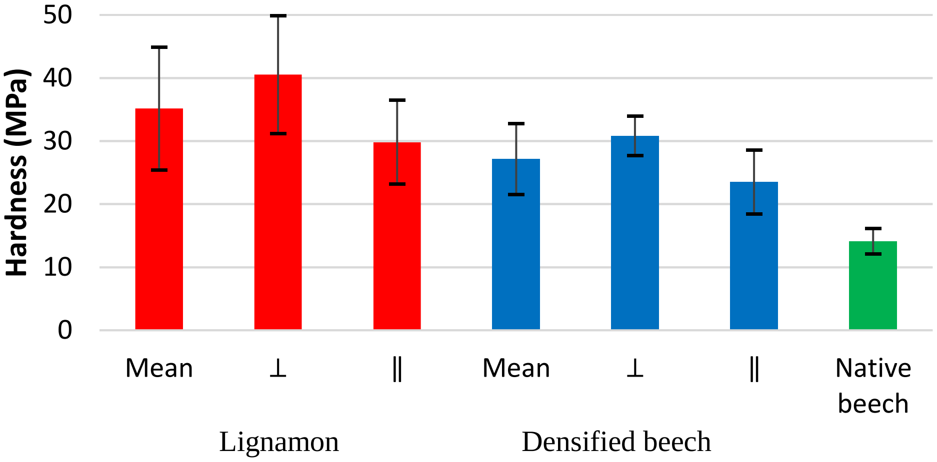
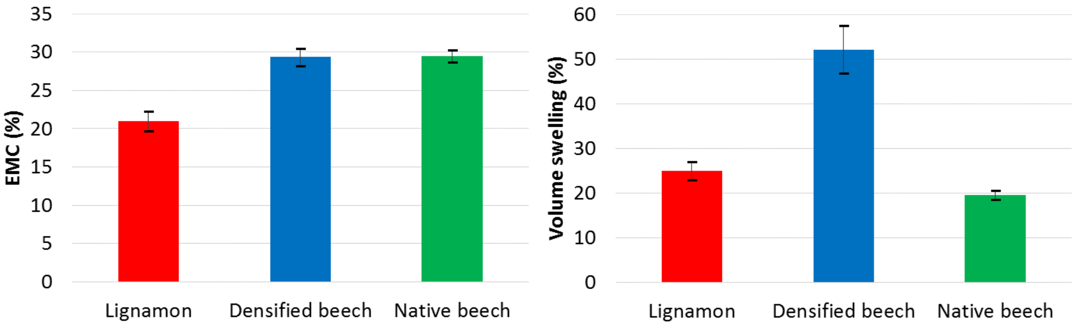


Figure III. 8 Hardness; Comparison of Brinell hardness and influence of the direction of compression (65 % rH, 20 °C); ⊥ = perpendicular to the direction of compression, ‖ = parallel to the direction of compression

Moisture absorption

The values of moisture content and volume swelling after conditioning (99 %, 20 °C) are shown in Fig. 9. The EMC (equilibrium moisture content) of Lignamon is 25 % lower compared to the EMC of native beech and densified beech. Volume swelling of lignamon is slightly higher compared to volume swelling of native beech and about 50 % lower compared to densified beech (see fig. 9b). Enhanced anti-swelling and moisture exclusion efficiency of lignamon is effected by a reduction of OH groups in the wood structure which is probably caused by heat treatment during the process. The process parameters of Lignamon are similar to the thermo-hydro-mechanical (THM) densification process. Tests of Navi and Girardet (2000) showed that the THM densified wood is less hygroscopic and more stable with a low set-recovery. It is known that heat treatment has a positive effect on the dimensional stability of densified wood (Boonstra and Blomberg 2007, Kamke 2006).



a b

Figure III. 9 Moisture absorption; EMC (a) and volume swelling (b) after conditioning (99 % rH, 20 °C) of Lignamon with an average density of 1073 kg·m^{-3}, of densified beech with an average density of 1077 kg·m^{-3} and of native beech with an average density of 689 kg·m^{-3}

CONCLUSIONS

Ammonia treatment provides plasticization superior to basic steaming which is supported by our measurement of slightly higher MOR and MOE of Lignamon compared to the densified beech. Advantage of Lignamon compared to steam-densified beech is the observed improvement of dimensional stability, hydrophobicity and hardness which was caused by heat treatment during process. Confirmation of added value leads to many potential applications for Lignamon (exterior cladding, terrace decking, sailboats, moulds etc.), which could motivate industrial partners to re-establish production. Further investigation will be carried out with self-produced Lignamon samples to determine the influence of particular process stages on changes of material properties. Similarity of Lignamon and THM process encourages comparison of these materials.

PAPER IV.

MOISTURE ABSORPTION AND DIMENSIONAL STABILITY OF POPLAR WOOD IMPREGNATED WITH SUCROSE AND SODIUM CHLORIDE

Pařil, P., Dejmal, A. (2014)

Maderas (16)3: 299–311.

Moisture absorption and dimensional stability of poplar wood impregnated with sucrose and sodium chloride

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ABSTRACT

This paper deals with the effect of vacuum-pressure impregnation of poplar wood (*Populus alba* L.) by aqueous solutions of sucrose and sodium chloride on its physical properties. Groups of samples with different concentrations of substances in the aqueous solution were compared within each other and also with a reference (non-impregnated) group. The specimens from all groups were tested for density, moisture absorption and dimensional stability. The obtained data were statistically analysed and compared each other. The most satisfying final properties were achieved in impregnation of sucrose with concentration of 6.25 g/100 ml H_2O. The retention was 31 kg/m^3 (WPG around 8 %). The values of ASE (anti-swelling efficiency) reached to 36 % and MEE (moisture exclusion efficiency) was reduced by 33 %.

Key words: poplar, wood modification, sodium chloride, sucrose, vacuum-pressure impregnation, swelling, equilibrium moisture content

INTRODUCTION

Today, wood is a very frequently used material. In comparison to other competitive materials it offers many advantages including the following ones: wood is a renewable material, given its weight it provides a very high strength and elasticity, it has good thermal insulating properties, it can be easily shaped, it is ecologically recyclable and, last but not least, it has its indisputable aesthetic qualities (Gryc et al. 2007; Baar and Gryc 2012). But there are also some disadvantages. One of them, hygroscopicity, which induces dimension changes, was examined in this study.

Wood impregnation by natural substances with the aim of modifying its properties has been well known for decades and even centuries. At the break of the industrial revolution mainly synthetic-based substances were preferred – these were artificially produced with frequent negative side effects both on human beings and on the environment. The current trend in many fields of human activity is to return to original harmony with nature and a harmless use of natural renewable resources (Hill 2006). Products made from materials which were modified by natural means can be recycled environmentally friendly. Advantages of the new generation of “eco-modified” products are: first, that the material comes from renewable resources (e.g. wood); and second, that also the impregnation substance is from such resources (e.g. substances obtained from plant processing or, ideally, as waste and by-products). Third, their energy efficiency should be low. One of such technologies is e.g. modification of wood impregnation by sugars (Vigué 2006).

Wood modification by pure sucrose is mainly used for conservation of wooden artwork. Sucrose (cane sugar, beet sugar, chemically α-D-glucopyranosyl-β-D-fructofuranoside, $C_{12}H_{22}O_{11}$), is easily dissolved in water, non-toxic and does not corrode metals. Its chemical structure is similar to cellulose, it has a low molecule weight and it penetrates wood easily and quickly. It has a crystalline structure suitable for wood reinforcement. It dissolves in water at a normal temperature so it does not have to be heated for impregnation. It has a chemical affinity to cellulose and diffuses in wood easily. A raster electron microscopic study found that sucrose penetrates cell walls where it crystallizes. This corresponds to its excellent stabilization of wood dimensions. Modified wood retains its natural appearance; and the price of sucrose is low compared to other substances (Morgós 1993).

Other research (Stamm 1955) compared impregnation by sucrose and impregnation by invert sugar with the aim to decrease water vapour absorption and water absorption. The invert sugar (obtained by acid or enzymatic sucrose hydrolysis) was found to decrease water absorption better than crystalline sucrose. Both ways achieved better results than unmodified specimens. However, the invert sugar does not increase the hardness of wood comparing to sucrose, which improves this property.

Another experiment published by Lesar et al. (2009) compared water vapour absorption in specimens impregnated by compounds of boron, sodium chloride and glucose. Impregnation by sodium chloride had a larger effect on the equilibrium moisture content (EMC) than impregnation by boron compounds. An increasing concentration of NaCl in wood was found to be accompanied by increase in EMC. Boric acid, borax, sodium chloride and glucose have all crystalline structures. The researchers assume that these substances are bound in wood mechanically (not chemically) and thus they do not cause any structural changes to wood. The substances are deposited in the form of smaller or larger crystals in cell walls and cell lumens. The crystals dissolve in an extremely humid environment and crystallize again when air humidity decreases. The absorbed and free water in wood works as a dissolvent. This process of crystallization and dissolution is reversible.

The difference between sodium chloride and sucrose is their water solubility – it is six times higher for sucrose than for NaCl. Thus we can assume smaller weight percentage gain (WPG) within NaCl impregnation. An important factor in the case of NaCl will be its hygroscopicity.

Modification of wood with sucrose is commonly used in the preservation of archaeological wood artefacts (Morgós 1993).

The use of these materials should be for interior due to increased hygroscopic properties of modified materials. Another alternative would be used for outdoor in small concentrations of sucrose when there is not such a large increase in EMC and adding some biocide compounds.

The main aim of this study was to provide better dimensional stability of the wood of poplar. The authors chose substances that are water soluble and come from natural sources and could replace e.g. synthetic resins. Changes in properties of solid wood in dependence on conditions of use can be huge and need to be eliminated as much as possible (Dejmal et al. 2009).

MATERIAL AND METHODS

Samples

Specimens of white poplar (*Populus alba* L.) with dimensions 30 × 20 × 20 mm (L × T × R) were oven dried in a laboratory drying chamber at a temperature of 103 ± 2 °C until constant mass was achieved. Then the specimens were weighed and dimensions were measured.

Vacuum-pressure impregnation

The impregnation solution contained water (dissolvent) and the impregnation substance, either sodium chloride or sucrose. Due to the lower water solubility of NaCl in comparison to sucrose, the impregnation solutions with NaCl were about 6 times less concentrated. In total, five different concentrations of water dilutions were prepared for each substance (Table 1). The mixture was mixed properly in a plastic container and then left standing for 24 hours at a temperature of 20 °C. After 24 hours all NaCl and sucrose were dissolved and homogeneous dilutions were gained.

Table IV. 1 Groups of samples and concentrations of substance in the solution

Group	Concentration (NaCl)	Concentration (sucrose)
I	1 g / 100 ml H_2O	6.25 g / 100 ml H_2O
II	2 g / 100 ml H_2O	12,5 g / 100 ml H_2O
III	4 g / 100 ml H_2O	25 g / 100 ml H_2O
IV	8 g / 100 ml H_2O	50 g / 100 ml H_2O
V	16 g / 100 ml H_2O	100 g / 100 ml H_2O
VI	unmod. (reference) specimens	unmod. (reference) specimens

The impregnation was conducted using the vacuum-pressure device JHP 1-072. Specimens from groups I–V were impregnated. For all groups a specific process of impregnation was chosen, based on vacuum phase only, without overpressure. The vacuum based impregnation was carried out in three steps. The pressure was decreased to 20 kPa of absolute pressure in each step and then maintained for chosen time. Breaks at atmospheric pressure followed after each vacuuming step and the impregnation solution was filled up (Table 2).

Table IV. 2 Pressures and times used for phases of vacuum-pressure impregnation

Phase	Time t (min.)	Absolute pressure (kPa)	Phase description
1	15/60	50/20	slight pressure decrease
relaxation	10	101.3 ± 1	filling up the impregnation solution
2	80	20	
relaxation	10	101.3 ± 1	filling up the impregnation solution
3	60	20	
conditioning	24	101.3 ± 1	removal of the impregnation solution

Testing of physical properties

The specimens were oven dried again after impregnation until the constant mass. Then they were weighed and dimensions were measured again. The weight percentage gain (1), longitudinal swelling due to modification (2) and surface swelling due to modification (3) was calculated as follows:

$$WPG = \frac{m_m - m_n}{m_n} \cdot 100 \tag{1}$$

Where: WPG is the weight percentage gain (%), m_m is the mass of an oven dried modified specimen (g) and m_n is the mass of an unmodified oven dried specimen (g).

$$\alpha_L = \frac{l_m - l_n}{l_n} \cdot 100 \tag{2}$$

Where: α_L is the longitudinal swelling due to modification (%), l_m is the length of an oven dried modified specimen (mm) and l_n is the length of an oven dried unmodified specimen (mm).

$$\alpha_S = \frac{s_m - s_n}{s_n} \cdot 100 \tag{3}$$

Where: α_S is the surface swelling due to modification (%), s_m is the surface dimension of an oven dried modified specimen (mm^2) and s_n is the surface dimension of an oven dried unmodified specimen (mm^2).

The specimens were conditioned in the laboratory (at temperature of 20 °C and a relative air humidity of 20 %) for 60 days until they reached equilibrium moisture content of 4,1 %.

The moisture absorption test was done by placing the specimens into the desiccator above the water level. The lid of the desiccator was hermetically sealed and the specimens were left inside for another 60 days. This time ensures that the equilibrium moisture content of wood was reached. We also checked that the mass of the specimens remained constant after this time. The environment inside the hermetically sealed desiccator became saturated with water vapours (the relative air humidity reached nearly 100 %). The conditioning process was conducted at a temperature of 20 °C. Xylene was used to prevent mildew in the desiccator. The measured values were used to calculate the anti-swelling efficiency (4) and moisture exclusion efficiency (5):

$$ASE = \frac{S_n - S_m}{S_n} \cdot 100, \tag{4}$$

Where: ASE is anti-swelling efficiency (%), S_n is volume swelling of an unmodified specimen (%) and S_m is volume swelling of a modified specimen (%).

$$MEE = \frac{EMC_n - EMC_m}{EMC_n} \cdot 100, \tag{5}$$

Where: MEE is moisture exclusion efficiency (%), EMC_n is equilibrium moisture content of an unmodified specimen (%) and EMC_m is equilibrium moisture content of a modified specimen (%).

Statistical methods

The data were processed in software STATISTICA 9.0. Extreme values were removed using a box-graph (box plot). It was also necessary to investigate the distribution of the data type using a normal probability graph. Shapiro-Wilks test verified the data normality. This information is obtained for further processing. Afterwards the important moment and quantile characteristics (median, arithmetic average, standard deviation, etc.) were calculated. Then we can perform statistical tests (ANOVA, linear regression, etc.), which can reject the null hypothesis or not.

RESULTS AND DISCUSSION

Treatments

One of the most important factors affecting the changes in wood properties is weight percentage gain (WPG). A close relationship between the concentration of the impregnation solution (content of the substance in water) and the reached values of WPG has been proved. The values of WPG fluctuated between 8 and 75 % after the modification by sucrose and between 0.6 and 30 % after modification by NaCl (Fig. 1). The values of WPG achieved with sucrose are higher, which correlates to the higher concentrations of sucrose in water dilutions compared to dilutions concentrations of NaCl. In spite of this, NaCl and sucrose penetrate wood very well and can crystallize in the wood after drying. According to Morgós (2003) sucrose penetrates cell walls easily and creates hydrogen bonds with cellulose molecules. On the other hand, Lesar (2009) assumes that NaCl is bound in wood only mechanically (not chemically) so no structural change of wood occurs. In the table 3 you can see also average retention of NaCl and sucrose.

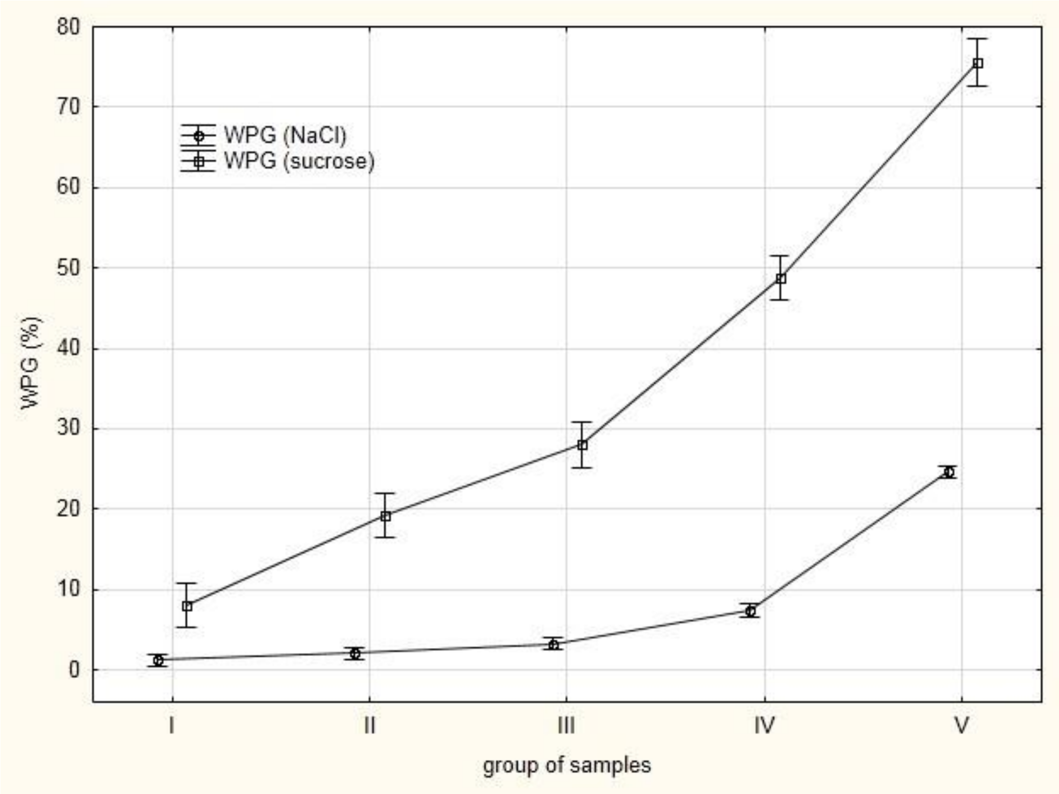

Figure IV. 1 Weight percentage gain dependence on the concentration of the impregnation solution by group

Table IV. 3 Average retention of NaCl and sucrose

Group	Retention (kg/m^3)
NaCl I	4,7
NaCl II	8
NaCl III	14
NaCl IV	27
NaCl V	72
Sucrose I	31
Sucrose II	63
Sucrose III	100
Sucrose IV	160
Sucrose V	258

Požgaj et al. (1997) states the density ρ_0 of poplar wood to be 390 kg·m^{-3}. The mean density (ρ_0) of reference (non-impregnated) specimens was 390 kg·m^{-3}. In dependence on the WPG the density of the specimens of *Populus alba* L. grew up to 676 kg·m^{-3} in the sucrose impregnated specimens and up to 510 kg·m^{-3} in the NaCl impregnated specimens.

The differences in density of specimens before and after modification (Fig. 2) showed that the NaCl impregnation in group I (1 g / 100 ml) caused a slight decrease in the density, which can be explained by larger swelling of wood and the slight increase in weight after modification with a very small concentration of NaCl in the impregnation solution. Starting from group II the density increased based on the concentration of NaCl in the impregnation solution. Group V reached an average density increase of 63 kg·m^{-3}, which means increase of 17 % compared to density before modification. Regarding sucrose impregnation (Fig. 2), the density of the group I increased as well (6.25 g / 100 ml). Group V reached an average density increase of 244 kg·m^{-3}, which means increase of 64 % compared to density before modification.

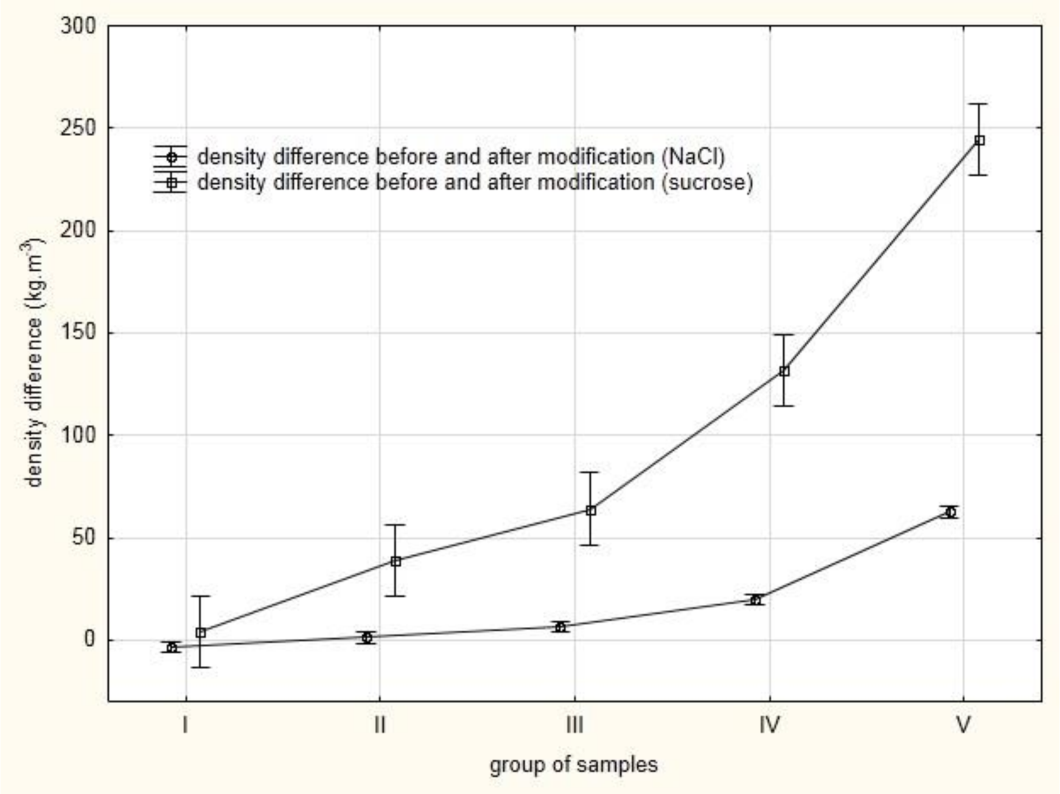

Figure IV. 2 Anova – dependence of density differences before and after modification on the concentration of the impregnation solution by group

Another indicator was swelling caused by the wood modification. Longitudinal swelling (α_L) due to modification follows the same rules as swelling due to moisture absorption. The average values in the longitudinal direction of group V are 0.6 % (NaCl) and 1.65 % (sucrose). The average values of swelling (αs) in the transverse directions due to modification did not differ much in groups I–IV – they ranged around 1.8 % (NaCl) and 3.6 % (sucrose). Group V (sucrose) also exhibited similar average values. Group V (NaCl) exhibited almost three times higher values – the average value of swelling was 5.2 %. The swelling of samples due to modification confirms the hypothesis that the wood expanded by the NaCl and the sucrose crystallization. This is consistent with that NaCl and sucrose were able to penetrate into cell walls, where they crystallized after drying. Further, we confirmed the influence of swelling due to modification on weight gain using linear regression model (Fig. 3 and 4). The dependence of swelling due to modification on WPG is higher for NaCl impregnation than for sucrose impregnation.

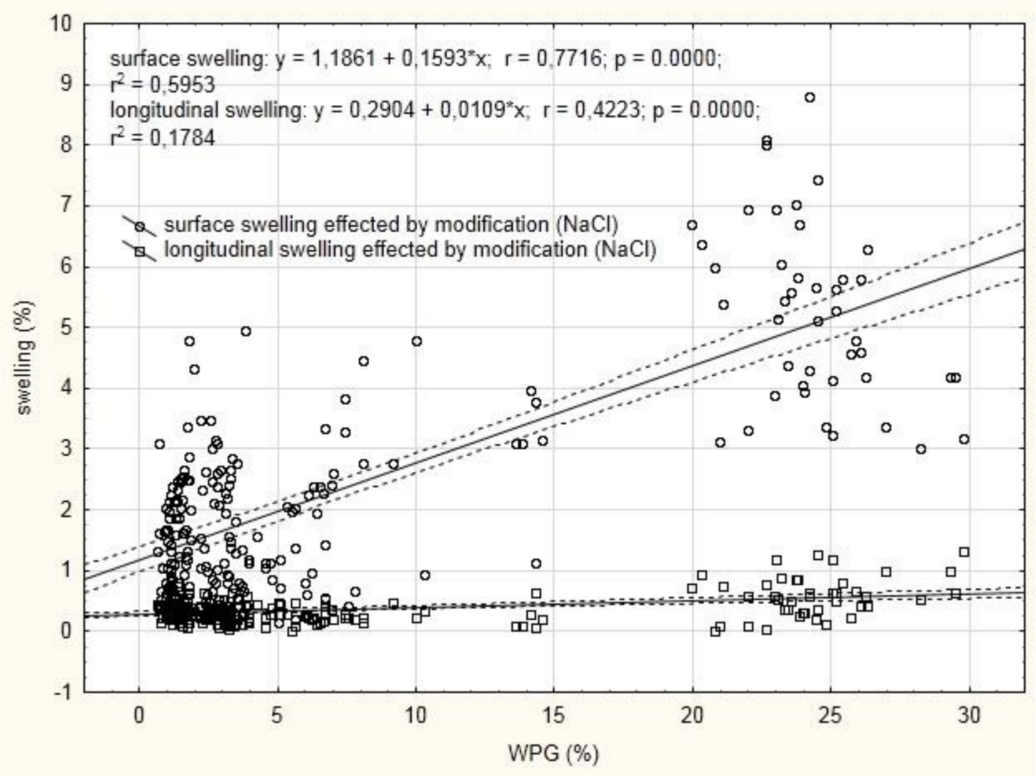

Figure IV. 3 Model of linear regression – dependence of swelling due to modification on WPG (NaCl)

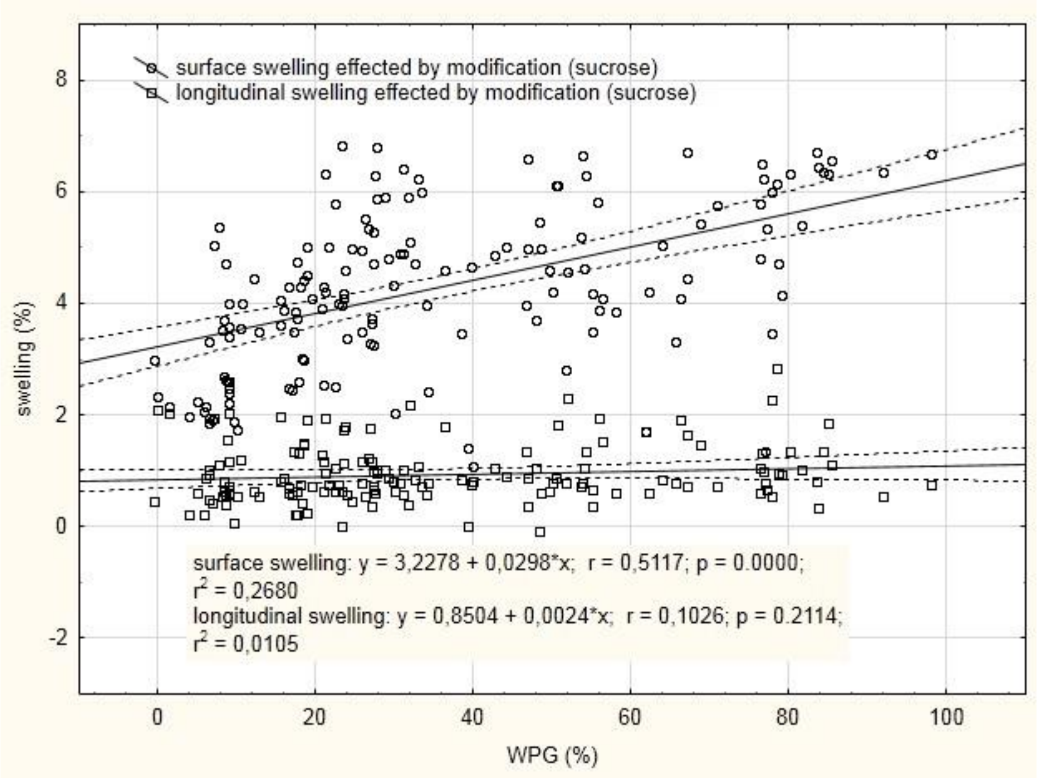

Figure IV. 4 Model of linear regression – dependence of swelling due to modification on WPG (sucrose)

Moisture absorption experiments

Swelling due to moisture absorption is the main investigated property of this research. In this case, the average values of volume swelling (S_n) were the highest in the reference group: 12.7 % (see fig. 6). Groups I (NaCl) and I (sucrose) exhibited average values of volume swelling (S_m) of 11.4 % and 8.1 %, respectively. Volume swelling in groups V (NaCl) and V (sucrose) was 9.6 % and 7.7 %, respectively. We found statistically significant differences when these groups (I and V) were compared with the reference group (VI). Impregnation by NaCl and sucrose manifested a positive effect on the dimensional stability of wood; the effect was higher in sucrose. It is probably caused by the preceding wood swelling caused by modification (NaCl and sucrose crystals in the cell wall) – moisture absorption does not increase the dimensions as much as it would in unmodified wood. The dimensional stability increases due to modification by these substances. Group I and V (sucrose) showed the best indicator ASE, 36 % (group I) and 39 % (group V). Group V showed the best result of ASE in case of NaCl (24 %).

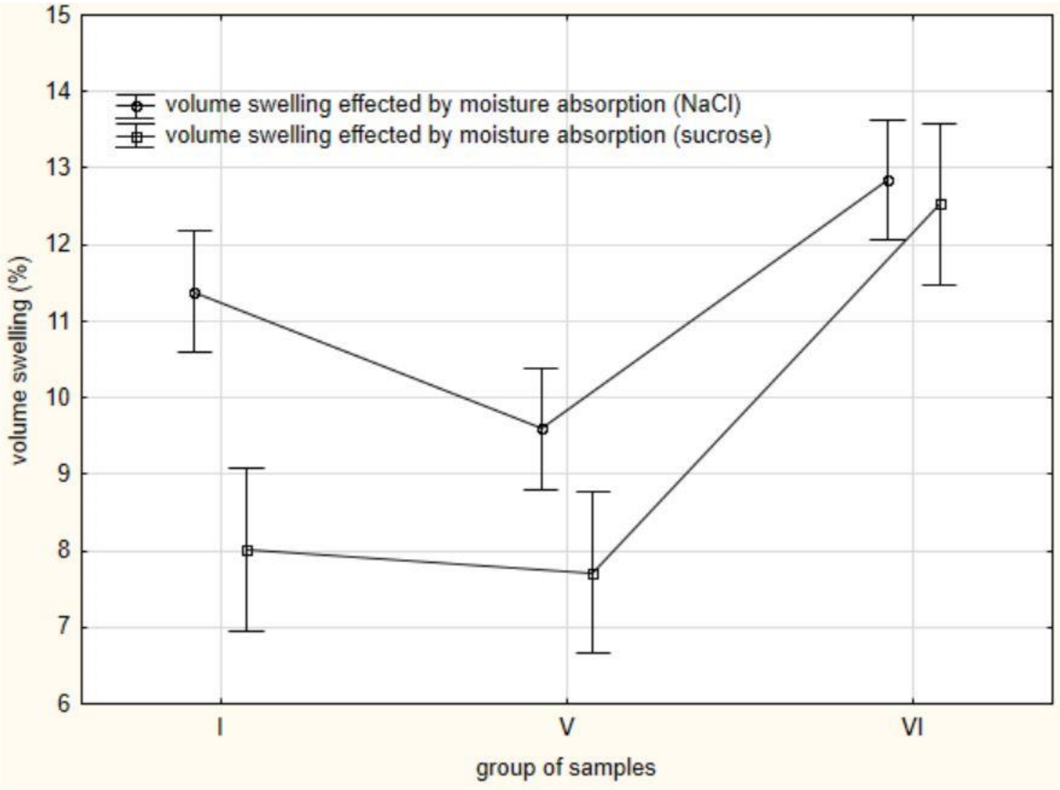

Figure IV. 5 Anova – dependence of volume swelling due to moisture absorption on the concentration of the impregnation solution by group

Another examined parameter was the average equilibrium moisture content ($\mathrm{EMC_n}$) was about 30 % in the reference group (Fig. 5). According to Siau (1995) the fibre saturation point is about 30 %; this means the maximum saturation of cell walls was achieved (wood contained the maximum amount of bound water). Group I (NaCl) reached an average $\mathrm{EMC_m}$ of 31.4 %, but no statistically significant differences were proved when compared with the reference group. On the other hand, in group I (sucrose) the average $\mathrm{EMC_m}$ was 35.7 % and statistically significant differences were found. The EMC in group V (NaCl) increased considerably – the average value was 66 %. The $\mathrm{EMC_m}$ in group V (sucrose) increased to 45 %. The $\mathrm{EMC_m}$ increases with an increasing NaCl concentration in the impregnation solution, as has also been confirmed by Lesar et al. (2009). These values in group V (NaCl) were achieved with an average WPG of about 22 %, while the value of EMC within sucrose impregnation was only 45 % with WPG of 70 %, which is three times more than in NaCl impregnation. With a relatively low content of NaCl in wood its hygroscopicity is considerably increased in contrast to sucrose impregnation. The model of linear regression (Fig. 7 and 8) shows that there is a statistically significant dependence between $\mathrm{EMC_m}$ and WPG: the higher WPG, the higher $\mathrm{EMC_m}$. This means that the more NaCl and sucrose there is in wood, the more the wood will absorb moisture, which affects the resulting $\mathrm{EMC_m}$. The MEE (moisture exclusion efficiency) indicator gained negative values. The average value of group I (NaCl) was 4.6 %, group V (NaCl) — 120 %, group I (sucrose) – 33 % and group V (sucrose) – 61 %. According to Morgós (2003), natural sucrose is highly hygroscopic at relative air humidity $\varphi > 85$ %. At lower ambient humidity sucrose manifests the opposite – it decreases wood hygroscopicity.

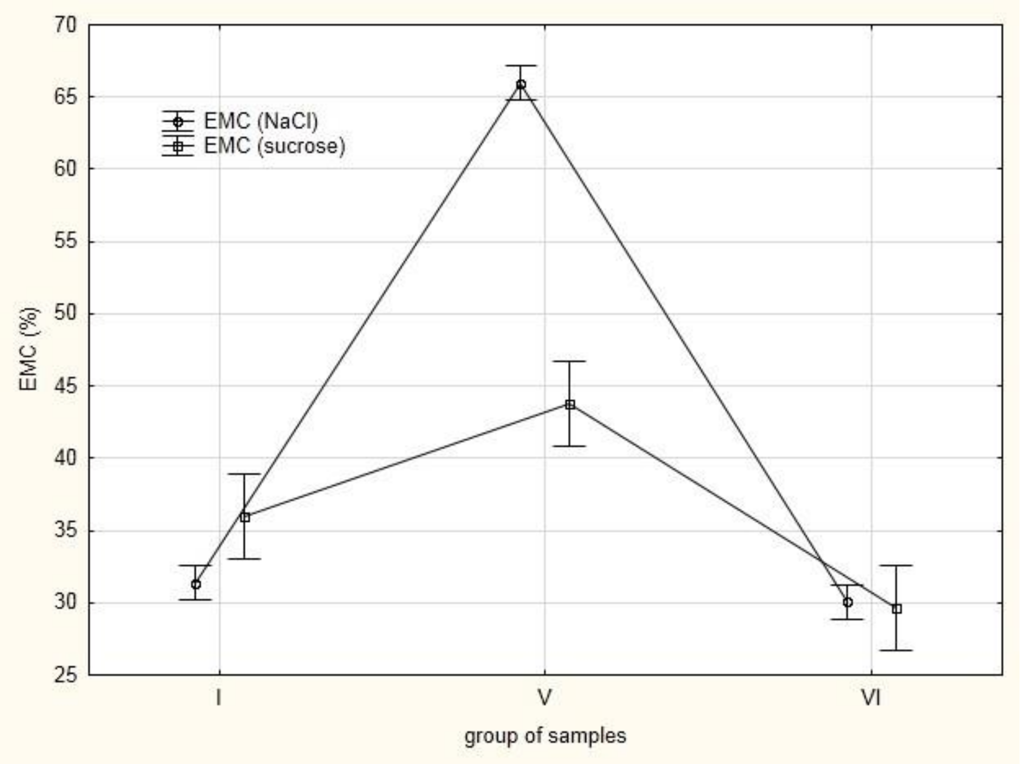

Figure IV. 6 Anova – EMC dependence on the concentration of the impregnation solution by group

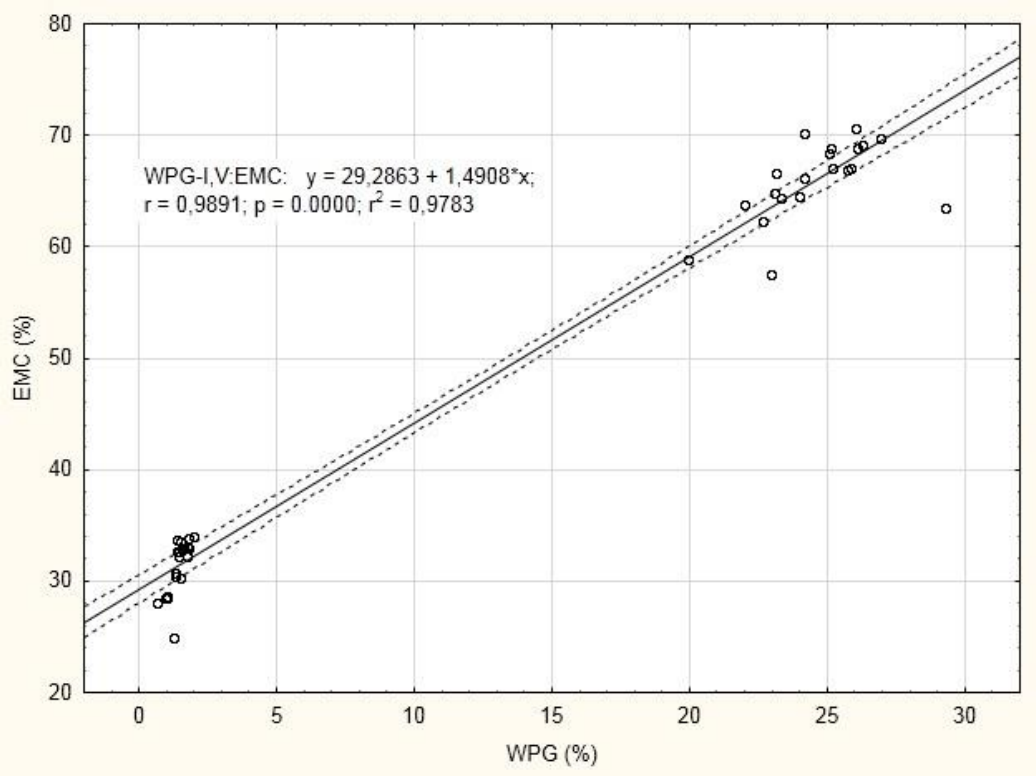

Figure IV. 7 Model of linear regression - EMC dependence on WPG (NaCl)

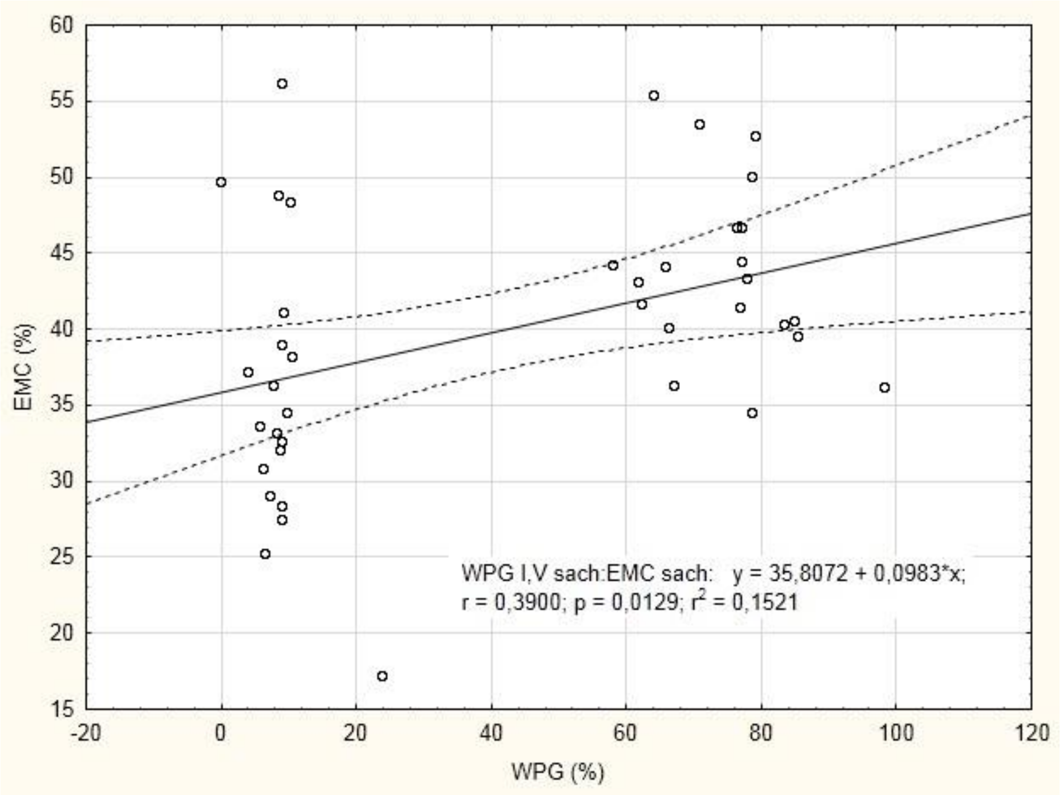

Figure IV. 8 Model of linear regression - EMC dependence on WPG (sucrose)

Group V (NaCl) exhibited enhanced properties of ASE but with the rapid increase in EMC, which is negative effect. Group I and V (sucrose) showed the best improvement of dimensional stability but group V provided little additional benefit while greatly increasing EMC_m. Higher EMC could cause increases susceptibility to mould and wood-decaying fungi. Impregnation with the lowest concentration of sucrose (group I) offers the best combination of reduction in swelling and relatively small increases in EMC and WPG.

CONCLUSIONS

Sucrose and NaCl impregnation are environment-friendly methods for wood modification using natural degradable substances. Poplar wood has a homogeneous structure and is fast-growing; its sapwood can be easily impregnated. The experimental measuring proves that crystallized sucrose and NaCl contained within wood can considerably affect its physical properties. The WPG increases with an increasing concentration of NaCl and sucrose in the impregnation solution and influences other wood properties. Tests also confirmed wood swelling due to modification. This evidences that NaCl and sucrose reached the cell walls where they crystallized after drying. Due to this wood swelled and its weight increased. Density increased in dependence on the concentration of the solution. Moisture absorption tests confirmed a high hygroscopicity of modified samples; the highest hygroscopicity was found in the highest concentration of NaCl. EMC of NaCl impregnation increased by 120 % on average in comparison with the reference group. Swelling caused by moisture absorption was lower in modified groups than in the reference groups, for both of the used substances. Modification reduced volume swelling caused by moisture absorption and thus we can state that it has a positive effect on the dimensional stability of wood. This is caused by wood swelling brought about by the modification itself. The lowest concentration of sucrose showed the best results from the perspective of improved dimensional stability and small increases in equilibrium moisture content.

Usage of the modified materials outdoors or in conditions of increased humidity cannot be recommended except small concentrations of sucrose when there is not such a large increase in EMC and adding some biocide compounds. Although there is still problem with potential leaching from wood. They are more suitable for interiors, e.g. for furniture, panelling and floors. Further research could ascertain how the modified wood would behave in lower relative air humidity. For this EMC in different ambient conditions could be ascertained, concentrations of NaCl and sucrose in the impregnation mixture could be increased and impregnation could be explored in combination of vacuum pressure and overpressure. It is also possible to combine impregnation with other ways of modification (e.g. thermal). Another topic for research could be the examination into the resistance to wood-destroying fungi and insects. Also an exploration should be conducted into fasteners regarding their potential corrosion.

PAPER V.

APPLICATION OF MICROWAVE HEATING FOR ACETYLATION OF BEECH (*FAGUS SYLVATICA* L.) AND POPLAR (*POPULUS HYBRIDS*) WOOD

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Application of Microwave Heating for Acetylation of Beech (*Fagus sylvatica* L.) and Poplar (*Populus hybrids*) Wood

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ABSTRACT

MW and conventional acetylation of wood was carried out to determine its efficacy on the material properties. Beech (*Fagus sylvatica* L.) and poplar (*Populus hybrids*) samples with dimensions 14 mm × 14 mm × 14 mm were impregnated using acetic anhydride, and chemical reactions were initiated by MW and conventional heating. The MW acetylation process was carried out using laboratory device at a frequency of 2.45 GHz in several testing modes to reduce time of the reaction. The uptake of substance, EMC, wood swelling, and dimensional stability were determined in order to evaluate the efficacy and degree of acetylation. Both MW and conventional heating positively affected the selected material properties. The results showed that no significant differences were found between MW and conventional heating; therefore, MW heating can be used as a valid replacement in the acetylation process. MW power of 2 kW and 0.1 $m \cdot min^{-1}$ conveyor speed were the optimum conditions for MW acetylation. These process parameters resulted in 39.4% ASE_T and 35.2% ASE_R for beech and 38.0% ASE_T and 16.3% ASE_R for poplar samples. This work provides insight into the details of wood acetylation using MW heating.

Key words: acetic anhydride; chemical reactions; dimensional stability; wood impregnation; microwave treatment; wood modification

INTRODUCTION

Wood, as an important renewable resource, has a broad range of material properties for various applications, *e.g.*, relatively high strength and stiffness, low specific weight, natural appearance with interesting texture, insulation properties, and machinability

(Kollmann 1951; Stamm 1964; Wagenführ 2000; Skodras *et al.* 2004). However, natural wood also has undesirable properties that might limit the range of feasible applications. Wood is a natural heterogeneous composite and is considered to be dimensionally unstable when exposed to wet conditions (Kumar 1957; Rowell 1983; Skaar 1988; Hunter 1995). Hydroxyl (-OH) groups of hemicellulose and cellulose chains are mainly responsible for the highly hygroscopic behaviour of wood (Stamm 1964; Rowell 1983). The dimensional instability of wood under different moisture/humidity conditions is considered a major drawback of wood performance (Stamm 1964; Hill and Jones 1996; Homan and Jorissen 2004; Popescu *et al.* 2013).

Wood modification techniques can be applied in order to improve certain wood properties, *e.g.*, bio-durability, dimensional stability, colour, wettability, etc. (Hill and Jones 1996; Militz 2002; Rowell 2005; Hill 2006; Čermák *et al.* 2015). Chemical modification can, for instance, be used as an efficient way to transform hydrophilic OH groups into larger hydrophobic groups (Kollmann 1951; Rowell 1983; Skaar 1988; Bodîrlău *et al.* 2009). Little to no water can penetrate the permanently swollen cell wall of wood as a result of chemical treatment (Homan and Jorissen 2004).

Acetylation of wood is one of the most commonly used chemical treatments to improve the dimensional stability and biological durability of wood (Tarkow *et al.* 1950; Larsson and Simonson 1994; Popescu *et al.* 2013). Moreover, this treatment retains to wood its original colour and improves acoustical, dielectric, and strength properties (Tarkow *et al.* 1950; Dreher *et al.* 1964, Homan *et al.* 2000).

Acetylation effectively changes free hydroxyls within the wood into acetyl groups (Rowell 1983; Hill and Jones 1996; Rowell 2013). This is done by reacting wood with acetic anhydride (Ac_2O) (Militz 1991; Sander *et al.* 2003). The standard acetylation process includes impregnation of oven-dried wood with Ac_2O, followed by conventional heating to initiate the chemical reactions with wood polymers (Bongers and Beckers 2003). Acetic acid is then released as a by-product of the reactions (Homan and Jorissen 2004). Application of the Ac_2O without a catalyst or cosolvent is the preferred method for wood acetylation (Rowell 2013). Time consumption is an important issue for the proposed acetylation method (Yang *et al.* 2014).

In order to reduce the reaction time and make the process more effective, an innovative wood acetylation process that uses MW energy has been recently studied

(Larsson *et al.* 1999; Larsson and Simonson 1999; Larsson 2002; Li *et al.* 2009; Diop *et al.* 2011; Yang *et al.* 2014). The application of MW energy rapidly heats the material throughout the whole cross-section using the dielectric properties of wood (Torgovnikov 1993; Larsson *et al.* 1999) instead of commonly used convection and conduction heat flux (Koskiniemi *et al.* 2013). The principle behind MW heating is based on the polar characteristic of molecules and their ability to absorb and transform MW radiation into heat (Metaxas and Meredith 1983; Torgovnikov 1993; Hansson and Antti 2003). Permanent dipoles of molecules begin to move with the same frequency as the electromagnetic field. Therefore, rapid changes in the field polarity cause vibration and rotation of molecules, which transforms the MW energy into frictional heat (Makovíny 2000; Hansson and Antti 2003; Dömény *et al.* 2014a). The polarizability of the Ac_2O in the MW field has been extensively studied (Baghurst and Mingos 1992; Larsson *et al.* 1999). Baghurst and Mingos (1992) stated that during MW heating, the temperature rise of the Ac_2O was about two times higher than water.

Unfortunately, published studies related to the acetylation process conducted using MW heating are still limited. Therefore, the present study aims to (1) analyse the acetylation process using MW heating, (2) evaluate the efficacy of MW heating on the chemical reactions during the process and its similarities with conventional methods, and (3) evaluate material properties (uptake of substances, equilibrium moisture content, wood swelling, and anti-swelling efficiency). This work should provide a better insight into details of the wood acetylation.

EXPERIMENTAL

Materials

Beech (*Fagus sylvatica* L.) and poplar (*Populus hybrids*) sapwood were studied. Samples with dimensions 14 mm × 14 mm × 14 mm were oven dried to 0% MC, according to EN 13183-1 (2002). The average oven-dry density (ρ_0) of testing samples was 694 $kg \cdot m^{-3}$ for beech and 316 $kg \cdot m^{-3}$ for poplar. Afterward, samples were sorted into groups of 10 for each species and acetylation treatment (Table 1).

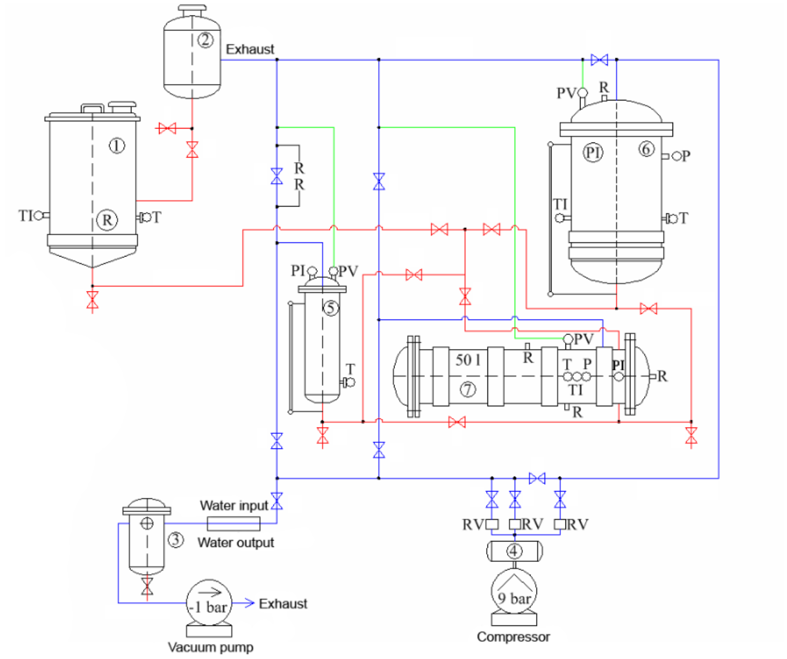
Table V. 1 List of treatments and process parameters

Material	No. of samples	Treatment	Mode	Speed of conveyor	Time
Beech/Poplar	10/10	Control	-	-	-
Beech/Poplar	10/10	MW I	1.5 kW	0.1 m·min^{-1}	15 min
Beech/Poplar	10/10	MW II	2.0 kW	0.1 m·min^{-1}	15 min
Beech/Poplar	10/10	MW III	2.0 kW	0.025 m·min^{-1}	60 min
Beech/Poplar	10/10	Conventional heat	100 °C	-	60 min

Methods

Acetylation process

Prior to treatment, samples were pressure impregnated with Ac_2O (Sigma-Aldrich, analytical grade ≥ 99%) in a laboratory plant JHP1-0072 (Figure 1).



Description:

1. Storage tank
2. Exhaust collector
3. Collector
4. Air eliminator
5. Sampling tank
6. Preheater
7. Impregnation tank

PV - Pressure regulator
TI - Thermal sensor
T - Thermometer
PI - Pressure sensor
P - Manometer
R - Reserve
RV - Control valve

Figure V. 1 Scheme of vacuum-pressure impregnation equipment (Dejmal *et al.* 2012)

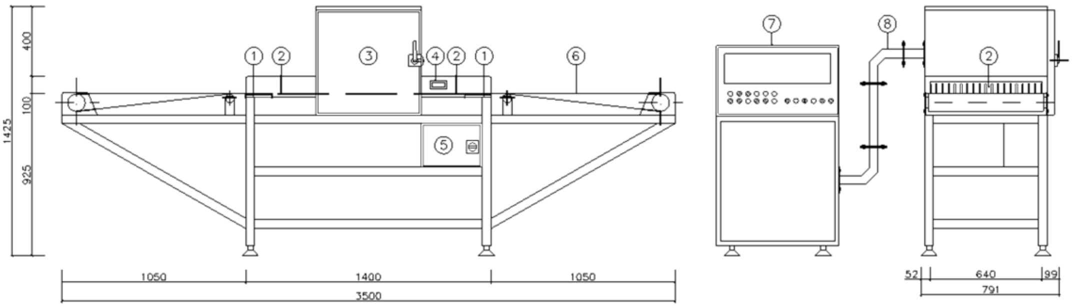
Wood species were impregnated separately using same process parameters, *i.e.* 0.8 MPa pressure for 120 min at 20 °C. Weight percentage gain (WPG) and retention (R) values were used as an indicator of substance uptake according to the following equations:

$$WPG\ (\%) = (m_2 - m_1)/\ m_1 \tag{8}$$

$$R\ (kg{\cdot}m^{-3}) = (m_2 - m_1)/V \tag{9}$$

where: m_1 is the sample weight before impregnation, m_2 is the sample weight after impregnation, and V is volume of the sample.

Afterward, MW and conventional heating were used to induce chemical reactions taking place during the acetylation process (Table 1). A continuous laboratory MW device (Figure 2) that operates at a frequency of 2.45 GHz with adjustable power from 0.6 to 5 kW was used for the MW heating. Conventional heating was carried out in a standard laboratory drying oven (Sanyo MOV 112).



Description: 1. Duced ceramics 2. Flexible copper plate 3. Modification chamber 4. Speed control panel 5. Power button 6. Conveyor 7. Microwave generator with control panel 8. Waveguide

Figure V. 2 Scheme of continuous MW device

Once chemical reactions took place, the testing samples were placed into the impregnation plant in vacuum at 10 kPa for 60 min to eliminate the residual acetic anhydride and acetic acid from wood structure.

Uptake of the substance was determined in two steps: after the impregnation of testing samples and after the chemical reaction when residuals were eliminated.

Surface temperature

The surface temperature of the testing samples was measured by a contactless infrared thermometer (Voltcraft IR-380, accuracy ±1.0 °C) during a short interruption of the chemical reactions (turning off the power and opening the modification chamber for a few seconds) for both methods of heating. Measurement was done in the middle of the reaction time.

Equilibrium moisture content and Dimensional stability

The samples were conditioned in a climate chamber (Sanyo MTH 2400) at different relative humidities (30%, 65%, and 99%) at 20 °C until the EMC was reached for certain conditions. Afterward, the MC was determined using the oven-dry method according to EN 13183-1 (2002).

Dimensional stability in radial and tangential directions was determined by estimating wood swelling ($S_{T,R}$) and anti-swelling efficiency ($ASE_{T,R}$). The swelling was calculated in dry and equilibrium states at the RH under study. ASE represents difference between the swelling of the treated and untreated wood. $S_{T,R}$ and $ASE_{T,R}$ were calculated according to the following equations:

$$S_{T,R}\ (\%) = 100\ (D_{T,R,2} - D_{T,R,1})/\ D_{T,R,1} \qquad (10)$$

$$ASE_{T,R}\ (\%) = 100\ (S_{T,R,u} - S_{T,R,t})/S_{T,R,u} \qquad (11)$$

where $D_{T,R,1}$ (mm) is the radial or tangential dimension of the oven-dried sample, $D_{T,R,2}$ (mm) is the radial or tangential dimension of the conditioned sample, and $S_{T,R,u}$ (%) and $S_{T,R,t}$ (%) are wood swelling of the untreated and treated sample, respectively.

Statistical analysis

The data were processed in STATISTICA 10 software (StatSoft Inc., USA) and evaluated using a one-factor analysis of variance (ANOVA), completed with Tukey's honest significance test (HSD test).

RESULTS AND DISCUSSION

Uptake of Substance

Average WPG and retention values are shown in Table 2. The amount of Ac_2O impregnated within the wood structure was identical for all testing groups (MW I, MW II, MW III, and conventional heating) after the impregnation process within the same wood species group. The results showed significant differences between the WPG of beech (66%) and poplar (211%), even though the impregnation process parameters were the same. The major differences can be explained by different densities of wood species, which is reflected in calculating of WPG (Eq. 25). In fact it was caused also by the structural and chemical composition of the different wood species. For practical applications, it is rather important to know the amount of the impregnated substance expressed by weight in the wood volume. Therefore, retention was used as a second indicator of the substance uptake.

Based on the Tukey's HSD test, statistically insignificant WPG and retention were found between conventional heating, MW I, and MW III treatments for beech and conventional heating, MW II, and MW III treatments for poplar. All other acetylation treatments were statistically significant in terms of substance uptake (Table 2). After the chemical reaction, the WPG decreased by ~57% for beech and ~202% for poplar. This shows that a relatively high uptake of substance was reached but a small amount of the Ac_2O reacted within and remained in the wood structure. This can also be seen from the retention results. After the chemical reaction, the retention decreased from 656.2 $kg \cdot m^{-3}$ to ~30 $kg \cdot m^{-3}$ for poplar and from 452.7 $kg \cdot m^{-3}$ to ~65 $kg \cdot m^{-3}$ for beech. Values of beech retention (after the reaction) were two times higher than poplar. However, this does not mean that the efficacy of acetylation was also higher because of the higher retention. The efficacy depends on the degree of substitution and the amount of free hydroxyl groups, which is associated with wood density. Therefore, WPG is an appropriate indicator of the substance uptake and the acetylation process efficacy. Some authors have evaluated the effectiveness of acetylation by acetyl content using HPLC analysis (Larsson and Simonson 1999) or by degree of substitution determined by a back-titration method (Li *et al.* 2009). However, WPG is a well-known indicator used in most studies dealing with wood acetylation. In the present study, WPG values of the acetylated beech and poplar samples were similar for all treatment modes, on average ~9%. Eranna and Pandey (2012) published data of the substance uptake for rubberwood (*Hevea brasiliensis*) conventionally treated at a temperature of 120 °C, after 15 min, 30 min, 60 min, and 120 min and reported that the WPG reached ~7%, ~8%, ~9%, and ~12%, respectively. Yang *et al.* (2014) compared the different types of acetylation reactions: liquid, MW, and vapour phase after 60 min of reaction time. Sugi wood (*Cryptomeria japonica*) acetylated using a MW reaction exhibited the highest WPG (19.4%), followed by the liquid phase reaction (19.1%), and vapour phase reaction (18.0%). Li *et al.* (2009) acetylated cellulose by MW heating with iodine as a catalyst. Results of the WPG after 15 min of the treatment at temperatures of 80 °C, 100 °C, and 130 °C were 13%, 16%, and 25%, respectively (Li *et al.* 2009). Pries *et al.* (2013) conventionally acetylated beech for a fungal decay test by Ac_2O at 120 °C for 120 min and observed 10.2% WPG. Results of the substance uptake (WPG, R) were difficult to compare with previously published data because of different wood species and process parameters used.

Table V. 2 Results of substance uptake (weight percentage gain and retention)

Uptake of substance	**Treatment**	**WPG (%)**		**Retention (kg·m^{-3})**	
		Beech	Poplar	Beech	Poplar
After impregnation	-	66.0 (3.8) ^{A}	211.3 (12.0) ^{A}	452.7 (23.2) ^{A}	656.2 (17.2) ^{A}
After chemical reaction	MW I	9.3 (1.1) ^{B}	7.7 (1.8) ^{B}	65.4 (6.4) ^{B}	24.2 (5.4) ^{B}
	MW II	10.2 (0.5) ^{C}	9.6 (0.8) ^{C}	70.0 (3.3) ^{C}	30.3 (2.3) ^{C}
	MW III	8.8 (0.8) ^{B}	9.3 (1.4) ^{C}	61.4 (5.5) ^{B}	30.1 (6.1) ^{C}
	Conventional Heat	9.5 (0.8) ^{B}	9.6 (1.3) ^{C}	64.7 (4.9) ^{B}	30.1 (4.1) ^{C}

Means sharing same letter in column are not significantly different (Tukey's HSD, $p < 0.05$)
Numbers in parentheses indicate standard deviation

Temperature

A maximum surface temperature was observed when MW treatment at 2 kW with 0.025 m·min^{-1} conveyor speed (mode MW III) was used, as well as conventional heating. The surface temperature increased from 20 °C to 103 °C and 100 °C, respectively. Moreover, when milder MW heating modes were used, the surface temperature increased from 20 °C to 83 °C (MW II) and 69 °C (MW I). The results showed that the MW power and conveyor speed had a substantial effect on the sample temperature, influenced by various radiation intensities converted directly to thermal energy by frictional heating.

Equilibrium Moisture Content

By converting the hydroxyl groups of cell wall polymers into hydrophobic acetyl groups, the hygroscopicity of the wood was reduced. Values of the EMC at different relative humidities are presented in Figure 3. Significant differences were found between the control, MW, and conventionally heated samples at all RH levels (30%, 65%, and 99%). However, insignificant differences were found between various modes of MW treatment. In the case of poplar, there were insignificant differences between MW II and MW III treatments. Similar results were recorded for beech in 99% RH. In that respect, 60 min (MW II) and 15 min (MW III) treatments had identical results for EMC.

Yang *et al.* (2014) reported that the acetylation efficacy increased with reaction time. Such a statement was not confirmed in the present study. From the results, it can be concluded that the MW treatment provided the same degree of acetylation independent of the duration of the reaction in the range of 15 to 60 min. However, it should be considered that only two time modes (conveyor speeds) were used in the experiment and deeper investigation is needed to confirm this statement. Larsson *et al.* (1999) studied the MW acetylation of pine and stated that the microwave-heated wood gives a higher degree of acetylation during the initial phase of the reaction compared to the conventional method. With a prolonged reaction time, the degree of acetylation was about the same, because only thermal effects are included when MW heating is applied to wood acetylation (Larsson *et al.* 1999).

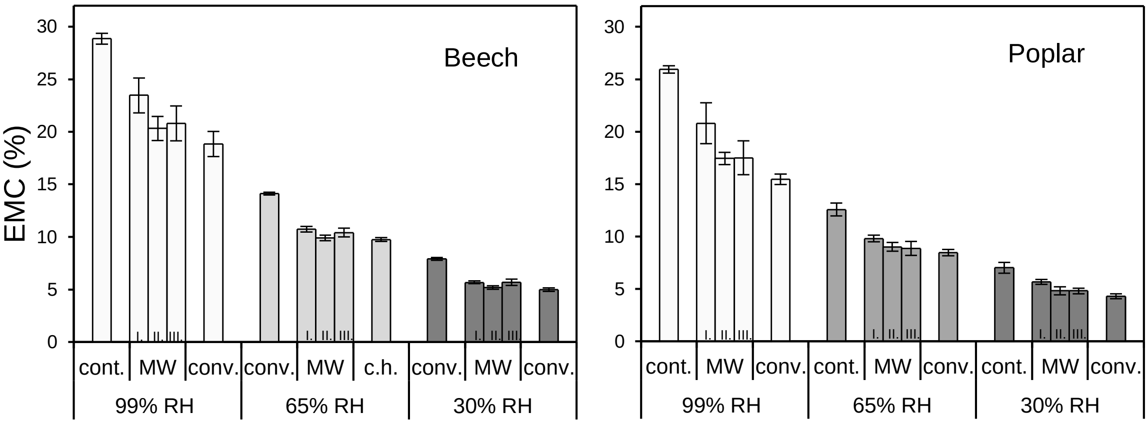


Figure V. 3 EMC of beech and poplar under different RH; Roman numerals indicate MW modes (MW I–III)

Using conventional heating for 60 min, the EMC of beech samples in 99% RH decreased by 35% when compared to the control. By using 2 kW MW heating for 15 and 60 min (MW II and MW III), the EMC decreased by ~29%. Similar results were found for poplar samples. The EMC of conventionally heated poplar decreased by ~40% and by about 32% for MW heating samples (MW II, MW III). The MW I mode provided a lower degree of acetylation even though a longer period (60 min) of heating was used. This was probably caused by a low increase of temperature during the acetylation process. EMC values at 65% and 30% RH showed a similar trend as 99% RH (Figure 3). The degree of acetylation increased with an increase in the MW power; therefore, it can be stated that MW power has a significant effect on wood acetylation.

Dimensional Stability

The radial and tangential swelling of wood (S_R and S_T) at different RH levels are presented in Figure 4. Results at 99% RH were used for the ASE, indicating the effectiveness of treatments on the dimensional stability (Figure 5).

The control samples had a higher radial and tangential swelling than acetylated samples. Since acetyl groups occupy space within the cell wall, the wood is not able to absorb water molecules and therefore wood swelling is reduced (Tarkow *et al.* 1950; Rowell 1983). When conventional and MW acetylation are compared, only very minor differences in the wood swelling can be found. Moreover, statistically insignificant differences were found between 60 min (conventional, MW III) and 15 min treatments. Heating by MW can accelerate chemical reactions in the acetylation process, whereby the same dimensional stability is reached. Therefore, the reaction time of acetylation can be reduced and the process made more effective.

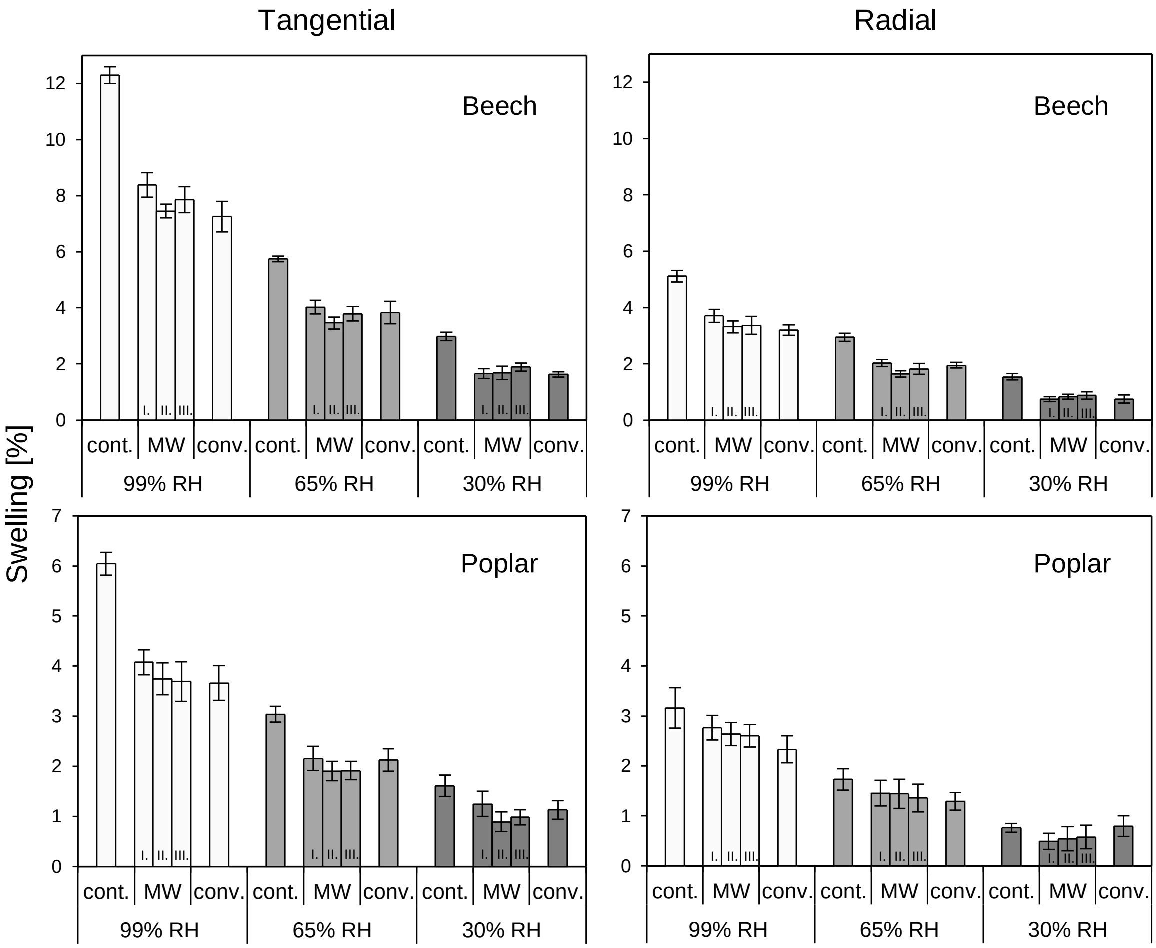


Figure V. 4 Swelling of beech and poplar in the tangential and radial directions

Anti-swelling efficiency is the most commonly used method to evaluate the dimensional stability of the modified wood (Santos 2000; Čermák *et al.* 2015). The dimensional stability was considerably improved for all applied acetylation treatment modes. The ASE of the acetylated beech in modes MW I, MW II, MW III, and conventional heating were 31.8%, 39.4%, 36.1%, and 41.0% in the tangential and 27.7%, 35.2%, 34.3%, and 37.6% in the radial direction, respectively. Similar values of ASE $_T$ and lower values of ASE $_R$ were found for poplar samples, *i.e.* 35.8%, 38.0%, 38.9%, and 39.4% in the tangential and 12.4%, 16.3%, 17.0%, and 26.1% in the radial direction, respectively.

Unfortunately, it was difficult to compare the ASE data of the acetylated wood, because no study dealing with the same wood species was found. Nevertheless, the data are comparable with previous studies published by Hill and Jones (1996) and Rowell *et al.* (2008). Hill and Jones (1996) stated that after the acetylation of Corsican pine (*Pinus nigra*), ASE reached 35% at 10% WPG. Similar results were found by Rowell *et al.* (2008), who reported 34% ASE (at 10% WPG) for southern pine (*Pinus taeda*).

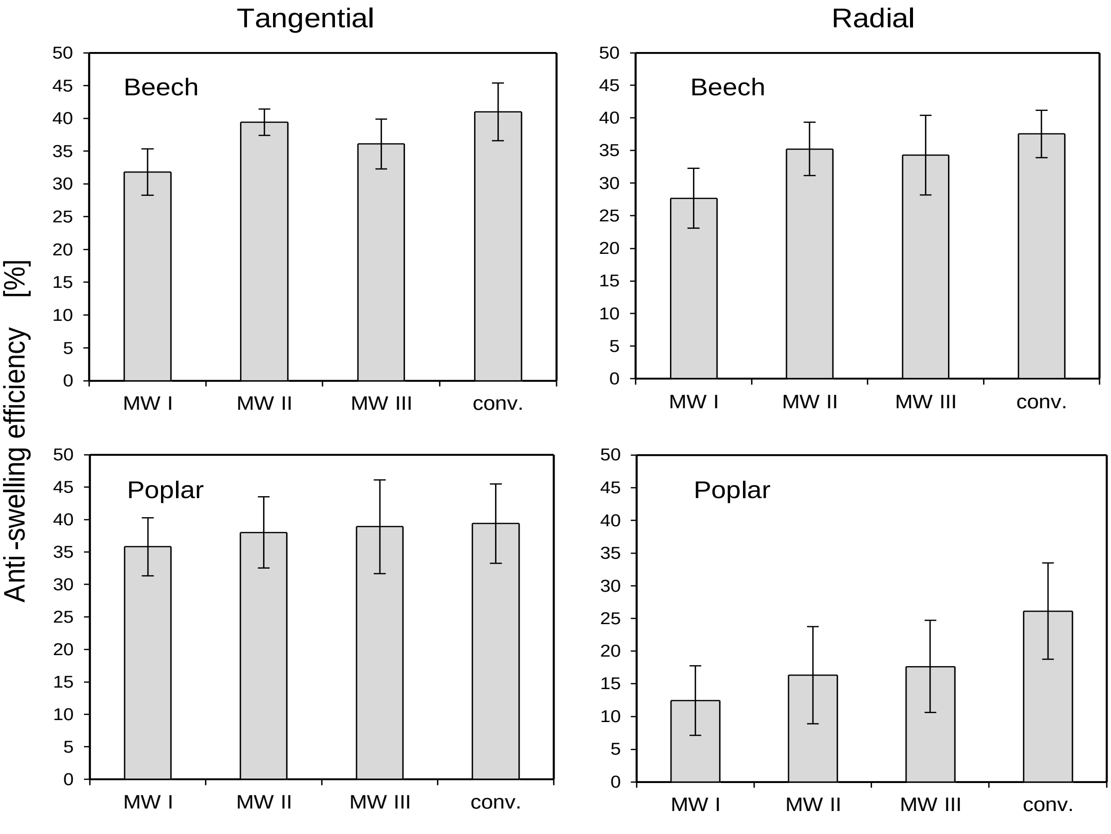


Figure V. 5 ASE of beech and poplar in tangential and radial directions in 99% relative humidity

It is well known that wood is an anisotropic material with different dimensional changes in different anatomical directions (Kollmann 1951; Boutelje 1962; Stamm 1964; Skaar 1988). According to Niemz *et al.* (1993), swelling in the tangential and radial directions can be expressed by a 2:1 (S_T:S_R) ratio. The tangential and radial swelling ratios ($S_{T,99\%}$:$S_{R,\,99\%}$) for control, MW, and conventional heating were 2.4:1, 2.3:1, and 2.3:1 for beech and 1.9:1, 1.4:1, and 1.6:1 for poplar. From the results, it can be concluded that acetylated beech samples provided negligible swelling ratio improvement. However, poplar samples showed much more significant swelling ratio improvement (S_T:S_R). This improvement is attributed to the lower ASE of poplar in the radial direction (Figure 5) compared to the tangential direction. The acetylated wood (species-dependent) can be therefore considered more homogenous, but anisotropy of swelling remains.

CONCLUSIONS

1. The acetylation of samples using different treatment modes (MW I, MW II, MW III, and conventional heating) provided similar WPG values after chemical reactions (~9%). Retention, expressed by weight in the wood volume, has been suggested as a better indicator of substance uptake. Beech wood had approximately two times higher substance retention compared to poplar, due to its structural and chemical composition.

2. The MW and conventional acetylation positively affected EMC, wood swelling, and consequently the dimensional stability. The improvement in the investigated properties was nearly identical in both types of treatment. Therefore, the efficacy of the acetylation process carried out using MW or conventional heating is comparable.

3. The rate of acetylation increased with an increase of MW power. However, the treatment time (15 and 60 min) did not affect the degree of acetylation. These results were confirmed for all RH levels (30%, 65%, and 99%).

4. The optimum mode of MW acetylation was found at the MW power of 2 kW using 0.1 m·min^{-1} conveyor speed (15 min). This mode resulted in 39.4% ASE_T and 35.2% ASE_R for beech and 38.0% ASE_T and 16.3% ASE_R for poplar samples.

5. MW heating was found to be an efficient rapid acetylation process (15 min, 0.1 m·min^{-1}). However, more detailed investigation of the time-dependency of MW heating should be done in the future.

PAPER VI.

IMPACT OF EXTRACTIVE CHEMICAL COMPOUNDS FROM DURABLE WOOD SPECIES ON FUNGAL DECAY AFTER IMPREGNATION OF NONDURABLE WOOD SPECIES

Sablík, P., Kyriaki G., Pařil, P., Baar, J., Rademacher, P. (2015)

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Impact of extractive chemical compounds from durable wood species on fungal decay after impregnation of nondurable wood species

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ABSTRACT

This study aims to evaluate the antifungal activity of extractive compounds obtained with fexIKA accelerate extraction process. Black locust *(Robinia pseudoacacia* L.*)* and African padauk *(Pterocarpus soyauxii* Taub.*)* heartwood, as well as black locust bark were used as the source material for investigation. After grinding, extraction, impregnation and rapid durability test, the efficiency of extractive compounds was assessed by the mass loss of European beech (*Fagus sylvatica* L.) samples used for impregnation and as reference samples. Results showed that the extractive compounds obtained from black locust heartwood were able to increase the native durability of European beech from class 5 (i.e. not durable with an average mass loss of 43.6 %) to class 3 (i.e. moderately durable with an average mass loss of 12.7 %), rendering this study's finding encouraging for the future use of extractive compounds as protective agents for wood.

Key words: Vacuum impregnation; extractive content; durability; fexIKA method; Trametes versicolor; Robinia pseudoacacia L.; Pterocarpus soyauxii Taub

INTRODUCTION

Wood as well as wood products manifest various physical and mechanical properties, which make them ideal for a wide range of applications. Nevertheless, wood durability, when attacked by wood-degrading organisms like fungi, bacteria or insects is often low. This is particularly the case of less durable wood species such as European beech (*Fagus sylvatica* L.) which is classified as 5 (i.e. not durable according to EN 350-2: 1994). Therefore, it is unfeasible to use wood in conditions of high humidity or contact with soil, where it is permanently exposed to degrading organisms, because of the high risk of rapid deterioration. This specific property renders the protection of wood against organisms mandatory. The most commonly suggested solution is the application of chemical preservatives, which significantly increases the life span of wood products. The degree of protection depends on many factors, like the protective agent used, the penetration depth and the retention of the chemicals in the wood (Bergman et al. 2010).

Only a few wood species growing in the temperate zone exhibit a similar high rate of natural resistance to degrading fungi and/or insects as tropical wood species (Rodrigues et al. 2012). In Europe only few tree species produce timber with a high natural durability (Grosser 2003). Black locust (*Robinia pseudoacacia* L.), a species native in North America, and cultivated in Europe for more than 400 years (Stringer 1992; Molnar 1995), deservingly represents this group. Many investigations have highlighted the fast formation of black locust heartwood in combination with its high natural durability (Hart 1968; Magel et al. 1991, 1994; Richter 2000). Scheffer and Morrell (1998) also rated black locust heartwood as very durable in regard to decay resistance, with a good weathering behaviour, mainly suitable for outdoor products.

The tropical wood species African padauk (*Pterocarpus soyauxii* Taub.), has bright red heartwood with a high hygroscopic stability and a good natural durability, due the high content of extractive compounds. It was found to contain approximately 13 % of soluble substances (Surowiec et al. 2004; Cardon 2007, Baar et al. 2014). African padauk medium-heavy heartwood manifests a remarkable decay resistance. It is rated as durable or very durable with resistance against termites and other insect species (Brémaud et al. 2011).

Nzokou and Kamdem (2003) attributed this high natural durability to the presence of specific extractive compounds found in heartwood, but also frequently observed in various plant parts like bark, roots, leaves, fruits and seeds (Yang 2009). Recent studies have applied the idea of utilizing extractive compounds obtained from corporation process waste products from various high durable wood species as antifungal agents (Novriyanti et al. 2010, Royera et al. 2012). Extractives from alternative sources can be deployed as organic preservatives for fungal control. Hence, waste products from the industrial processing have the potential to serve as an important source for economically produced industrial natural biocides (Singh and Singh 2012). There have also been studies that dealt with practical problems such as impregnation into wood and mainly fixation in the wooden matrix, appearing during the leaching test or the durability test, which limited a wide commercial utilization of these processes and products (Furuno et al. 2004, Sen et al. 2009).

Although, Soxhlet extraction has been the most commonly used method, this technique is time consuming and requires quite big amounts of organic solvents. Recently, new extraction techniques, like *fex*IKA (Schwanninger and Hinterstoisser 2002), have been established in order to reduce the volume of solvents used during the process, to improve the precision of the results and to reduce the extraction time needed (Szyrwińska and Lulek 2001).

Wood preservative agents are under constant supervision because of their potential negative impact on the environment and human health. As a result of an increasing interest in and public perception of environmental aspects, protective agents have to fulfil two basic criteria: the first one is the desired efficiency and second, low or non-toxicity. This encourages researchers all around the world to design new alternative protective methods based on natural products or chemical compounds, to replace currently used treatments with higher toxicity. Kartal et al. (2006) implied that besides natural oils and other known treatments also extractive compounds obtained from high durable species have the potential to achieve the required efficiency and serve the environmental demands.

Considering the fact that numerous factors are impeding the progress necessary to develop technologies deploying natural products for wood protection, these issues need to be addressed and solutions have to be found (Singh and Singh 2012). Objectives of this study were: first, to determine the amount of extractive compounds possible to obtain from black locust (*Robinia pseudoacacia* L.) and African padauk (*Pterocarpus soyauxii* Taub.), and second to use these solutions for impregnation of European beech (*Fagus sylvatica* L.) wood and evaluate their antifungal activity.

MATERIAL AND METHODS

Wood sampling and preparation

Naturally durable wood species, black locust (heartwood, internal and external bark mixture) harvested in the Czech Republic and African padauk (heartwood) harvested in Gabon were chosen to obtain extractive compounds, one 60-years-old, air dried trunk for each species. Material from four different heights (0, 1.3, 4, 6 meters) was used (Fig. 1), in order to obtain random mixture of each specimen class. Grinding was done using Retsch SM300 mill and the final material separation by sifting on a 50-mesh (0.500 mm analytical screen). After the preparation of the specimens, four successive steps were performed: extraction, impregnation, rapid durability test and evaluation of the results.

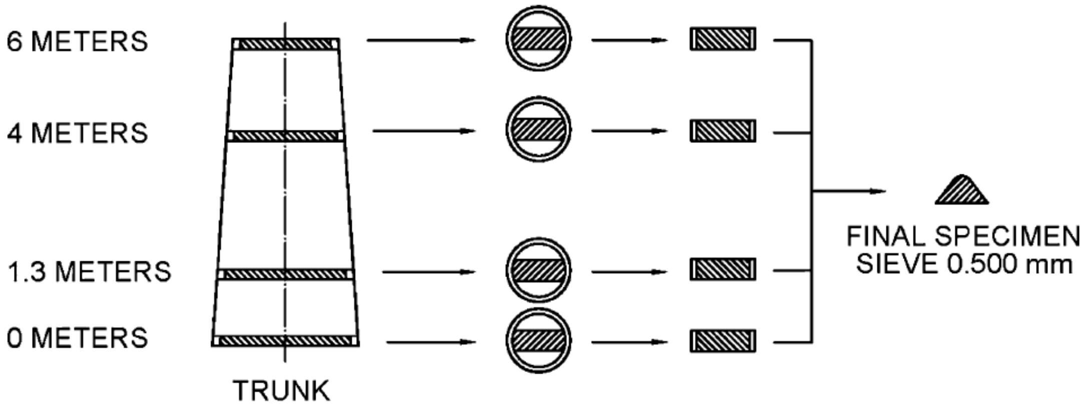

Figure VI. 1 Scheme of the specimen preparation form the trunk

Extraction

Specimens of weight 10 ± 0.01 g were used for extraction with the *fex*IKA vario control apparatus (Schwanninger and Hinterstoisser 2002). Powder was extracted with 100 ml mixture of methanol and distilled water (1:1, v/v), at 110 °C for 1.5 hour during 4 extraction cycles. The extractive compounds obtained were filtered, filled up to the original solvent volume of 100 ml and divided into two groups. Eight samples from the first group were oven dried at 103 ± 1 °C to the constant weight and then cooled in the desiccator. Subsequently, the quantitative amount of extractive content was determined gravimetrically from the dry weight of the wood powder. The second group of forty samples was concentrated in 10:1 ratio. The obtained solutions were stored in a cold and dark place and later used for samples impregnation.

Impregnation

The rapid durability test was used for the evaluation of the extracts efficiency against wood-rotting fungi (Bravery 1979). Air dried sapwood beech samples were obtained from a 50-year-old log (trunk harvested in the Czech Republic). The wood used for the experiment was without cracks, coloration, rot, insect damage or any other visible defects.

The sample impregnation was conducted and the process of impregnation chosen, was based on the vacuum phase only, avoiding the overpressure phase. The impregnation was carried out in one step. The pressure was decreased to 20 kPa of absolute pressure and then maintained for one hour. Solution excesses were tapped after the treatment and the samples were weighted to quantify the uptake. The impregnated samples were placed into the condition chamber with a temperature of 22 °C and 60% relative humidity.

The rapid durability test

The methodology used, employed 40 wood blocks with a length of 30 mm and a cross section of 10*5 mm^2 for each solution prepared from the reference beech wood. Impregnated and non-impregnated wood samples were sterilized by gamma radiation (28 kGy) and put into Petri dishes with malt extract agar medium covered by *Trametes versicolor* culture. Three treated and one reference untreated sample were placed into each Petri dish on a stainless mesh. Petri dishes were stored in the climate box for 6 weeks at a temperature of 22 °C and 65% relative humidity. After this period, the samples were carefully cleaned, dried at 103 ± 1 °C and the mass loss was calculated gravimetrically for each sample. Samples were classified into durability classes in compliance with EN 350-2.

RESULTS

African padauk heartwood showed a higher yield of extractive compounds (11.2%) compared to the total extractives of black locust heartwood (7.4%) and bark (9.6%) (Fig. 2). The extractive yield obtained from African padauk heartwood using methanol-water mixture (1:1, v/v) as a solvent was on average 11.2% higher than the average amount for tropical woods (Brémaud et al. 2011).

Three solutions obtained from black locust (heartwood, bark) and African padauk (heartwood) were used for European beech wood block samples impregnation. After six weeks of durability testing, the samples treated with African padauk extractive compounds showed an average mass loss of 16.5%, meaning an increase from the original beech durability class 5 (i.e. not durable) to class 3 (i.e. moderately durable). The samples treated by extractive content of black locust bark showed an average mass loss of 29.1%. This result ranks wood into durability class 4 (i.e. slightly durable). The durability test of samples treated with black locust heartwood extractives showed an average result of mass loss 12.7% (i.e. durability class 3 moderately durable). Detailed examination of this group results shows that 20 out of the total 40 treated samples manifested a mass loss from 8.7% to 11.9%. This means that the samples can be classified into durability class 2 (i.e. durable). The average mass loss was higher than in the case of samples impregnated with black locust heartwood extractive compounds, the treatment significantly increased the resistance of wood to decay in comparison to untreated European beech reference samples. Black locust bark extraction content impregnated into European beech samples showed the lowest results of durability against *Trametes versicolor* fungus. The mass loss ranged between 18.7 % and 37.5 % (Fig. 3).

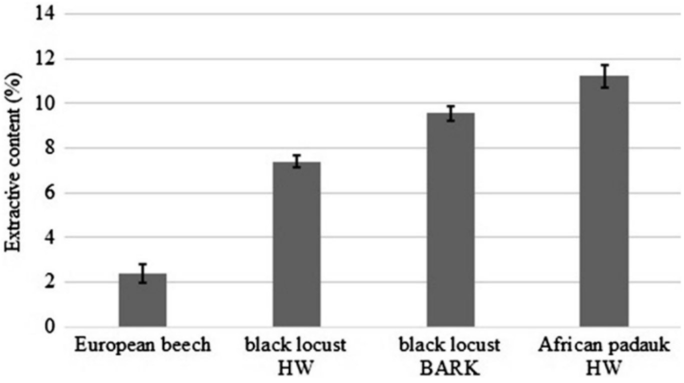

Figure VI. 2 Quantitative amount of extracted compounds, n = 8

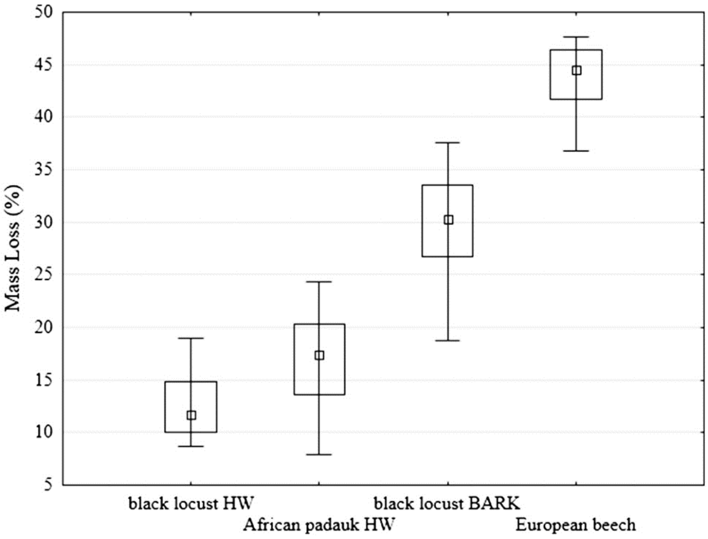

Figure VI. 3 Mass loss of samples after the durability test, Bravery samples, n = 40

DISCUSSION

Bark generally contains a higher amount of extractive compounds including phenolics, flavanones and flavonoids, having the purpose to act as a plant biocide chemical defensive mechanism against a wide range of harmful microbes and herbivores (Patten et al. 2010). Also in this study, black locust bark shows a higher extractive yield than its heartwood.

Much of the main-stem volume of black locust consists of heartwood, characterized by the presence of dark yellow-brown colour. Extractive compounds present in black locust give the heartwood its distinctive colour and decay resistance and their content extracted with hot water ranges from 5.2% to 8.6% (Hart 1968, So et al. 1980). Mészáros et al. (2007) extracted 1-year-old black locust shoots, obtained from a Hungarian energy plantation, with different solvents (95% Ethanol, Acetone, Distilled water, Ethanol). The amounts of extractive compounds in their study varied between 2% and 8%. The extractive yield results of this study showed 7.4 % for black locust heartwood and 9.6% for bark. Comparing with other literature results, the extractive content depends on the extraction process, solvent type, wood origin and type of chemical compounds present in the wood. Even though *fex*IKA extraction process was used in this study instead of Soxhlet apparatus, the results are in accordance with literature.

Extractive compounds can represent only a low percentage in some woods, while the mean for tropical hardwoods is 7.6% of total extracts (4.6% for ethanol–benzene extracts), based on 653 species from the CIRAD database (Brémaud et al. 2011). In some species, extractive content equals to one-third of the wood mass, e.g. 35 % of total extractive compounds in *Excoecaria parvifolia* (Gérard 1991). Extraction of African padauk heartwood in this study reached the total amount of 11.2% of extractive compounds. Brémaud et al. (2011) reached 13.4% of total extractive compound using methanol as a solvent for extraction. Another recent study has achieved a lower range of total extractive yield (from 4.0% with acetone as a solvent, to 9.1% with water as a solvent) using the “Accelerated Solvent Extraction” system ASE 200 (Saha et al. 2013). The results of this study mostly followed Brémaud et al. (2011) probably because of the similarity of the solvents used.

During this research it was possible to achieve an increase in native European beech durability by impregnating it with native extractive compounds. Specifically, black locust heartwood extractive content showed the best result, with 50% of the samples under the upper limit of durability class 2 (i.e. durable wood with mass loss from 6.0 to 12.0%) in laboratory test on Petri dishes. These results are promising data for the future research. There is still the question how extractives are stored in the wood after impregnation, if they are placed in the cell wall or in the lumina and how they really contribute to wood durability. Also the results of samples treated with black locust bark and African padauk heartwood extractive content confirm that the decay resistance of non-durable European beech wood could be increased using native chemical compounds from durable species under laboratory conditions. However, the retention levels necessary to obtain adequate protection (i.e. durability class 1) of European beech wood blocks are higher than thresholds reached in the present work. This can be explained by macro- and micro-distribution of extractives in the specimens and binding between the impregnated solution and the wooden matrix.

CONCLUSION

In order to obtain new environmentally friendly wood-preservative agents based on chemical compounds without any additives, the efficiency of extractive compounds against wood-decaying fungi was investigated in this study. Heartwood extractive compounds obtained from black locust showed strong antifungal activity in laboratory tests. Besides the promising results, the steps needed for the future were identified: primarily, do the leaching test (which was not part of this study) before the durability test to evaluate the fixation of extracts in the wood and the detection of phenolic compounds in wood after impregnation.

PAPER VII.

IMPROVEMENT OF WOOD PROPERTIES DUE TO IMPREGNATION OF WOOD WITH RENEWABLE LIQUIDS FROM DIFFERENT PROCESS RESIDUES OF NATIVE ORIGIN

Rademacher, P., Pařil, P., Baar, J., Čermák, P., Rousek, R., Meier, D., Koch, G., Schmitt U. (2015)

Conference paper (Cost action FP1407), Koper, Slovenia

Improvement of wood properties due to impregnation of wood with renewable liquids from different process residues of native origin

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Key words: wood modification, native resources, cell wall bulking, volumetric swelling, durability

INTRODUCTION

Wood modification treatments using non-toxic components are becoming more prevalent and are often used in place of biocides with negative environmental effects. However, many modification processes remain dependant, if only partly, on fossil resources. Wood modification processes, based on renewably sourced solutions, have a lesser impact on the environment and can be produced in a sustainable way (Ermeydan *et al*. 2012). The following investigations show first screening of started research project, carried out by the wood research group of Mendel University, Brno (Rademacher *et al*. 2014).

MATERIAL AND METHODS

- Swelling measurement: 10 samples of 14 x 14 x 28 mm^3 for each treatment
- Durability: 9 samples of 5 x 10 x 30 mm^3 (Bravery Test) for each treatment
- Production of liquid residues from thermal treatment (TT)-, Hydro-Thermal-Carbonisation (HTC)-, and pyrolysis-processes; impregnation to increase weight-percent-gain (WPG)
- Impregnation of Beech and Poplar sets of samples using vacuum 20 kPa/ 1 hour (EN 113)
- Concentrations: Pyrolysis 1:10; 1:2, original (1:1 = 100%); TT and HTC concentrated 10:1

- Conditioning, drying, volume/weight, leaching, bulking measurement following standards
- Durability tests: Bravery Test; fungi: *Trametes versicolor,* decay 6 weeks acc. to EN 113
- UMSP: UV-light absorption at 278nm, using Zeiss-UMSP 80 (Koch and Grünwald 2004)

RESULTS AND DISCUSSION

WPG after impregnation was about 5 % - 8 % in case of hydrothermal carbonisation (HTC) and 10 % - 15 % with thermal treatment (TT) residues. Impregnation with pyrolysis liquids from Beech wood powder (liquefaction under heat and pressure) produced 40 % WPG in Beech and 60 % in Poplar (Fig. 1). After leaching, high amounts of TT and HTC solution were washed out, whereas Pyrolysis liquids stayed with 25 % to 40 % remaining in the wood. Despite higher wash out rates following the EN 84 leaching test, all treatments had a positive effect on the tested properties.

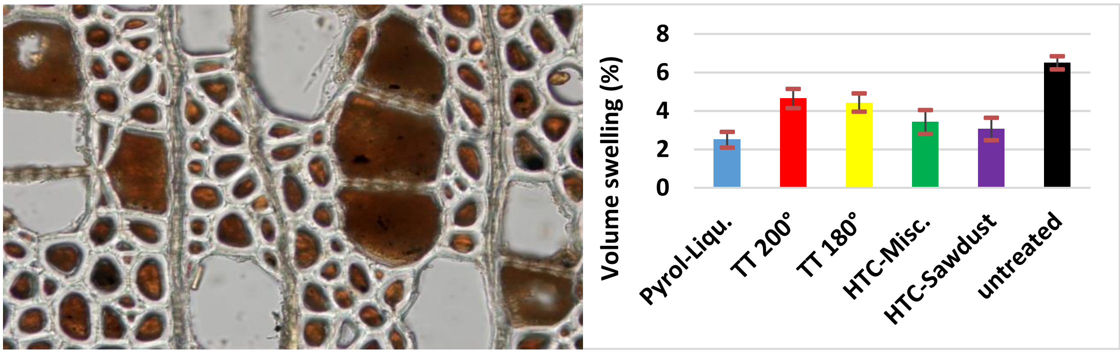

Figure VII. 1 Pyrolysis-liquid impregnated Poplar and volumetric swelling of Poplar wood.

Volumetric swelling in 65 % relative humidity at 20 °C was reduced from 6.5 % in untreated poplar to 5 % in impregnated samples with process residues of thermal treatment using 180 °C or 200 °C. The processes using HTC liquids from *Miscanthus sp.* (Misc.) or Sawdust showed reduction to 3.0 % - 3.5 % and Pyrolysis liquid treatment to 2.5 % (Fig. 1). The mass loss of untreated Beech (30 % - 35 %) and Poplar (40 % - 50 %) was reduced to 2 % in case of Pyrolysis- and 4 % in case of TT-treatment, depending on wood species and impregnation- or leaching- process (Fig. 2). Attendant bulking tests and UV scans prove the high inclusion of phenolic compounds in cell walls (Fig. 2).

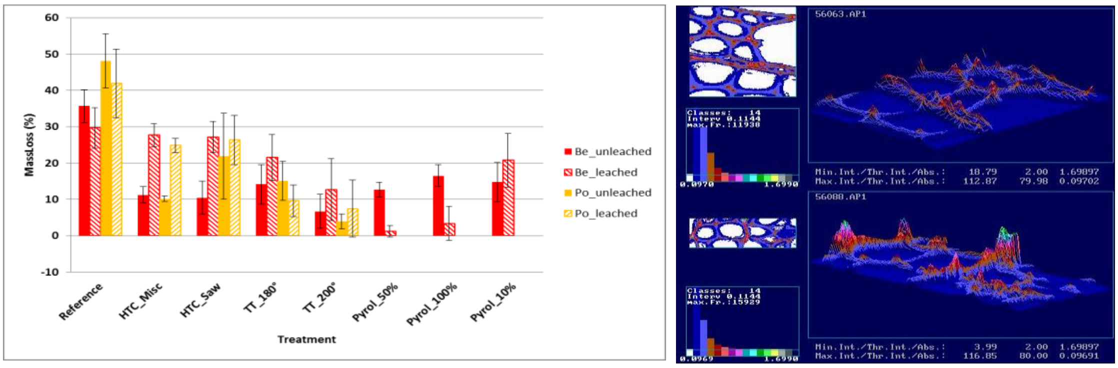

Figure VII. 2 Mass loss of Beech (Be) and Poplar (Po) Bravery samples due to fungi decay; UMSP-Scans of untreated and treated poplar fibres.

4 CONCLUSIONS

The doctoral thesis summarizes the research in the area of wood impregnation. Patent and results of scientific papers published in peer review journals (proceedings) may be concluded as follows:

I. The patented process (iron oxide nanoparticles) is characterized by impregnation with a product containing iron oxide nanoparticles, in a concentration of 0.4 g/l to 42 g/l, an average particle size in the range of 1 to 100 nm, and a liquid medium. Impregnation can be performed as pressure impregnation, followed by soaking, or the product can be applied by brushing or spraying. This method is an alternative to wood ammonification. This leads to colouring and UV stabilizing of treated wood, which is proved by Paper I and other already unpublished investigations.

II. This research has shown that copper nano-particles at the concentration of 3 g/l are effective against both tested fungi (under 5 % of mass loss) but it seems to be ineffective after leaching. Nano-silver treatment shows very low ML (under 1 %) and high efficiency against Trametes versicolor fungi for leached and unleached specimens, but very low efficiency against Poria placenta decaying. Further steps for research in this area should be to improve fixation and determinate the influence of nanoparticles form (preparation method/technique).

III. Advantage of Lignamon compared to steam-densified beech is the observed improvement of dimensional stability, hydrophobicity and hardness which was caused by heat treatment during process. Confirmation of added value leads to many potential applications for Lignamon (exterior cladding, terrace decking, sailboats, moulds etc.), which could motivate industrial partners to re-establish production. Further investigation will be carried out with self-produced Lignamon samples to determine the influence of particular process stages on changes of material properties.

IV. The experimental measuring proves that crystallized sucrose and NaCl contained within wood can considerably affect its physical properties. Tests also confirmed wood swelling due to modification. This evidences that NaCl and sucrose reached the cell walls where they crystallized after drying. Due to this wood swelled and its weight increased. Moisture absorption tests confirmed a high hygroscopicity of modified samples; the highest hygroscopicity was found in the highest concentration of NaCl. The lowest concentration of sucrose showed the best results from the perspective of improved dimensional stability and small increases in equilibrium moisture content.

V. The rate of acetylation increased with an increase of MW power. However, the treatment time (15 and 60 min) did not affect the degree of acetylation. These results were confirmed for all RH levels (30%, 65%, and 99%).

VI. Heartwood extractive compounds obtained from black locust showed strong antifungal activity in laboratory tests. Besides the promising results, the steps needed for the future were identified: primarily, do the leaching test (which was not part of this study) before the durability test to evaluate the fixation of extracts in the wood and the detection of phenolic compounds in wood after impregnation.

VII. After impregnation of residuals and leaching, high amounts of TT and HTC solution were washed out, whereas Pyrolysis liquids stayed with 25 % to 40 % remaining in the wood. Volumetric swelling in 65 % relative humidity at 20 °C was reduced from 6.5 % in untreated poplar to 5 % in impregnated samples with process residues of thermal treatment using 180 °C or 200 °C. The processes using HTC liquids from Miscanthus sp. (Misc.) or Sawdust showed reduction to 3.0 % - 3.5 % and Pyrolysis liquid treatment to 2.5 % (Fig. 1). The mass loss of untreated Beech (30 % - 35 %) and Poplar (40 % - 50 %) was reduced to 2 % in case of Pyrolysis- and 4 % in case of TT-treatment.

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