PRODUCTION OF HARDBOARDS MADE WITH TANNIC ACID AND PHENOL-OXIDIZING ENZYMES

Master Thesis

Submitted by
Alfred Andreas Hummer, Bakk.tech.

Supervisor:
Univ.Prof. Dipl.-Ing. Dr.nat.techn. Alfred Teischinger
Co-Supervison:
Dipl.-Ing. Dr. Andreas Kandelbauer

Institute of Wood Science and Technology
Department of Material Sciences and Process Engineering
University of Natural Resources and Applied Life Sciences
BOKU – Vienna

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Abstract - Zusammenfassung

Abstract

Fibres derived from three different wood mixtures were used to fabricate hardboards. The fibres were obtained from an industrial manufacturing process and formed into fibre mats. The mats were impregnated according to two different laboratory scale methods (conventional and non-conventional). In the conventional method the fibres were suspended in water and a solution of tannic acid and/or laccase was added to the suspension. The fibres were formed into mats and subsequently pressed into hardboards on a laboratory press. In the non-conventional method fibre mats were formed and in a second step impregnated with tannic acid and/or laccase solution. The mats were incubated/dried in an oven at 40°C until a moisture content of about 50% was reached and then pressed into hardboards.

The hardboards were tested for internal bond strength (IB), modulus of elasticity (MOE), modulus of rupture (MOR) and thickness swell after 24h of water immersion. The effects of laccase dose, tannin concentration, pH of impregnation solution, mat moisture content before pressing, press temperature and board density on board properties were investigated.

The best results were achieved with a laccase dose of 500 nkat/g d.f., tannic acid concentration of 10%/g d.f. and pH 6 of the impregnation solution. An addition of Hydrowax to the impregnation solution was beneficial for the dimensional stability but not for the mechanical one. Press temperatures above 190°C and moisture contents below 50% of the fibre mat before pressing had an adverse effect on board parameters. Even the fibre mixture was an issue, the best results were achieved with mixtures rich in softwood.

Zusammenfassung

Fasern drei verschiedener Holzmischungen wurden verwendet um Hartfaserplatten herzustellen. Die Fasern wurden einem industriellen Herstellprozess entnommen und im Labor-

maßstab zu Fasermatten weiterverarbeitet. Die Fasermatten wurden mittels zwei verschiedener Methoden (konventionelle und nicht-konventionelle) im Labormaßstab imprägniert. Bei der konventionellen Methode wurden die Holzfasern in Wasser suspendiert und mit einer Lösung aus Tanninsäure und/oder Laccase versetzt. Die Fasern wurden zu Matten und diese anschließend zu Hartfaserplatten verpresst. Bei der nicht-konventionellen Methode wurden die Fasermatten gepresst und in einem weiteren Schritt mit einer Lösung aus Tanninsäure und/oder Laccase imprägniert. Die Matten wurden in einem Ofen bei 40°C inkubiert/getrocknet, bis eine Restfeuchte von ca. 50% erreicht war, um anschließend zu Hartfaserplatten weiterverarbeitet zu werden.

Die so produzierten Platten wurden hinsichtlich Querzugfestigkeit, Biegebruchverhalten, Elastizitätsmodul und Dickenquellung (nach 24h Wasserlagerung) getestet. Die Auswirkungen veränderter Laccase Dosen, Tanninsäurekonzentrationen, pH-Werte der Imprägnierlösungen, Fasermattenfeuchte vor Verpressung, Presstemperatur und Plattendichte auf die Eigenschaften der Faserplatten wurden untersucht.

Die besten Ergebnisse konnten mit einer Laccasedosis von 500 nkat/g d.f., einer Tanninkonzentration von 10%/g d.f. und einem pH von 6 der Imprägnierlösung erzielt werden. Ein Zusatz an Hydrowax zur Imprägnierlösung wirkte sich günstig auf die Dimensionsstabilität aber negativ auf die mechanische Stabilität aus. Presstemperaturen über 190°C und ein Feuchtegehalt unter 50% der Fasermatten vor Verpressung hatten einen negativen Einfluß auf die Plattenparameter. Die Fasermischung zeigte erkennbare Auswirkungen auf die Platteneigenschaften und Mischungen mit hohem Weichholzanteil erzielten die besten Ergebnisse.

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Abbreviations

General

°C	degree Celsius
10TA	10% per g dry fibre tannic acid
A	enzyme activity
bar	bar = 100000 Pascal
d	thickness of absorbing sample solution (normally 1 cm)
d.f.	dry fibre
e.g.	for example
eq.	equation
et.al.	et alii
fig.	figure
FM	fibre mixture
g	gram
h	hour
HB	hardboard
HDF	high density fibre board
IB	internal bond strength
l	litres
m	meter
M	molar mass [mol/kg]
MDF	medium density fibre board
MF	melamine-formaldehyde
min	minutes
MOE	modulus of elasticity
MOR	modulus of rupture
nkat	nano-katal
noE	no enzymes
PF	phenol-formaldehyde

s	seconds
TA	tannic acid
tab.	table
TF	tannin-formaldehyde
TS	Thickness Swelling
U	Units
UF	urea-formaldehyde
V	volume of the enzyme solution
ΔE	change in extinction over time (e.g.: 1 min)
ϵ	molar extinction coefficient, ϵ = 29 mmol^{-1}cm^{-1}

Sample Codes

10TA_500_pH4_2HW_imp_D1402h

10TA	10% tannic acid per g dry fibre
500	500 nkat enzyme dose per g dry fibre
pH4	impregnation solution adjusted to pH 4
2HW	addition of 2% per g dry fibre Hydrowax
imp	non-conventional method
D1402h	dried at 140$°$C for 2h after incubation at 40$°$C and before pressing into boards

10TA_500_30min_preinc

10TA	10% tannic acid per g dry fibre
500	500 nkat enzyme dose per g dry fibre
30min	enzyme solution stirred for 30min at 40$°$C before impregnation
preinc	preincubation of enzyme solution before impregnation

10TA_500_5CaCl2_conv

10TA	10% tannic acid per g dry fibre
500	500 nkat enzyme dose per g dry fibre
5CaCl2	5% CaCl$_2$ per g dry fibre
conv	conventional method

10TA_500_1,5HW_pre_2h104pre

10TA	10% tannic acid per g dry fibre
500	500 nkat enzyme dose per g dry fibre

1,5HW_pre   1,5% Hydrowax per g dry fibre added before pressing of fibre mat
2h104pre   2h preincubation at 104°C of fibre mat before impregnation

noTA_noE
noTA   no tannic acid addition
noE   no enzymes added

Chapter 1

Preface

The use of enzymatic systems for surface activation of wood particles to form binderless composites has been the subject of study for over 20 years. Enzyme-catalysed bonding of wood can be achieved either by activation of lignin, which is mixed with wood particles, or by surface activation of the wood particles directly (Hill, 2006; Grönqvist et al., 2003).

Laccase is such an enzyme and its use in wood processing industry takes place mainly in the pulp and paper sector. There is no industrial scale application of this enzyme in the fibreboard sector, except some pilot-scale approaches. The most promising possible application could be in the MDF production sector where the resin content is very high. These resins have two drawbacks, first they are derived from fossil fuels and second they contain hazardous compounds like formaldehyde. In this study hardboards (HB) were produced at laboratory scale, in a process similar to the industrial wet-process for this type of board. In addition to laccase, tannin (a natural binder) was added to increase the laccase-induced radical formation. The fibres used were produced at the FunderMax GmbH hardboard plant in St.Veit/Glan, Austria, and the experiments were conducted in the laboratories of the Wood Carinthian Competence Center "W3C" (St.Veit/Glan, Austria) and FunderMax GmbH (St.Veit/Glan, Austria), respectively.

Fibres of different wood species were used and formed into mats, which were impregnated with solutions of laccase, tannic acid and additives in different concentrations and at different pH. After a drying process the mats were pressed to hardboards and tested according to their internal bond strength, modulus of elasticity, modulus of rupture and thickness swelling behaviour.

In the following thesis a short introduction to fibreboard production, binding mechanism and laccase/fibre interaction will be given, followed by a brief description of the experimental procedure. A presentation of the results as well as a discussion will be given.

Chapter 2

Introduction

2.1 General Introduction

The forest based industries sector can be divided into main groups: pulp and paper and allied groups, and lumber and wood-based panels and materials and their further processing to final products (load bearing, non-load bearing, furniture, etc.). A good documentation of the forest-based industries sector is given by the homepage of the EU "Enterprise and Industry Sector" (http://ec.europa.eu/enterprise/forest_based/index_en.html) and the COST Action E44 "Wood Processing Strategies" (http://dfwm.ugent.be/woodlab/CostE44/). The challenges of research and development are provided in the forest-based sector Technology Plattform (http://www.forestplatform.org/).

Regarding wood-based products such as medium-density fibreboards (MDF) and particleboards (PB), structural panels such as plywood and oriented strandboard (OSB); solid-wood joints, made with the increasingly expensive petroleum-derived adhesives, manufacturers are under pressure. Production costs and harmful formaldehyde emissions from the adhesives need to be reduced, and product recyclability to be improved (Widsten and Kandelbauer, 2008b).

2.2 Application of laccase in wood processing industry and target of the thesis

One step towards the prior mentioned goals is the enhanced employment of enzyme technology, which is a sustainable and energy saving method, due to the mild reaction conditions at which enzymes work. Whereas the application of enzymes, like laccase, in the pulp and paper industry is more common and has already reached a higher status of integration, it is not the fact for the lumber and wood products industry sector, especially board

production.

Research work in the Competence Center for Wood Composites and Wood Chemistry (Wood Kplus) puts much emphasis on this issue (Gradinger et al., 2004; Kuncinger et al., 2004; Srebotnik and Boisson, 2004; Fackler et al., 2007; Kandioller, 2004; Wulz, 2005).

The introduction of this new technology is rather slowly and the implementation has still to overcome some problems. The compliance with existing production technologies and facilities, the cost-competitiveness in comparison to crude-oil or gas derived chemicals and additives, and the fulfilling of all quality standards, especially dimensional stability, are some issues that have to be faced (Widsten and Kandelbauer, 2008b).

First approaches of implementation into an industrial process have already been done and one of the most promising is the application of laccase in the MDF production. Felby et al. (2004) already showed the producibility of MDF boards from laccase treated fibres, whereby Widsten et al. (2003, 2004) had the most applicable implementation of laccase treatment into an existing production plant so far, by spraying the laccase solution into the refiner blow-line instead of the conventional ureaformaldehyde resin.

It was the target of this thesis to involve covalent bonds, beside the hydrogen bonds, in the board forming process by application of laccase and tannic acid. The laccase created phenoxy radicals which were able to form covalent bonds during the hot pressing step. The tannic acid as a poly-phenolic compound enhanced the radical formation and served as a natural binder.

2.3   Fibreboard production

Fibreboards are defined according to the European standard EN-316 as a plate-type material, thicker than 1,5 mm, made of lingo-cellulose fibres linked together with the use of heat and pressure.

Fibreboards can be divided into different groups as a function of the manufacturing process, density, specific properties and field of application. The two main criteria for distinguishing the different board classes are the manufacturing process and density. Further, the European standard EN-316 distinguishes between two kinds of manufacturing processes:

- the wet process:
  The main group of fibreboards made with this process are hardboards (HB) with a density more than 900 kg/m^3.

- the dry process:

  The most important groups of boards made with this process are medium density fibreboards (MDF) and high density fibreboards (HDF) with densities between 450-800 kg/m^3 and more than 800 kg/m^3, respectively.

The main difference between the wet and the dry process is the mat forming agent, which is water in the former and air in the latter. This has also a significant effect on the press times which are shorter in MDF/HDF production (5-3 s/mm) than in hardboard production (2-3 min/mm), where the water has to be evaporated. The boards in this study are made according to a procedure similar to the wet process. Therefore it is not possible to cross-grade results from this study to MDF/HDF experiments. A further study will be necessary to evaluate optimal parameters for the MDF/HDF production process to obtain improved properties.

2.4 The wet process

Hard- and softwood chips are mixed, dried and stored in a bunker where they are taken from and pumped into the pre-heater. The pre-heater is a vertical pipe where the wood chips are cooked with hot steam at approx. 180°C and about 8 bar in a counterflow process. At the bottom of the pre-heater the cooked chips are disintegrated in the defibrator, a grinder with a fixed and a rotating disk. Because of the temperatures of about 180°C the lignin is softened and the wood cells are separated along the lignin-rich middle lamella region. During this process parts of the lignin are depolymerized and are more reactive towards a laccase treatment later on. With adjusting the steam temperature and pressure and the disc clearance of the defibrator, the amount of lignin present on the fibre surfaces and the length of the wood fibres can be modulated.

Subsequently, the fibres are mixed with water in tubs and the pH is adjusted to 4.5-5.5 with sulphuric acid. This mixture is pumped through screw conveyors, where resins and hydrophobicity agents are added, to the mat forming strainer and roller machines. These machines press and suck of the water, so the dry mass content is raised to about 50-60%.

The endless fibre mat is cut into pieces by a disk saw and runs onto metal plates with sieve overlays, which drain the water at the hot pressing step. The fibre mats are then pressed into hardboards in a continuous or stepwise working press at temperatures at about 200°C (Soine, 1995).

2.5   The dry process

In this process, the fibres are made in the same way as in the wet process. After the defibrator, the fibres are dried in a so called blow-line, where the resin and the hydrophobicity agent are sprayed onto the fibres. After the drying step the fibres have a dry mass content of about 97%. This mixture of dry fibres, resin and hydrophobicity agent is stored in a bunker and taken from there to be scattered as homogeneous as possible onto a conveyor belt, where the mat is formed by use of air instead of water. Following to the mat forming step the MDF boards are pressed at temperatures of 180- 200°C on a continuously working day light press. One advantage of this manufacturing process is the fact that MDF boards don't have a sieve structure on one side (Soine, 1995).

2.6   MDF, HDF and HB

Medium density fibreboards (MDF) and high density fibreboards (HDF) are made with the same process and in the same way but with different press parameters, so the density of HDF is higher. MDF boards have an uneven density profile with lower density in the middle layer of the board and increasing densities forwards the surfaces. This gives a lightweight board with increased mechanical strength in comparison to a board with same density but even density profile. Further, both sides of a MDF board have a smooth surface, because they are pressed on a daylight press with fibres of low moisture content. This makes MDF boards to one of the most used boards in the furniture industry nowadays. The main disadvantage of MDF boards is their relatively high content of resins of up to 10% per fibre dry weight. As mentioned before, this is a main problem in times of stricter regulations relating to formaldehyde emissions, a major component of most resins in use today.

Hardboards (HB) are made with the wet process and show a density of more than 900 kg/m^3. HB have a uniform density profile and are mainly used for backplanes of cupboards, door production, drawer bottoms or support materials for floors (Soine, 1995).

An advantage of HB is their low resin content of approx. 0.5-2%, depending on the quality standards to be reached. Nevertheless, the most used resins for HB are phenol-formaldehyde (PF), ureaformaldehyde (UF) and melamine-formaldehyde (MF). Disadvantages of HB are the production process itself, with a higher energy demand in comparison to the dry process, the complex waste water recycling process and the fact that there is only one smooth side per board and one with the sieve structure on it.

2.7 The enzyme laccase and its interaction with lignin

Laccase is a multi copper enzyme, to be more precise a phenoloxidase (EC 1.10.3.2), and one of the glycoprotein enzymes expressed by white-rot fungi and other organisms. These play a crucial role in the terrestrial carbon cycle by helping to degrade lignocellulosic material such as wood (Widsten and Kandelbauer, 2008b). White-rot fungi are basidiomycetes, and the enzymes they express are able to degrade all the main components of lignocellulosic material, i.e.: cellulose, hemicelluloses and lignin (Widsten and Kandelbauer, 2008a).

Biochemically, laccase is an enzyme which oxidizes a variety of hydrogen donors. Thus, it catalyzes the removal of an electron and a proton from phenolic hydroxyl or aromatic amino groups to form free phenoxy and amino radicals, respectively (Leonowicz et al., 2001). For this master thesis study, the enzymatic catalysis of phenoxy radicals is of special interest (see figure 2.1).
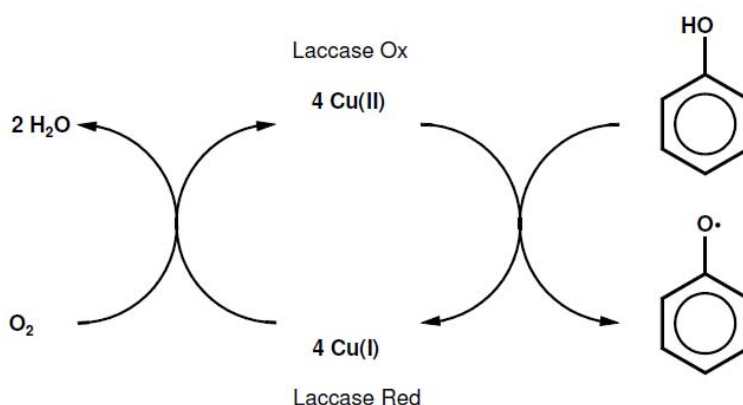
Figure 2.1: Laccase catalyzed oxidation of phenolic hydroxyl groups to phenoxy radicals (Pronk and Leclercq, 2004)

Figure 2.1 shows the catalyzed redox reaction, where oxidation of four mole phenolic hydroxyl groups to phenoxy radicals and the reduction of one mole oxygen to two mole of water. The reaction takes place at the active site of the enzyme, which contains four copper ions. Two of them are involved in the reduction of oxygen.

The enzyme itself is a very large molecule (MW ˜ 70.000) which cannot penetrate deep into wood; moreover, due to its rather low-redox potential (˜ 0,5-0,8 V), it is unable to oxidize non-phenolic (C4- etherified) lignin units, which have a high redox potential (>1,5 V). Because of this limitation, laccase alone can only oxidize phenolic lignin units (<20% of all lignin units in native wood) at the substrate surface. Therefore, laccase is often applied with an oxidation mediator, a small molecule able to extend the effect of laccase to non-phenolic lignin units, in order to overcome the accessibility problem. These systems are called laccase mediator systems (LMS). In a LMS the mediator is first oxidized by laccase

and diffuses then into the cell wall, where it oxidizes lignin inaccessible to laccase (Widsten and Kandelbauer, 2008b).

A mechanical pulp consists not only of a fibre fraction but also of approximately 10% of low molecular weight carbohydrate and lignin extractives generated during the pulping process. It was shown that the water extractable lignin components were interacting as redox mediators with the fibre surface lignin and the oxidizing enzyme (Felby et al., 2004). For this thesis the effect of radical formation and fibre cross-linking was enhanced by adding tannic acid to the impregnation solution, which served as a natural binder.

Lignin is an amorphous polymer which functions as a cementing material in wood cells; it comprises approximately 20-30% of the dry wood mass. Lignin consists of p-hydroxyphenyl, guaiacyl and syringyl-type phenylpropane units in which the aromatic units bear 1-3 free or etherified hydroxyl groups. The phenylpropane units are linked together by ether and carbon-carbon bonds (Widsten and Kandelbauer, 2008b).

Figure 2.2 shows a possible structure of lignin and illustrates the complexity of this macro-molecule.
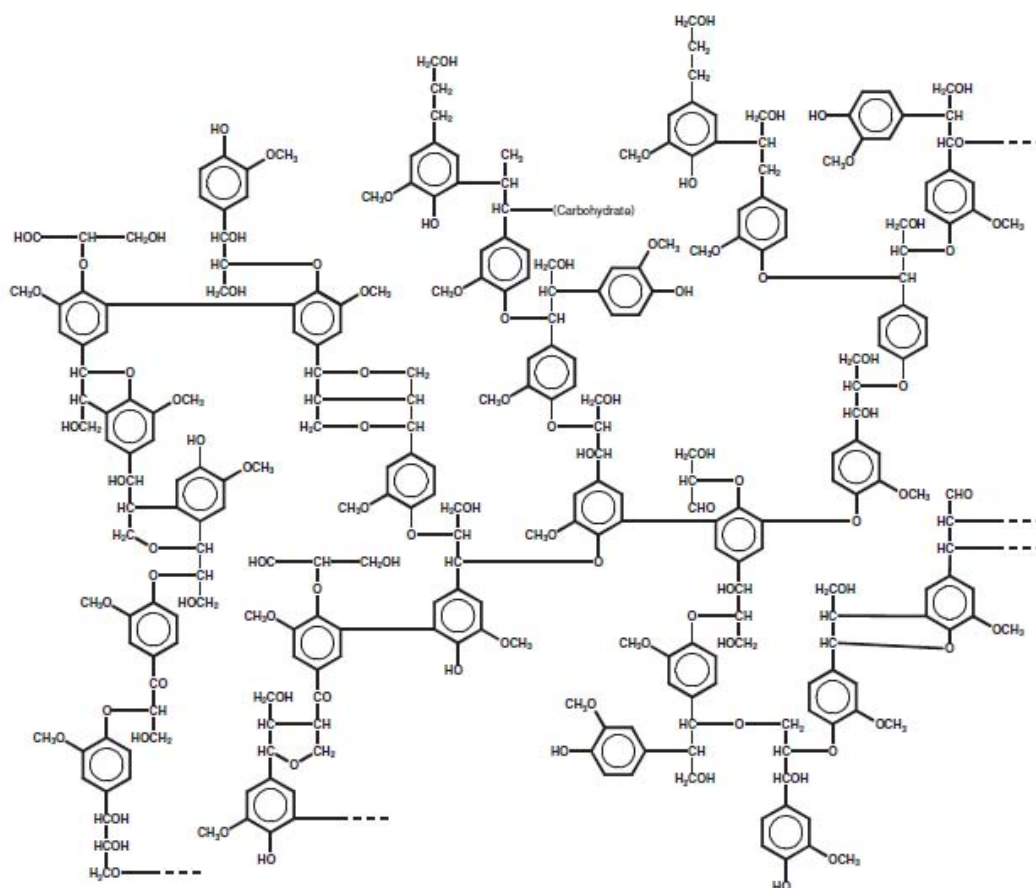
Figure 2.2: Possible complex lignin structure (Glazer and Nikaido, 1995)

Defibration of wood causes depolymerisation of the main components as covalent

bonds connecting lignin and carbohydrate molecules are ruptured. The relative proportions of cellulose, hemicelluloses and lignin differ from each other in the various layers of the wood cell. However, in high temperature TMP pulping or mechanical pulping according to the Asplund process, which is carried out at temperatures exceeding the glass transition temperature of lignin, wood failure mainly takes place in the highly lignified middle lamella region (Widsten et al., 2001).

As defibration was performed at about 170°C and 8,5-9,0 bar, in this setting, the fibre surface was rich in lignin, which was in turn beneficial for laccase treatment. Besides the laccase induced radical formation, mechanoradical formation as a form of thermo mechanical pulping took place as well.

2.8 Tannins as a binder

Beside the well known standard adhesives urea-, phenol- and melamine-formaldehyde used in the wood-based industries nowadays, there is also a growing interest in renewable and/or more ecofriendly alternatives like the lignosulfonates (by-product of sulfite pulping) or flavanoid-based tannins obtained from certain trees. Pizzi (1994) gives an overview of the most common binders in use and alternatives which will become more important in the near future.

Tannins are derived through extraction with water or aqueous alkalis from barks, woody material, pods, nut shells and other plant material. Often used tannins are the ones derived from Black Wattle (*Acacia mearnsii*) and Quebracho (*Quebracho colorado*). Tannins are polyphenolic compounds and their composition varies depending on the raw-material and the solvent used for extraction. Besides the tannins, compounds such as resins, fatty acids, carbohydrates and starch can be found in the extracts. In this study nearly pure tannic acid was used as a binder or enhancer of self binding forces of defibrated wood (Rosamah, 2003).

Up to now pure tannic acid, tannins alone or tannins in combination with phenol oxidizing enzymes, such as laccase, are not in use in the industrial wood processing industry. But condensed tannins in combination with formaldehyde, so called TF-resins, are in use for industrial scale production of wood based materials in South Africa, Australia and Germany. The knowledge of the binding attributes of tannin in combination with formaldehyde date back to the early 1940's. Since the oil-crisis in the 1970's the interest in the technical application and use of tannins as a surrogate for synthetic binders such as urea-formaldehyde, phenol-formaldehyde or melamine-formaldehyde resins was fast growing. New developments in lowering formaldehyde emission enhanced that movement (Rosamah, 2003).

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The use of tannins as binders is due to their relatively high content of reactive polyphenols. Tannins are divided into two main groups, hydrolyzable and condensed tannins. All tannins, except the larger condensed ones, are water soluble.

2.8.1 Hydrolyzable tannins

Hydrolyzable tannins are derivatives of gallic acid (3, 4, 5–trihydroxyl benzoic acid). Gallic acid is esterified to a core polyol and the galloyl groups may be further esterified or oxidatively crosslinked to yield more complex hydrolyzable tannins. The most simple ones are the gallotannins. Figure 2.3a and figure 2.3b show gallic acid and one simple core structure of tannic acid. Normally more than three galloyl groups are coupled to one glucose molecule and a polygalloyl–glucopyranoside is formed. Other more complex structures are the so called ellagitannins, where the galloly groups are crosslinked with each other (Hagerman, 1998).

(a) Gallic acid   (b) Tannic acid – One possible core structure
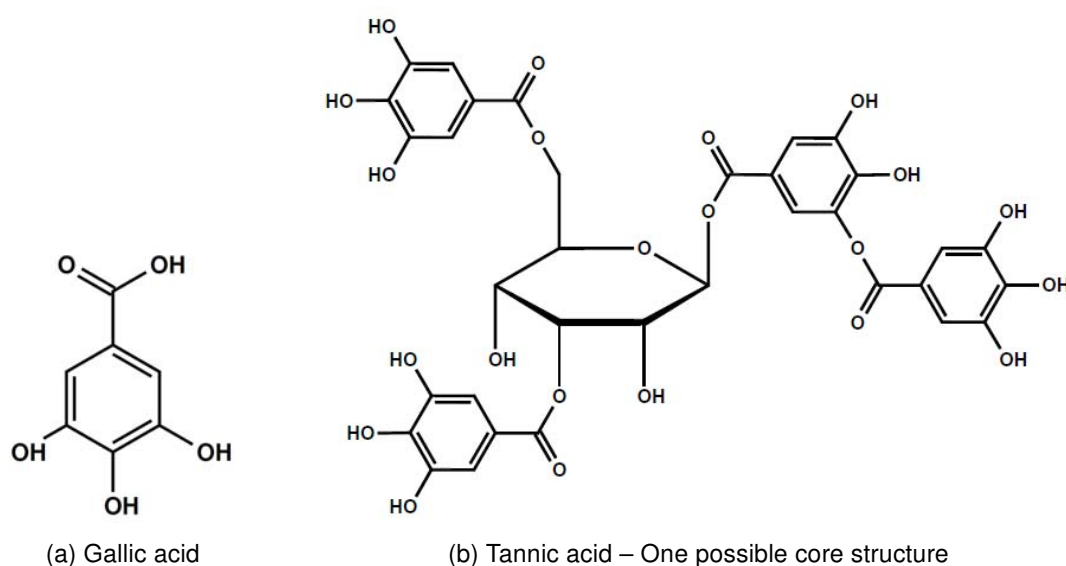
Figure 2.3: Tannic acid and their base units

2.8.2 Condensed tannins

They are polymeric flavanoids whose subunits are linked by carbon-carbon bonds and they are therefore not susceptible to being cleaved by hydrolysis. The flavanoids are a diverse group of metabolites based on a heterocyclic ring system derived from the amino acid phenylalanine (figure 2.4b (A)) and through polyketide biosynthesis (figure 2.4b (B)). Although the biosynthetic pathways for flavanoid synthesis are well understood, the steps leading to condensation and polymerization have not been elucidated (Hagerman, 1998).

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(a) Phenylalanine   (b) Flavanoid core structure
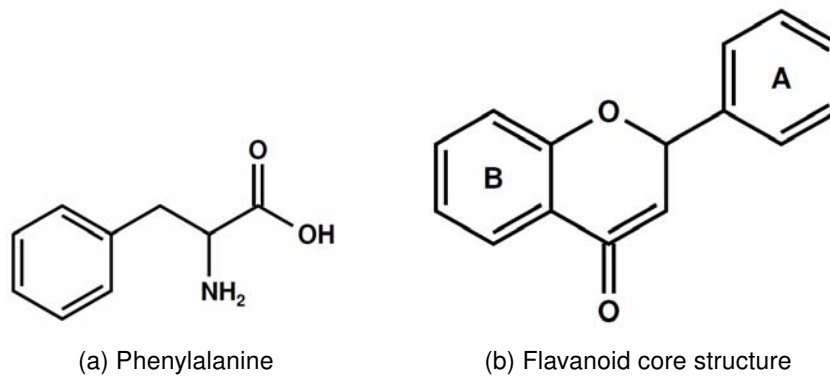
Figure 2.4: Phenylalanine and the flavanoid core structure

Generally, it has to be distinguished between two types of condensed tannins, the resorcin-type and the phloroglucin-type. The first one dominates in extractes of *Accacia mearnsii* (Wattle tannins) and *Quebracho colorado*, the second one in extractes derived from conifers (e.g.: *Pinus radiata*) (Zeppenfeld and Grunwald, 2005).

Condensed tannins are able to interlink with formaldehyde over a wide pH range and the resulting ability to form water resistant inter-fibre bonds is the basis for their application as a binder for wood based materials. Due to their high molecular weight the density of the condensed TF-resin polymer is relatively small in comparison to UF- or PF-resins.

Next to the application of tannins in combination with formaldehyde, the use of tannins solely in combination with phenol oxidizing enzymes is a new field of investigation. The applied principle relies on the ability of tannins to form polymers and water resistant inter-fibre bonds, but the enhancing factor in this case is the phenoxy-radical producing enzyme laccase. The coupling reagents, which form the rigid polymer, are the enzyme activated tannin and lignin, instead of the previously mentioned formaldehyde. As already mentioned some half industrial scale approaches have been made.

2.9   Bonding mechanisms in fibreboards

Hardboard as well as paper has some characteristics of composites materials as compared to a homogenous polymer structure. Main bonding forces in fibreboards are:

- covalent bonds (lignin)

- hydrogen bonds (cellulose and hemicelluloses)

- London-van der Waals dispersion forces

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The covalent bonds are the strongest, the hydrogen bonds are intermediate and the non polar London-van der Waals dispersion forces are the weakest. The bonding energies in kJ/mole are about 800, 50 and 20, respectively (Frihart, 2006).

2.9.1 Hydrogen bonds

Cellulose and hemicelluloses are mainly involved in this type of inter-fibre bonds. Beneficial for hydrogen bond formation is a lower defibration temperature at about 160°C, which yields some fracture in the cellulose rich secondary wall surfaces. Also at this temperature less carbohydrate material is hydrolysed and removed from the middle lamella and primary wall. Thus, the fibre surface is partially more active in hydrogen bonding. The addition of cellulose rich pulps to the hardboard fibres has also a positive effect on board strength as it supports the formation of hydrogen bonds.

Hydrogen bonds are not as strong as covalent bonds and the strength of these falls of significantly with increasing moisture present in the bonding area. In amorphous areas hydrogen bonds are broken by water layers. When boards are made up of fibres with low lignin content, e.g. hardwood and grasses, it is necessary to add resins or hydrophobation additives to increase the moisture resistance and dimensional stability. Differences between hardwoods (with 20% lignin) and softwoods (with about 28% lignin) are quite obvious in this context (Back, 1987).

2.9.2 London – van der Waals dispersion forces

Especially oleophilic low molecular weight material, such as extractives inherent in wood or waxes added for hydrophobation, have a very low cohesive strength. These substances have excellent adhesive forces to wood fibres but the cohesive strength of the oleophilic interphase is low. The surface of the fibres is sealed by the additives and the formation of hydrogen and covalent bonds is not or only to a minor degree possible, so just the weak London-van der Waals dispersion forces are acting. Thus, hydrophobation additives lower the strength of fibreboards, but improve the moisture and dimensional stability (Back, 1987).

2.9.3 Covalent bonds

Covalent bonds are formed through crosslinking of the wood polymer chains, to a minor degree during the late phase of the press-drying process and to a larger extent during an eventual post-pressing heat treatment. Lignin appears the most reactive among wood polymers in this type of auto-crosslinking reactions. As covalent bonds are the strongest

inter-fibre bonds and because they are oriented mainly perpendicular to the board plane, their influence on the internal bond strength (z-direction) is significant. A measure for covalent binding is the difference in dry and wet state mechanical strength after 24 hours of water immersion, because of the ruggedness against water layers in comparison to hydrogen bonds. The covalent bonds are only broken to a minor extend by excessive swelling forces. The formation of covalent bonds is favoured by lignin rich fibre surfaces as they are produced through a thermo-mechanical treatment under pressure and temperatures well above the glass transition temperature of moist lignin (approx. 115°C). Such a treatment yields to a fracture in the lignin rich middle lamella (at least 40% lignin) of the cell-wall and therefore produces surfaces high in lignin. This in turn is beneficial for radical and covalent bond formation during the enzyme pre-treatment and hot-pressing step.

Higher pressure and temperature is also beneficial for covalent bonding due to a boosted entanglement of the fibres and better plastification of the wood polymers, so that they are able to move and organise themselves in the board plane (x,y directions). It is also important to ensure a temperature above the glass transition temperature of ligning even in the core of the board during the hot-pressing step. The temperature ranges normally from 150°C in the board core to 220°C when the board is almost dried and ready for release (Back, 1987).

Which type of bonds are predominant in the final board depends on the production process and the chosen parameters. The main influencing factors are:

- Bonding area achieved

- Directional distribution of the fibres and of the bonding area within the board

- Defibration method used

- Pressure/ temperature/ time schedule used at the hot pressing step

- Possible pre– or post-treatment of fibres (e.g.: enzyme treatment, heat treatment)

Discussion of all these factors and possible impacts on board-strength are beyond the scope of this thesis, and the reader is referred to the relevant literature.

2.10 Production of fibreboards with phenol-oxidizing enzymes

Production of boards made with phenol-oxidizing enzymes has only been done at laboratory or semi-industrial scale until now. Main drawbacks of these methods were the weak

moisture resistance and dimensional stability of the boards. Also, the implementation into existing manufacturing plants is not possible without cost-intensive adaptations. Another problem, especially in wet processes, is the loss of reactive lignin and water soluble additives (e.g.: tannic acid) at the mat forming step. Part of the lignin and additives is extracted with water and pressed out when the fibre mat is formed.

Regarding the methods used on a pilot-scale, the application of enzyme in the atmospheric refining stage during the fibre production (Felby et al., 2004) has the advantage that the fibres are not exposed to high temperatures, which may result in premature radical cross-linking and deactivation of the enzyme. Nevertheless, the separate required incubation stage reduces the attractiveness of this approach. An advantage of the method of spraying the enzyme onto fibres in the refiner blowline (e.g. at the UF resin application point) (Widsten et al., 2003, 2004) is that it requires no changes to existing manufacturing facilities and equipment. A drawback of this method is that the conditions prevailing in the blowline (high-temperature and low fibre moisture content) may reduce radical formation and stability in the fibres and deactivate the enzymes (Widsten and Kandelbauer, 2008a).

In the laboratory-scale experiments by Felby et al. (1998) and Kharazipour et al. (1997, 1998), fibres were either incubated with laccase (see Felby et al., 1998; Kharazipour et al., 1997) or peroxidase (see Kharazipour et al., 1998) at low consistency in a water medium at a suitable pH, or laccase solution was sprayed onto the fibres (see Kharazipour et al., 1997). The activated fibres were formed into mats and their water content adjusted to the desired level for wet- and dry-process boards. After that the mats were pressed into 3-6 mm thick fibreboards with densities in the medium-density fibreboard (MDF, 700-800 kg/m^3) or high-density fibreboard (HDF, >800 kg/m^3) range. Unbehaun et al. (2000) manufactured dry-process MDF from rape-seed and pine fibres treated with laccase or enzyme culture media but provided no experimental details (Widsten and Kandelbauer, 2008a).

Chapter 3

Materials and Methods

3.1 Experimental design

During the whole experiments two main methods were used for producing fibreboards. The one was the non-conventional method and the other the conventional method for making fibreboards in the wet process. The defibration of wood chips and the fibre mat preparation was the same for both methods. Both methods will be briefly described and each step will be annotated in detail.

The non-conventional method:

Wood chips of a defined composition were defibrated and pressed into fibre mats. The fibre mats were impregnated with a laccase/ tannin solution and dried/ incubated at 40°C until a moisture content of 50% was reached. Afterwards these impregnated fibre mats were pressed into hardboards at a laboratory press. The so produced boards were tested in terms of density, internal bond strength (IB), modulus of rupture (MOR), modulus of elasticity (MOE) and thickness swelling in water over 24h.

The conventional method:

The defibration was performed the same way as at the non-conventional method. Afterwards the wood fibres were mixed with water and the enzymes and tannin was added to this mixture. Now the whole mixture was stirred for 20min, let rest for 20min and stirred again for additional 20min. Subsequently, the fibres were pressed into mats and the mats immediately pressed into hardboards on a laboratory press.

3.2   Defibration of wood chips

The wood was first chopped up into chips and stored on an outside storage area. Afterwards chips of different wood species were mixed by tipping them into a water blow line with a shovel loader. The so mixed wood chips were stored in a bunker and dried at about 70°C. After this pre-drying step the chips were processed to fibres in a defibrator. The defibrator is a vertical pipe were the temperature and pressure is raised to 170-180°C and 8,5-9,0 bar, respectively. At the bottom of the pipe two grinding disks, one fixed and the other rotating, are situated. Depending on the disk clearance and temperature/pressure in the defibrator fibres of different length and surface properties (amount of activated lignin on surface) can be produced.

The fibres used for the experiments in this study are taken directly after the grinding step. All further working steps are made at laboratory scale. So the whole defibration process is performed at the hardboard plant and the fibres are of the same quality as used for hardboard production in an industrial process. The main components of the fibre mixtures were beech (*Fagus sylvatica*) and spruce (*Picea abies*). Following fibre mixtures were taken from the defibrator:

Mixture 2a: 17% beech, 83% softwood (mainly spruce without bark)
Mixture 4a: 33% beech, 66% softwood without bark (mainly spruce)
Mixture 6:   66% beech, 33% softwood without bark (mainly spruce)

3.3   Preparation of fibre mats

The fibres from the defibrator were filled into barrels of 180L and stored in an horizontal position for two hours to let the fibres cool down and equilibrate the moisture distribution in the barrels. Depending on the hardboard thickness which should be reached, different amounts of fibres were taken for mat preparation, but same amounts for all fibre mixtures were used.

4-4,5 mm boards: 1300g fibres
3-3,5 mm boards: 1050g fibres

The fibres were mixed with hand-warm water in a 30l pot so consistencies of 2,6% and 2,1%, respectively, were reached (calculated on fibre dry-mass with an average moisture content of 40%). The water fibre mixture was stirred for 1-2 min until the fibres were homogenously distributed. The fibres were pressed into mats on a modified cider press. First the water/ fibre mixture was poured into the press and the water drained of until the

cake did not move anymore. In a second step the dewatered fibres were pressed into mats under a pressure of 100 bar for about 2-3 minutes, whilst at the same time the water was sucked of with a vacuum membrane pump.

As soon as possible after pressing the mat with a size of 43x43 cm, the mats were cut into four pieces of 17x17 cm on a disk saw, whereby the mat was placed between two hardboards of the same size so no pieces were sheared off the mats edges during cutting. Immediately afterwards the pieces were sealed in plastic bags to avoid desiccation and stored in a freezer until they were used for impregnation.

3.4   Non-conventional method

The non-conventional method was the most used method in all the experiments made, although it did not really meet the needs of an industrial applicable process but was quite useful in bench scale testing. The method comprised the following steps:

1. The fibre mats made as described before were defreezed and weighed.

2. On basis of the determined weight and moisture content, which was identified by dry mass determination (see below), the amount of enzyme, tannin and additives, like Hydrowax or $CaCl_2$, could be calculated. All chemicals added were calculated on fibre dry-weight.

3. The tannin was weighed out and dissolved in water. Depending on the additives used, the tannin was dissolved in 1000 ml and 750 ml tap water, respectively, if Hydrowax was applied later on.

4. In a subsequent step the pH of the solution was adjusted to a desired value (pH of 4, 5, 6, or 7) with sodium hydroxide (NaOH, 1 mol/L) or sulfonic acid (H2SO4, 48%). The solution was gently stirred all the time.

5. The enzymes were pipetted into the adjusted solution and stirred for further 5 min (or longer in some experiments) with a magnetic stirrer.

6. In the meanwhile the fibre mats were put into wooden molds of 17x17 cm, so they were ready for impregnation.

7. The solution was poured over the mats, which sucked off most of it and were covered with the rest of the mixture.

8. The impregnated mats were put into a compartment drier and dried at 40°C. In some experiments the mats underwent a thermal pre- or post-treatment at higher temperatures.

9. After 70 hours of drying, a moisture content of 50-70% was reached and the mats were taken out of the oven.

10. The dried mats were weighed and an exact determination of the moisture content was possible.

11. The mats were packed into airthight plastic bags and were ready for pressing into hardboards.

All steps from 1-11 were made for each sample separately. For this study, 16 samples a week could be made due to the 70 hours drying time.

3.5   Conventional method

This method corresponds more or less to the way the hardboards are made in an industrial wet process. The fibres were taken from the defibrator and directly used to make hardboards. The steps of cutting and freezing were skipped as well as the impregnation and drying steps. All chemicals and additives were added after the fibres were mixed with water in the 30L pot. In detail, the method comprised the following steps:

1. The fibres were taken from the defibrator and filled into barrels of 180L.

2. The barrels were stored in an horizontal position to let the fibres cool down and equilibrate the moisture distribution all over the barrel.

3. Depending on the required final hardboard thickness, 1300 g or 1050 g were weighted.

4. The necessary amount of tannin, enzyme and additives, like Hydrowax or $CaCl_2$, were calculated on fibre dry-weight, where an average moisture content of 40% was taken into account.

5. Afterwards, the fibres were mixed with 40°C warm water in a pot of 30L (consistencies of 2,6% and 2,1%).

6. In the next step the tannin was first weighed out and added to the mixture and thereafter the enzyme solution.

7. After about 2min of stirring the Hydrowax or $CaCl_2$, also calculated on fibre dry-weight, was added.

8. The whole mixture was stirred for further 20 minutes.

9. The water/ tannin/ enzyme/ additives solution was let rest for 20 more minutes.

10. In a final step, stirring continued for additional 20 minutes. The loss of temperature during this 60 minutes of incubation was less than 3°C.

11. The whole mixture was poured into the modified cider press and pressed into fibre mats of 43x43cm in size at about 100bar for 1-2min. During pressing the pressed out water was sucked of with a vacuum membrane pump.

12. The so made fibre mats were now ready for pressing, as described below.

The conventional method was only applied to a few of the test-points and was performed to have some comparative values of a method similar to the industrial wet process for producing hardboards.

3.6   Pressing of fibreboards

The fibreboards were pressed on a Bürkle LA 160 laboratory press with different press parameters depending on the required hardboard thickness and size of the samples. The press temperatures ranged from 180°C to 200°C. The following press parameters were used:

Press plunger face: 616 cm^2

For hardboards 4-4,5mm:
board size 43x43cm:

p_1 = 114bar	t_1 = 10s	ramp = 5s
p_2 = 18bar	t_2 = 7min	

board size 17x17cm (2 boards):

p_1 = 38bar	t_1 = 10s	ramp = 5s
p_2 = 6bar	t_2 = 7min	

For hardboards 3-3,5 mm:
board size 43x43cm:

p_1 = 133bar	t_1 = 14s	ramp = 10s
p_2 = 20bar	t_2 = 5min	

board size 17x17cm (2 boards):

p_1 = 44bar t_1 = 14s   ramp = 10s

p_2 = 7bar t_2 = 5min

ramp   this is the time the press is given to raise or lower the pressure to the desired values

p_1 pressure at the short high pressure phase

p_2 pressure at the longer low pressure phase

t_1 time p_1 was hold

t_2 time p_2 was hold

The press cycle consisted of three phases. In the first phase the press closed and the pressure was raised to p_1 in a time window which was given by the ramp parameter. The pressure was hold for the time given by t_1. In the second phase the pressure was lowered to p_2 within the ramp time and hold for the time t_2. In the third phase the pressure was lowered to the start value of 2 bar and hold for 5s. Thereafter the press opened and the hardboard could be removed.

3.7   Testing of fibreboards

After pressing size, weight and density of the fibreboards were determined and they were tested with regard to IB strength, modulus of rupture (MOR), modulus of elasticity (MOE) and thickness swelling behaviour.
After density determination the boards were cut into smaller pieces for further tests. Figure 3.1 shows how the samples were cut out.

6 x 5 x 5cm pieces for IB strength (IB) and thickness swelling (TS)

1 x 5 x 15cm piece for bending strength test (MOR/MOE)
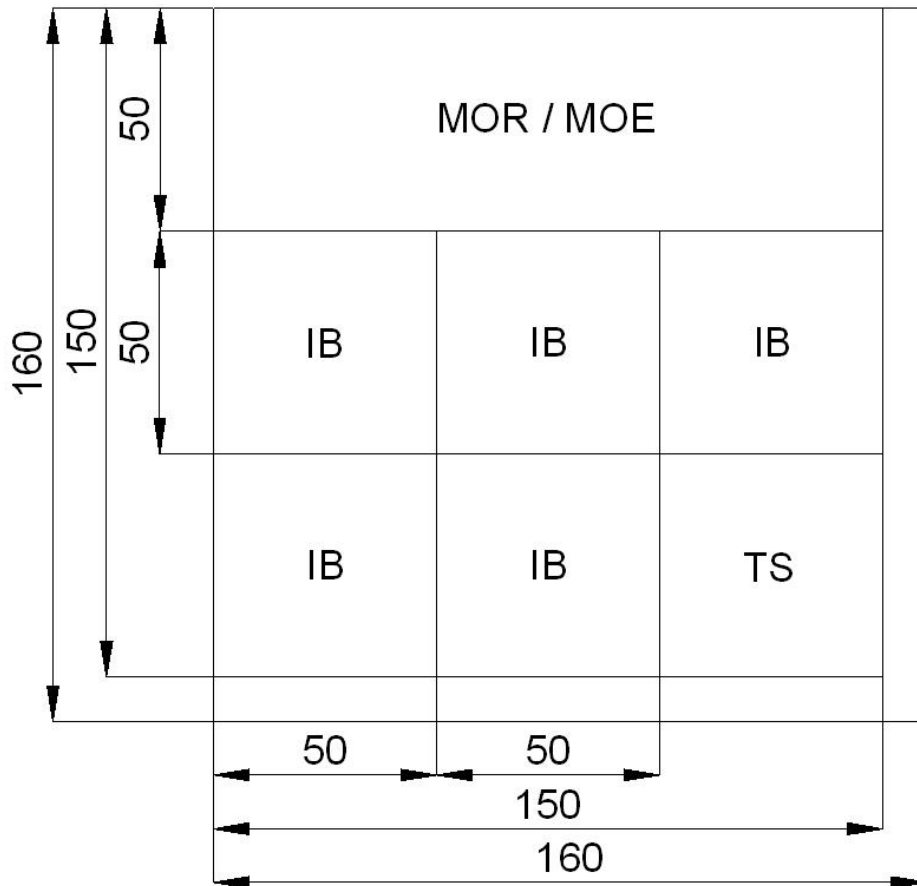
Figure 3.1: Cut out pattern in [mm]

The tables A.1-A.3 show which samples with which fibre mixture were prepared, and the amount of boards made for each sample and fibre mixture. The samples in the tables A.1, A.2 and A.3 were made with the non-conventional method, the samples in table A.4 with the conventional method.

Table A.1 shows the samples made with 500 nkat/g d.f.
Table A.2 shows the samples made with 1000 nkat/g d.f.
Table A.3 shows the samples made of fibremats pretreated with Hydrowax
Table A.4 shows the samples made with the conventional method

For each board IB strength was tested five times. Thickness swell, modulus of ruputure and modulus of elasticity was determined once only.

3.7.1 Density determination

According to an internal laboratory method.

The hardboards were cut into pieces of 16x16 cm (non-conventional method) or 40x40 cm (conventional method). Thereafter the mass and board thickness (as an average of three different measurements on the board) was determined and through the calculation of the board volume the density could be determined.

3.7.2 IB strength test

According to EN 319.

Five samples for IB strength testing were taken from each board. Before gluing the samples onto the brass test blocks the sieve pattern had been grinded of in order to avoid a bursting in the sieve structure. After the samples were glued onto the test blocks and the blocks were cooled down to room temperature, the IB strength could be determined.

3.7.3 Bending strength test

According to EN 310.

The bending strength tests are done with the 15x5cm samples. Before testing the thickness of each sample had been determined (accuracy 0,5mm). According to the thickness of the sample, the support distance on the test device had been adjusted (apparent from a table at the test device).

3.7.4 Thickness swelling test

According to EN 317.

The thickness swelling was determined by storing one sample of 5x5cm for 24h in a water bath tempered to 20°C. The board thickness was determined before and after the test and the thickness swelling in percent compared to the initial thickness could be calculated.

3.8 Calculations

3.8.1 Amount of tannin

Equation (3.1) shows an example how the amount of tannic acid per gramm dry fibre has been calculated.

$$m_{mat} = 302,756g$$
$$DM_{mat} = 36\%$$
$$DM_{mat} = 108,992g$$

$$c_{tannin} = 10\%$$
$$DM_{tannin} = 95\%$$
$$purum_{tannin} = 87,9\%$$

(3.1)

$$c_{tannin} = \frac{DM_{tannin} * c_{tannin}}{100} * \frac{100}{DM_{tannin}}$$
$$c_{tannin} = \frac{108,992 * 10}{100} * \frac{100}{95}$$
$$c_{tannin} = 11,47g$$

11,47g corresponds 9,57g pure tannin or 8,78% dry fibre

3.8.2 Enzyme dose

Equation (3.2), (3.3) and (3.4) show an example how the enzyme dose per g dry fibre has been calculated.

$$m_{mat} = 302,756g$$

$$DM_{mat} = 36\%$$

$$DM_{mat} = 108,992g$$

$$c_{tannin} = 10\%$$

$$DM_{tannin\%} = 95\%$$

$$m_{tannin} = 11,47g$$

See also calculation (3.1)!

(3.2)

$$DM_{tannin} = \frac{c_{tannin} * DM_{tannin\%}}{100}$$

$$DM_{tannin} = \frac{11,47 * 95}{100}$$

$$DM_{tannin} = 10,9g$$

(3.3)

$$DM_{total} = DM_{mat} + DM_{tannin}$$

$$DM_{tannin} = 108,992g + 10,9g$$

$$DM_{tannin} = 119,892g$$

$$A_{lac} = 8121\frac{nkat}{1000\mu l} \quad \text{laccase activity}$$

$$500nkat = x\mu l$$

$$500nkat = \frac{500nkat * 1000\mu l}{8121nkat}$$

$$500nkat = 61,57\mu l$$

$$dose_{lac} = 500\frac{nkat}{\text{g of dry fibre}}$$

$$dose_{lac} = 61,57 * DM_{total}$$

$$dose_{lac} = 61,57 * 119,892$$

$$dose_{lac} = 7382\mu l$$

(3.4)

7382μl enzyme solution were neccessary to get an enzyme activity of 500nkat/g dry fibre.

3.8.3   Amount of Hydrowax

Equation (3.5), (3.6) and (3.7) show an example how the amount of Hydrowax per g dry fibre has been calculated.

$$m_{mat} = 304,648g$$
$$DM_{mat} = 37,7\%$$
$$DM_{mat} = 114,852g$$

$$c_{tannin} = 10\%$$
$$DM_{tannin\%} = 95,24\%$$
$$m_{tannin} = 12,06g$$

See also calculation (3.1)!

(3.5)

$$DM_{tannin} = \frac{c_{tannin} * DM_{tannin\%}}{100}$$
$$DM_{tannin} = \frac{12,06 * 95,24}{100}$$
$$DM_{tannin} = 11,49g$$

(3.6)

$$DM_{total} = DM_{mat} + DM_{tannin}$$
$$DM_{tannin} = 114,852g + 11,49g$$
$$DM_{tannin} = 126,338g$$

$$HW_{conc} = 60\%$$
$$dose_{wax} = 2\frac{\%}{\text{g of dry fibre}}$$

$$m_{wax} = DM_{total} * \frac{dose_{wax}}{100} * \frac{100}{HW_{conc}}$$
$$m_{wax} = 126,338 * \frac{2}{100} * \frac{100}{60}$$
$$m_{wax} = 4,21g$$

(3.7)

3.8.4 Amount of calcium-chloride CaCl$_2$

Equation (3.8) shows an example how the amount of CaCl$_2$ per g dry fibre has been calculated.

$$m_{mat} = 284,440g$$
$$DM_{mat} = 37,7\%$$
$$DM_{mat} = 107,234g$$

$$dose_{CaCl_2} = 5\frac{\%}{\text{g of dry fibre}}$$

(3.8)

$$m_{CaCl_2} = DM_{mat} * \frac{dose_{CaCl_2}}{100}$$
$$m_{CaCl_2} = 107,234 * \frac{5}{100}$$
$$m_{CaCl_2} = 5,36g$$

3.9 Additional methods

3.9.1 Dry mass determination of fibremats

Equipment: Sartorius MA 30 moisture analyzer

                             Heraeus UT 6 drying oven

The dry mass was determined at 103°C and 24h in a compartment drier. This dry mass determination was done for each batch of fibre mats made, whereby each time two determinations were performed at the same time. This data was used to calculate the necessary amount of laccase, tannin and additives, like Hydrowax or CaCl$_2$. The determination of dry mass was important for calculation and weighing out of the right amount of chemicals used for impregnation. Equation (3.9) shows the calculation of consistency.

$$\text{consistency} = \frac{\text{dry mass of wood}}{\text{dry mass of wood + mass of water or buffer}}$$

(3.9)

$$10\% \text{ consistency} = \frac{\frac{1}{10}\text{oven dry wood}}{\frac{9}{10}\text{water or buffer}}$$

3.9.2 Determination of enzyme activity

The volume of a disposable cuvette was 2500 μl.

The laccase activity was determined by a dynamic method with ABTS (Niku-Paavola et al., 1988). The assay was carried out as follows:

Equipment: Shimadzu UV-1800 spectrophotometer

Jensen Systems SensoLab CDV with Schott pH-elcetrode SteamLine SL80-225 pH

Used chemicals: Succinic acid, ACS reagent (Sigma Aldrich), purum = 99%, M = 118,09 g/mol

ABTS (Sigma Aldrich), purum = 98%, M = 548,68 g/mol

Myceliophtora thermophila laccase enzyme (Novoyzmes) 51002(frozen)

Made solutions: ABTS solution c= 275 mg/25 ml in distilled water

25 mM succinate buffer, pH = 4,5 adjusted with NaOH

Procedure:

1917 μl of enzyme dilution (diluted in succinate buffer) was combined with 583 ìl ABTS reagent in a disposable cuvette. The extinction increase was measured over 120 sec every second at 436 nm. The spectrophotometer was zeroed with ABTS (583 μl)/ succinate buffer (1917 μl) solution. Every dilution was measured two times and absorption values were recorded by the spectrophotometer every half second.

Dilution of enzyme:

Three different laccase enzyme-solutions were tested and each enzyme-solution was first diluted 1:10 in 2000 μl buffer.

The following dilution steps were 1:100 and 1:1000. From the last dilution (1:1000) the dilutions of 1:40 000, 1:50 000 and 1:60 000 were made for each enzyme-solution. The dilutions of 1:40 000-1:60 000 were directly made in the cuvette.

Table 3.1: Dilution scheme

Dilution	μl Pure enzyme/ Prev dilution	μl Buffer	Total volume
1:10	200	1800	2000 μl
1:100	20	180	200 μl
1:1000	30	270	300 μl
enzyme solution for the following dilutions was taken from the 1:1000 dilution			
1:40000	48	1869	1917 μl
1:50000	38	1879	1917 μl
1:60000	32	1885	1917 μl

Determination of activity:

The activity was calculated according to the formula:

$$A\left[\frac{\text{nkat}}{\text{ml dilution}}\right] = 16,67 * \frac{V_{total}}{V_{enzyme}} * \frac{\Delta E}{\epsilon * d} \tag{3.10}$$

A	Activity
V_{total}	Total sample volume
V_{enzyme}	Volume of the enzyme solution
ΔE	Change in extinction over time (e.g.: 1 min)
ϵ	Molar extinction coefficient, ϵ = 29 mmol^{-1}cm^{-1}
d	Thickness of absorbing sample solution (normally 1 cm)
16,67	Relation between 1 U and 1 nkat (1U = 16,67 * 10^{-9} kat)

Activity in [nkat/ ml pure enzyme solution]:

$$A_{pure} = 16,67 * \frac{V_{total}}{V_{enzyme}} * \frac{\Delta E}{\epsilon} * \text{dilution factor} \tag{3.11}$$

where V_{total} = 2500 μl, V_{enzyme} = 1917 μl and ϵ = 29 mmol^{-1}cm^{-1}

Equation (3.12) shows the conversion between Units and katal.

$$1kat = 1mol/s = 1 * 10^{-6}\mu mol/s = 60 * 106\mu mol/min$$
$$1U = 1\mu mol/min = 1 * 10^{-6}mol/min =$$
$$= 1,667 * 10^{-8}mol/s = 16,67 * 10^{-9}mol/s$$

$$\tag{3.12}$$

$$1U = 16,67 * 10^{-9}kat = 16,67nkat$$
$$1kat = 6 * 10^{-7}U = 60mU$$
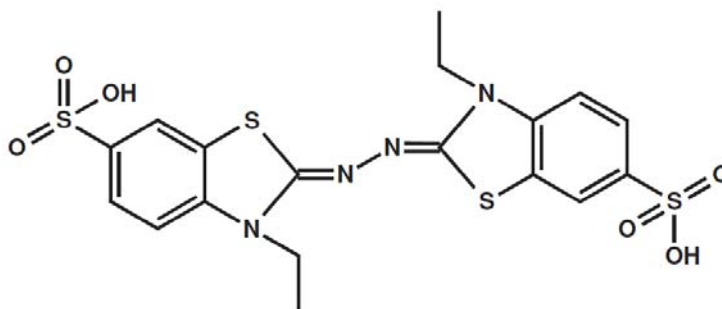
Figure 3.2: ABTS = 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic) acid

3.9.3   Calibration of pipettes

Before the beginning of the experiments and in regular intervals of 8 weeks the pipettes were calibrated with water. The calibration took place at a lab scale with an accuracy of $\pm 0,01$ mg. Each calibration was performed with a volume that lay in the middle of the pipettable volume-range of the pipettor.

Choosen volumes:

Table 3.2: Volumes pipetted

Pipette	Pipetted volume
0,5-10μl	5μl
5-50μl	25μl
10-100μl	50μl
20-200μl	100μl
100-1000μl	500μl
1-5ml	2,5ml

Equipment: Mettler Toledo lab scale (d = 0,01mg)

Procedure:

Each volume was pipetted 10 times and the changes in mass were recorded. The mass differences between each step could be calculated and transformed to the corresponding volume through the density of the water at the temperature the calibration was made. Now the difference between the real and the theoretical volume could be calculated and the arithmetic mean value of the whole set of 10 pipetted volumes could be determined. Further information about calibration procedure and allowed inaccuracy of the pipettes can be gathered from the instruction manual.

Chapter 4

Results

4.1   Sample plan

On basis of pre-tests the following standard conditions where defined:

Table 4.1: Standard conditions

Laccase dose	500 nkat/g dry fibre
Tannic acid concentration	10 %/g dry fibre
Fibre mixture	4a
pH	6
Drying temperature	40°C
Press temperature	190°C

In comparison to these standard conditions, the parameters where changed and the influence of the changes studied. The following parameters where changed:

- Fibre mixture, 2a; 4a and 6 ,respectively

- Laccase dose of 0; 500 or 1000 nkat/g dry fibre

- Tannic acid concentration of 0, 2.5; 5; 7.5; 10; 12.5 or 15 %/g dry fibre

- The pH of impregnation solution of 4; 5; 6 or 7

- Addition of Hydrowax of 1; 2 or 5 %/g dry fibre

- Change in press temperature to 180; 190 or 200°C

- Post-treatment through drying at $140°$C for 2h

- Different pre-incubation time of 30 and 60 min

For some boards instead of the non-conventional method, the conventional method was used (see below). In the following tables the results of the experiments are presented. Tables 4.2, 4.3 and 4.4 describe the boards made with 500 nkat/g d.f. laccase dose, followed by tables 4.5, 4.6 and 4.7 describing the boards with 1000 nkat/g d.f. laccase dose, table 4.8 with the boards made with the conventional method and at the end table 4.9 with the boards made from mats pre-treated with additives. An overview which experiment was made with which fibre mixture is given in the appendix in the sample plan. The following abbreviations are used:

FM	Fibre mixture
IB	Internal bond strength
MOR	Modulus of rupture
MOE	Modulus of elasticity
TS	Thickness swelling
Density	Density of the hardboard
Moisture	Moisture after drying/ incubation step
Thickness	Thickness of the hardboard

4.2 Boards made with 500 nkat/g d.f. laccase dose

4.2.1 Fibre mixture 2a

Table 4.2: Boards made from fibre mixture 2a and 500 nkat/g d.f.

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,54	23,1	2676	100	891	79	2,70
noTA_500	0,94	50,1	4466	58	918	81	3,33
5TA_500_1HW_imp	0,67	28,8	3124	51	922	60	2,57
5TA_500_2HW_imp	0,71	33,1	2707	50	907	60	2,67
5TA_500_5HW_imp	0,74	29,1	2882	45	979	86	3,20
7,5TA_500_1HW_imp	1,12	29,4	3136	54	952	84	3,33

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, **u** moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
7,5TA_500_2HW_imp	1,07	27,2	2870	46	955	82	3,43
7,5TA_500_5HW_imp	0,99	29,6	3512	31	960	82	3,50
10TA_noE	0,84	43,2	3608	60	947	78	3,33
10TA_500	1,22	46,9	3941	49	946	78	3,37
10TA_500_pH4	1,13	58,3	4684	55	980	81	3,37
10TA_500_1HW_imp	0,93	28,9	2990	42	905	75	3,07
10TA_500_2HW_imp	0,93	34,5	3333	43	942	72	3,67
10TA_500_D1402h	0,95	58,8	4860	51	939	43	3,13
10TA_500_pH4_D1402h	1,26	61,4	5145	41	991	58	3,47
10TA_500_pH4_1HW_imp	1,10	32,1	3542	41	965	82	3,50
10TA_500_pH4_1HW_imp_D1402h	0,93	36,4	4281	42	952	51	3,57
10TA_500_pH4_2HW_imp_D1402h	1,10	36,8	3890	38	986	68	3,53

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

4.2.2 Fibre mixture 4a

Table 4.3: Boards made from fibre mixture 4a and 500 nkat/g d.f.

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_500	0,85	37,2	3522	70	914	59	4,23
2,5TA_500	0,78	33,6	3566	86	917	74	4,13
2,5TA_500_pH4	0,82	43,1	3943	67	886	73	3,47
2,5TA_500_1HW_imp	0,76	35,3	3866	83	911	84	3,33
2,5TA_500_2HW_imp	0,92	37,8	3793	62	923	79	3,30
2,5TA_500_5HW_imp	0,76	36,4	3458	55	921	80	3,30
5TA_500	1,09	32,2	3543	60	899	55	4,38
5TA_500_1HW_imp	0,94	42,5	4061	56	951	73	3,27
5TA_500_2HW_imp	0,84	29,8	3833	49	921	53	4,53
5TA_500_5HW_imp	0,76	41,6	3802	52	901	77	3,33

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
7,5TA_500	0,98	32,2	3529	55	896	57	4,58
7,5TA_500_pH4	1,15	49,5	3062	50	929	77	3,27
7,5TA_500_1HW_imp	0,83	37,8	3458	54	923	81	3,10
7,5TA_500_2HW_imp	0,83	40,1	3682	52	945	82	3,30
7,5TA_500_5HW_imp	0,95	34,6	3323	53	952	59	3,20
7,5TA_500_pH4_D1402h	0,88	41,1	3526	54	930	70	3,40
10TA_noE	0,74	28,4	3400	49	930	44	4,33
10TA_500	1,41	42,5	4223	47	933	58	4,27
10TA_500_pH4	1,14	49,0	4629	35	970	61	4,20
10TA_500_pH5	1,12	42,8	4261	49	951	61	4,48
10TA_500_pH7	0,79	35,2	4182	62	944	53	4,83
10TA_500_1HW_imp	0,90	42,4	4290	33	943	80	3,43
10TA_500_2HW_imp	0,84	29,1	3433	44	943	59	3,57
10TA_500_5HW_imp	0,92	32,7	3227	48	917	58	3,37
10TA_500_5CaCl2_imp	0,61	21,4	3353	44	954	41	4,53
10TA_500_30min_preinc	1,04	45,8	4118	57	911	59	3,13
10TA_500_60min_preinc	1,14	39,3	3914	53	937	59	3,20
10TA_500_D1402h	1,06	42,3	4024	44	941	68	3,65
10TA_500_pH4_D1402h	0,74	38,0	3467	49	943	44	3,48
10TA_500_P180	1,18	43,6	4285	54	949	66	4,37
10TA_500_P200	0,87	34,8	3619	52	922	56	4,70
10TA_500_pH4_1HW_imp	1,00	34,6	3823	46	928	80	3,10
10TA_500_pH4_2HW_imp	0,89	36,4	3518	52	926	79	3,40
10TA_500_pH4_1HW_imp_D1402h	0,93	41,8	4128	51	919	52	3,43
10TA_500_pH4_2HW_imp_D1402h	0,96	35,9	3845	50	928	46	3,33
12,5TA_500	1,50	43,3	4059	41	923	65	4,43
12,5TA_500_pH4	1,00	54,4	4652	50	907	70	3,80
12,5TA_500_5CaCl2_imp	0,61	32,6	4551	38	963	35	4,67
12,5TA_500_P200	0,45	22,2	2367	112	868	20	4,73
15TA_500	1,37	54,6	4868	43	945	48	4,50
15TA_500_pH4	1,01	56,4	4526	46	914	60	3,63

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

4.2.3 Fibre mixture 6

Table 4.4: Boards made from fibre mixture 6 and 500 nkat/g d.f.

Sample code	IB [N/mm²]	MOR [N/mm²]	MOE [N/mm²]	TS [%]	ρ [kg/m³]	u [%]	d [mm]
noTA_noE	0,40	32,0	3697	114	870	73	3,03
noTA_500	0,78	35,9	3140	70	892	72	3,10
2,5TA_500_1HW_imp	1,26	27,1	3316	87	906	81	3,47
5TA_500_1HW_imp	1,03	21,5	2629	78	890	82	3,37
5TA_500_2HW_imp	1,06	23,2	2639	69	907	80	3,43
5TA_500_5HW_imp	1,01	20,5	2876	65	889	76	3,47
7,5TA_500_1HW_imp	1,06	23,3	3006	62	894	77	3,47
7,5TA_500_2HW_imp	0,73	20,4	2630	55	855	68	3,57
7,5TA_500_5HW_imp	0,98	24,2	2597	57	879	69	3,77
10TA_noE	0,55	29,4	4063	60	920	63	3,50
10TA_500	0,82	36,6	3715	56	916	75	3,63
10TA_500_pH4	0,88	32,7	3360	62	932	76	3,80
10TA_500_1HW_imp	1,08	32,9	3349	53	918	76	3,40
10TA_500_2HW_imp	0,86	20,6	2601	53	874	76	3,37
10TA_500_5HW_imp	1,30	27,1	3320	37	901	79	3,73
10TA_500_D1402h	0,84	36,4	3435	56	901	53	3,50
10TA_500_pH4_D1402h	0,63	28,0	2873	62	878	42	3,57
10TA_500_pH4_1HW_imp	1,10	31,2	3094	51	906	68	3,70
10TA_500_pH4_2HW_imp	1,15	26,6	2647	49	883	68	3,33

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

4.3 Boards made with 1000 nkat/g d.f. laccase dose

4.3.1 Fibre mixture 2a

Table 4.5: Boards made from fibre mixture 2a and 1000 nkat/g d.f.

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,54	23,1	2676	100	891	79	2,70
noTA_1000	0,96	43,4	4182	61	933	82	3,00
10TA_1000	1,34	59,7	4220	47	969	75	3,10
10TA_1000_pH4	1,00	60,3	5048	42	953	82	3,47
10TA_1000_1HW_imp	1,13	37,1	3799	36	932	81	2,57
10TA_1000_2HW_imp	1,18	43,4	4075	48	985	82	3,33
10TA_1000_D1402h	0,85	49,2	4605	47	923	37	3,40
10TA_1000_pH4_D1402h	1,23	47,1	4463	40	986	60	3,43

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

4.3.2 Fibre mixture 4a

Table 4.6: Boards made from fibre mixture 4a and 1000 nkat/g d.f.

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_1000	0,86	41,1	4002	62	879	72	3,30
2,5TA_1000	0,71	34,0	3432	83	908	72	4,20
5TA_1000	0,79	37,0	3561	61	919	77	4,17
5TA_1000_2HW_imp	0,84	24,2	2841	47	915	73	4,37
7,5TA_1000	0,93	43,3	4384	60	928	79	4,30
7,5TA_1000_2HW_imp	0,77	25,9	2707	40	922	70	4,20
7,5TA_1000_pH4_D1402h	0,87	40,5	3403	51	940	67	3,40
10TA_1000	1,44	55,3	4625	52	939	65	3,95
10TA_1000_pH4	1,16	64,4	5359	40	949	82	3,40

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
10TA_1000_1HW_imp	1,38	46,9	4255	50	918	73	3,83
10TA_1000_2HW_imp	0,84	28,1	3468	27	920	51	4,37
10TA_1000_5HW_imp	1,20	27,7	3972	28	962	69	4,80
10TA_1000_D1402h	0,98	46,2	4075	49	932	74	3,68
10TA_1000_pH4_D1402h	1,05	45,7	4624	43	950	46	3,63
12,5TA_1000	1,06	49,5	4690	44	926	76	4,23
12,5TA_1000_pH4	1,12	46,9	4011	44	890	62	3,73
15TA_1000	1,28	40,3	3883	47	939	75	4,33
15TA_1000_pH4	1,23	48,2	4417	46	959	69	3,60

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

4.3.3   Fibre mixture 6

Table 4.7: Boards made from fibre mixture 6 and 1000 nkat/g d.f.

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,40	32,0	3697	114	870	73	3,03
noTA_1000	0,79	36,9	3789	73	888	66	3,47
10TA_1000	0,88	39,8	3656	53	915	75	3,57
10TA_1000_pH4	0,90	35,0	3497	58	902	76	3,60
10TA_1000_D1402h	0,84	36,7	3321	61	896	45	3,52
10TA_1000_pH4_D1402h	1,10	36,0	3487	49	927	61	3,53
10TA_1000_pH4_D1402h	0,95	33,8	3372	53	899	52	3,58

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

4.4 Boards made with the conventional method

Table 4.8: Boards made with the conventional method

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE_conv	0,63	26,5	2846	100	904	–	4,27
noTA_500_conv	0,74	26,5	2932	88	904	–	4,70
10TA_noE_conv	0,70	25,2	2759	74	923	–	4,50
10TA_500_conv	1,05	39,4	3949	95	931	–	4,47
10TA_500_1,5HW_conv	1,26	36,1	3756	88	901	–	4,43
10TA_500_2HW_conv	0,60	21,3	2663	33	925	–	4,37
10TA_500_5CaCl2_conv	1,13	38,3	3501	81	903	–	4,20

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, **u** moisture content fibre mat, **d** board-thickness

4.5 Boards made from mats pre-treated with additives

Table 4.9: Boards made from mats pre-treated with additives

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
7,5TA_1000_1,5HW_pre	0,23	28,6	3358	68	877	42	4,33
7,5TA_1000_2HW_pre	0,23	27,6	3312	42	866	64	4,23
7,5TA_1000_5CaCl2_pre	0,95	37,3	4219	77	874	42	4,50
10TA_500_1HW_pre	0,74	41,2	3978	55	944	63	4,30
10TA_500_1,5HW_pre	0,49	32,4	3903	34	926	57	4,30
10TA_500_2HW_pre	0,28	28,5	3277	46	919	48	4,53
10TA_500_5CaCl2_pre	1,04	35,9	3773	65	943	48	4,57
10TA_500_1HW_pre_2h104pre	0,47	33,5	4408	67	873	50	4,50
10TA_500_1,5HW_pre_2h104pre	0,33	28,9	3965	62	875	57	4,37
10TA_500_2HW_pre_2h104pre	0,32	27,2	3700	33	886	59	4,50
10TA_1000_1HW_pre	0,49	35,8	3980	63	888	62	4,43
10TA_1000_1,5HW_pre	0,21	35,4	4205	45	880	49	4,23

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, **u** moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
10TA_1000_2HW_pre	0,31	31,9	3982	34	909	74	4,30
10TA_1000_5CaCl2_pre	1,21	39,7	4034	56	877	56	4,47

Abbreviations: **IB** internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, **u** moisture content fibre mat, **d** board-thickness

Chapter 5

Discussion

In this chapter, the effect and influence of variations in the production parameters onto the measured board properties internal bond strength (IB), modulus of rupture (MOR), modulus of elasticity (MOE) and thickness swelling (TS) will be discussed and illustrated through diagrams. The used datasets for the diagrams are summarized in the appendix.

Wood is a natural compound and thus, it is normal that boards made from two fibre mixtures produced the same way with the same hardwood to softwood relations will always give boards with different properties. So if someone would conduct the experiments described here the results could be the same, slightly, or in the worst case, totally different. For that reason the discussion of the influence of the parameter changes will be done from a broader perspective and the outcome of the consideration can be seen as a rough guideline in which direction further experiments should be conducted.

5.1 Effect of enzyme dose and tannin concentration

These two parameters work together, as the added tannic acid functions as a substrate for the enzymes and enhances the radical formation during the drying/ incubation step. The effect of laccase dose was studied based on two different doses (500 and 1000 nkat/g d.f.) and the tannic acid concentration was raised from 0 to 15%/g d.f. in steps of 2,5%. Figure 5.1 shows the correlation of tannic acid concentration and laccase dose. The results presented here were all received from boards made from mats of fibre mixture 4a. The results used in the following diagram are shown in the appendix.

As it can be seen, the effect of higher enzyme dose is relatively small and the increase in IB strength is mainly correlated to an increase in the amount of tannic acid. It is also obvious that the IB strength level of 1000 nkat/g d.f. treated samples is the same or less than the one of 500 nkat/g d.f. samples. This can be explained by an enzyme

overload of the fibres and a competing of radical formation and destruction reactions. In summary it can be said that an increase in tannin concentration increases the IB strength until a level of about 1,4-1,5 N/mm^2 is reached. Above a concentration of 10% tannic acid the enhancement of IB strength is relatively low and the additional costs are in no relation to the gathered improvement. A raise in enzyme dose does not bring any effect and is not a practicable way for board improvement.

Figure 5.2 demonstrates the dependency of modulus of rupture (MOR) and modulus of elasticity (MOE) from tannin concentration and laccase dose. As well as the IB strength MOR and MOE can be improved with raised tannin content, but stagnate at a level of about 50 N/mm2 and 4500 N/mm2. This level is reached with concentrations of about 10% tannic acid and there is no effect if the laccase dose is raised, as discussed before, or this has even an adverse effect on MOR and MOE. A correlation between MOR and MOE, which is not always the case, is also visible.

Figure 5.3 shows the thickness swelling after 24 hours of water immersion at 20°C. The thickness swelling is given as a percentage of the initial board thickness, which is given on the secondary y-axis. The board thicknesses are quite similar, so the thickness swelling is comparable for each tannin concentration. As in the diagrams before the thickness swelling improves until a concentration of 10% tannic acid is reached and barley drops with a further raise in tannin content.
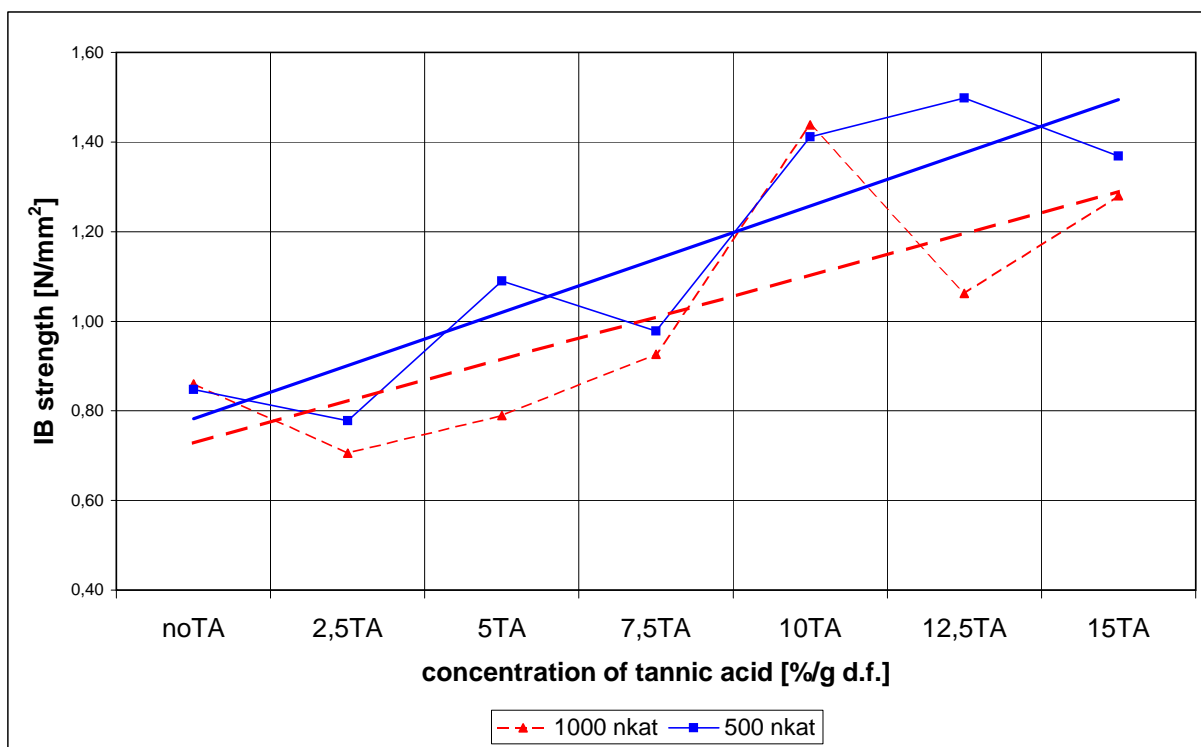

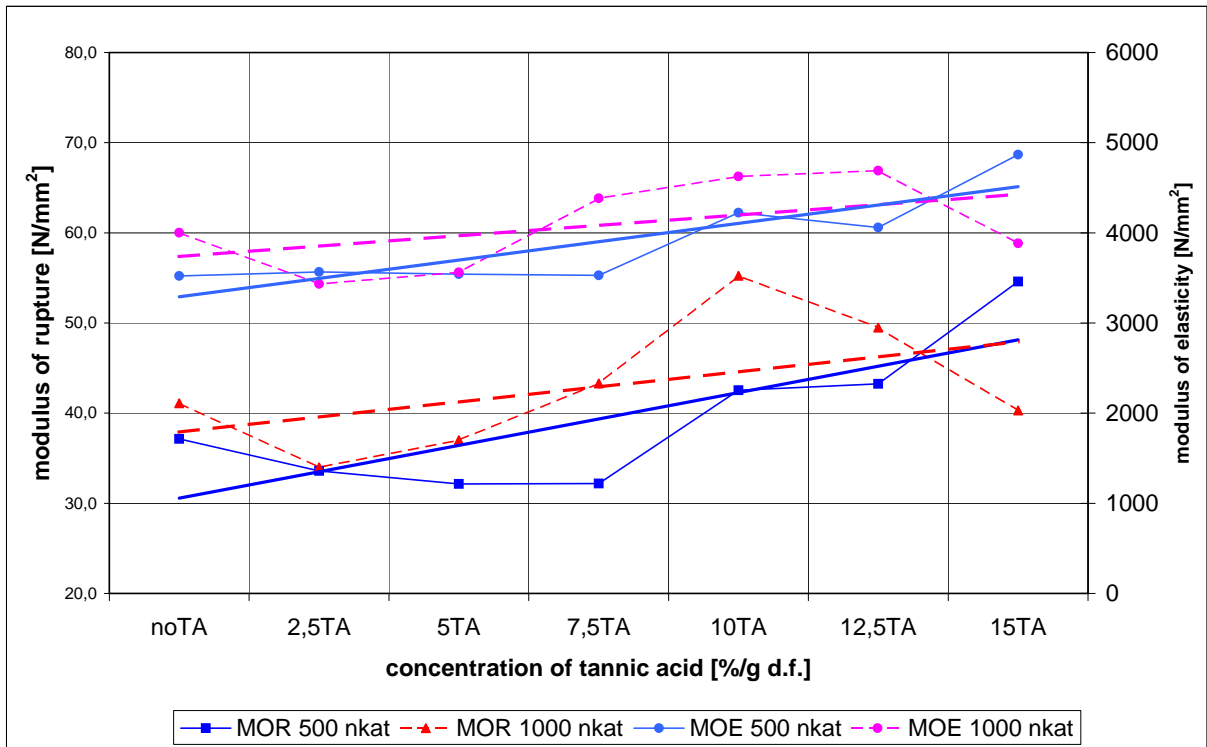Figure 5.1: IB strength depending on laccase dose and tannic acid concentration

Figure 5.2: MOR and MOE in correlation to laccase dose and tannin concentration
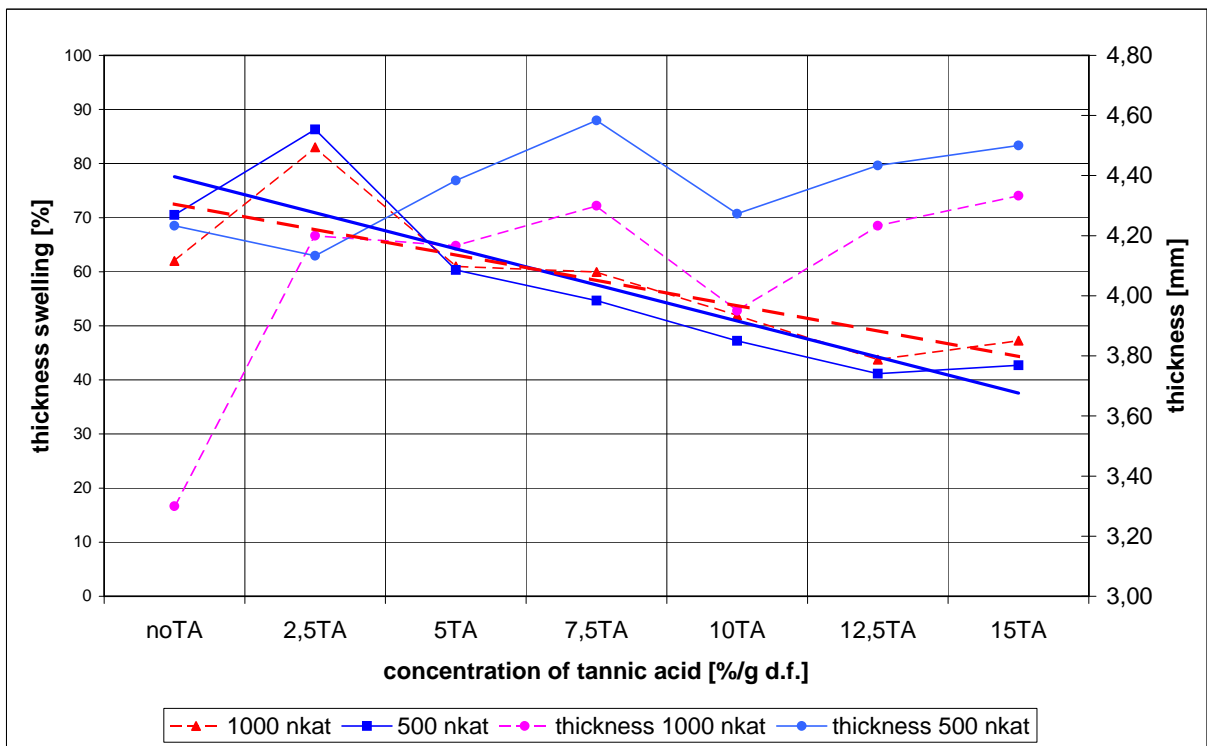
Figure 5.3: Thickness Swelling in comparison to laccase dose and tannin concentration

5.2   Effect of different pH

The effect of pH was studied at different tannin concentrations and with different fibre mixtures. The following diagrams illustrate the influence of the pH shift onto the measured properties (IB, MOR, MOE, thickness swelling). The diagrams were split up into two groups (500 and 1000 nkat) and in each group different tannin concentrations with different pH values were compared (e.g.: 7,5% tannic acid at pH 6 and 4). The values for boards made without any tannic acid or only with enzyme addition were added as well.

Figure 5.4 and figure 5.5 illustrate the IB strength shifting with changes in the pH of the impregnation solution. Alltogether the values are the best for pH 6, or the same as for other pH values. Significant drops are visible were no enzyme was used (noTA_noE, 10TA_noE) and mixtures 2a and 4a have similar values, whereas boards made from mixture 6 have worse results.

Figure 5.6 and figure 5.7 display the MOR and MOE values with changing pH. In contrast to the IB strength values, the best results are gathered with boards impregnated with a solution of pH 4. This can be said for 500 nkat as well as for 1000 nkat/g d.f. treated boards. The MOR values are changing markedly whereas the MOE values are shifting between 4000 and 500n N/mm^2 and not directly correlate with the MOR values. It can also be seen that MOR and MOE values do not correlate with the IB strength values, and boards with low IB strength achieve better results at MOR/MOE or reverse. For the thickness swelling (TS) no tendencies could be found and the pH shift does not really influence this parameter (figures 5.8 and 5.9). The improvement of TS goes hand in hand with a raise in tannic acid concentration and reaches the best values at 10TA_pH4. These results are similar to the ones illustrated in figure 5.3, and a direct correlation between TS and pH cannot be postulated.

As a final conclusion to pH adjustment it is noteworthy, that the pH of the solution always drops to a lower pH because of the acidification through the impregnated wood fibres. In summary it has been shown that a pH between 4 and 6 is most beneficial for the enzyme activity of laccase, which has also been observed in other studies (see Widsten et al. (2009)). This corresponds to the Novozymes (Novozym 51003) technical bulletin as well, where the highest enzyme activity was achieved under close-to-neutral conditions.
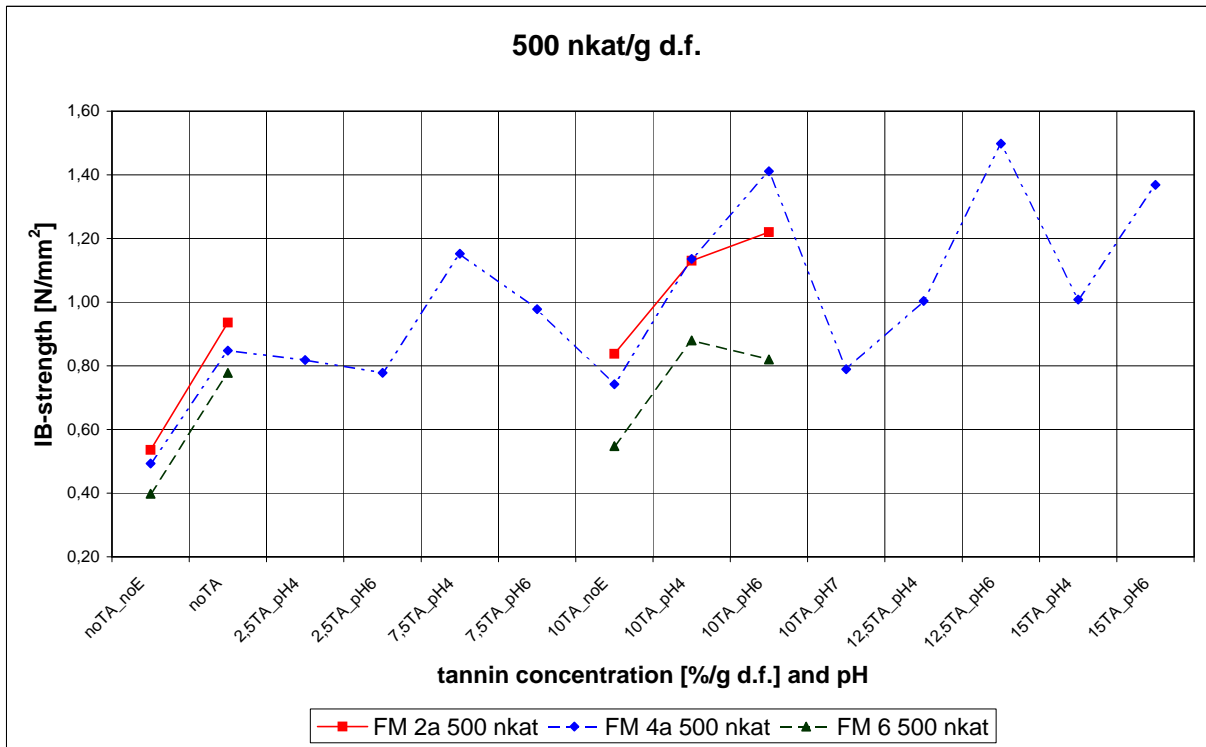
Figure 5.4: IB strength at diff. pH at 500 nkat/g d.f.
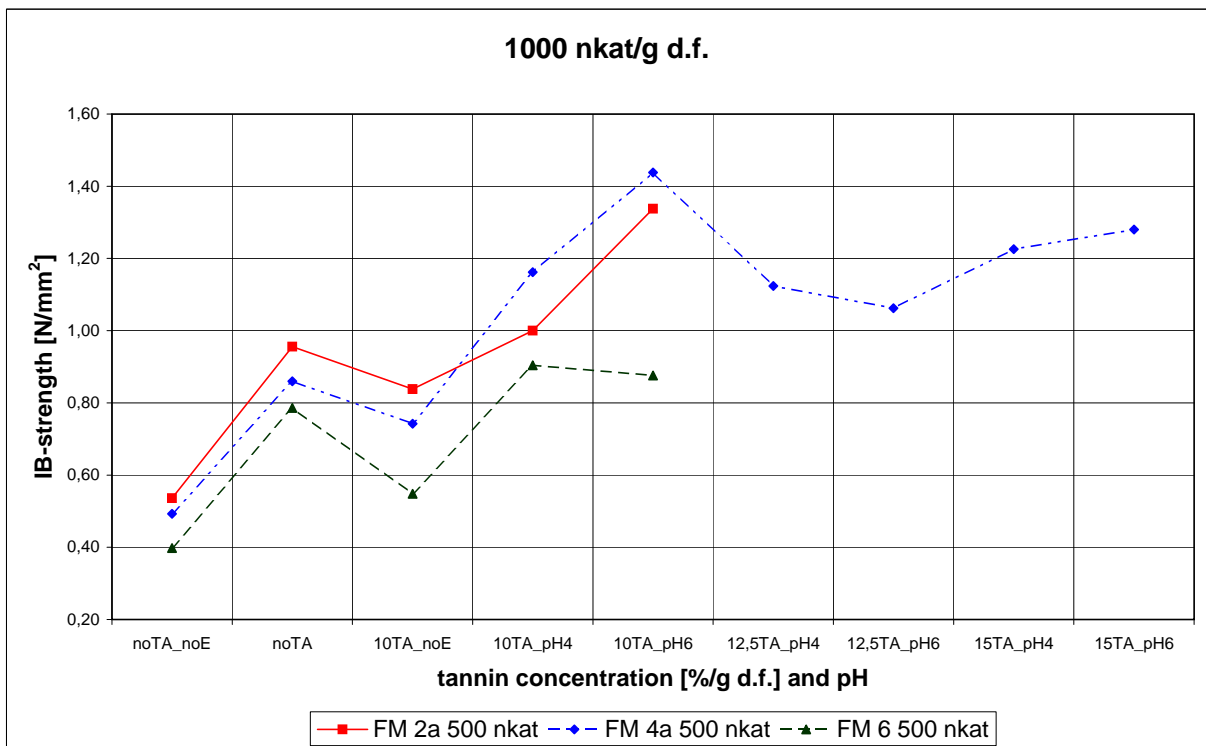
Figure 5.5: IB strength at diff. pH at 1000 nkat/g d.f.
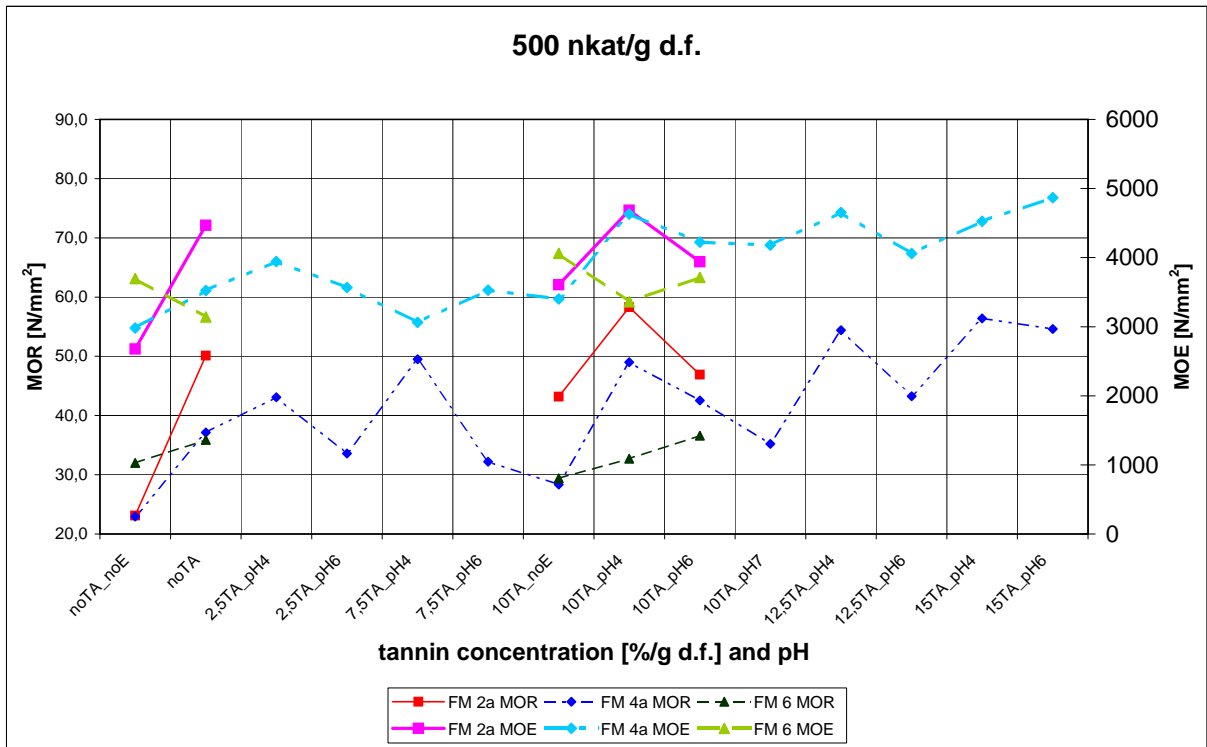
Figure 5.6: MOR and MOE in correlation to diff. pH at 500 nkat
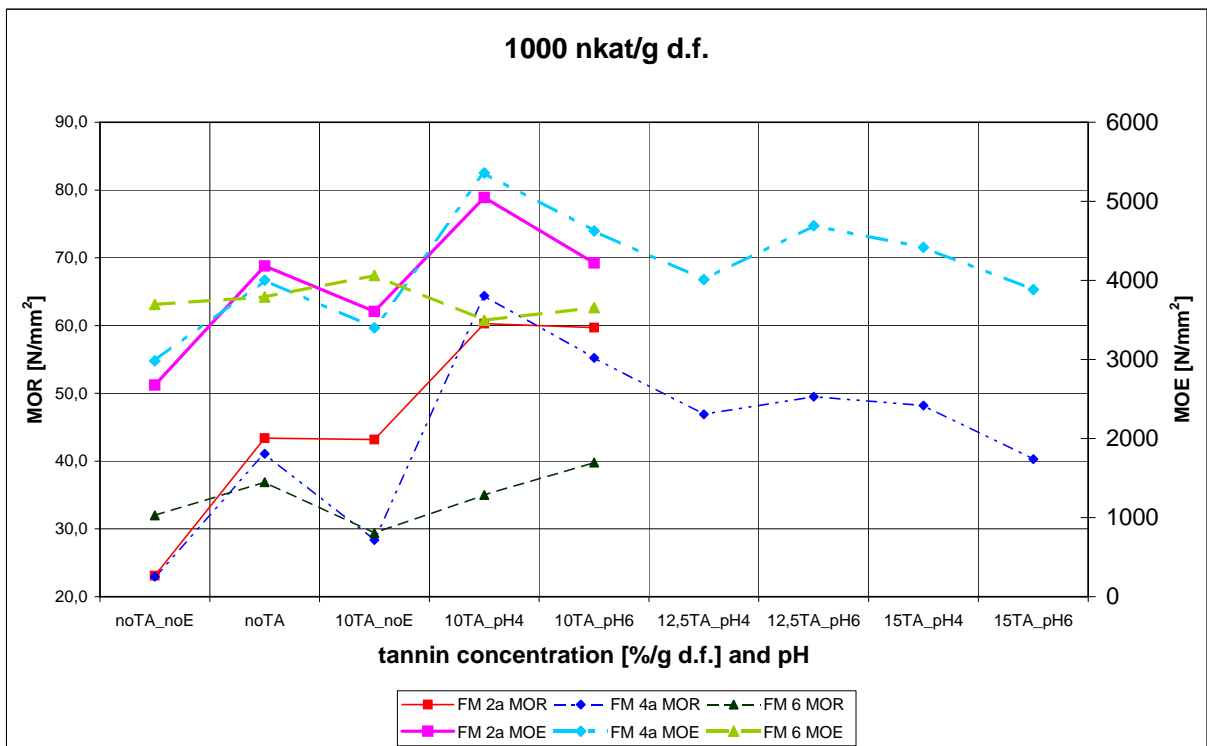
Figure 5.7: MOR and MOE in correlation to diff. pH at 1000 nkat
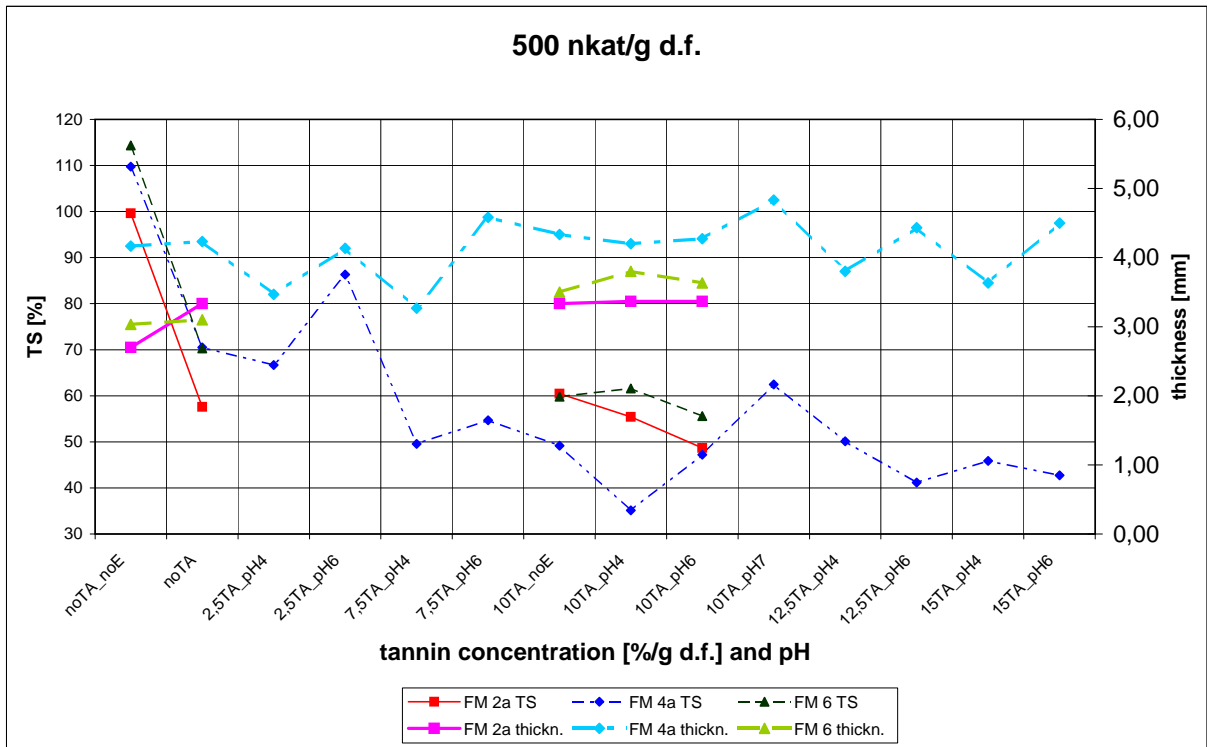
Figure 5.8: Thickness Swelling in corr. to diff. pH at 500 nkat/g d.f.
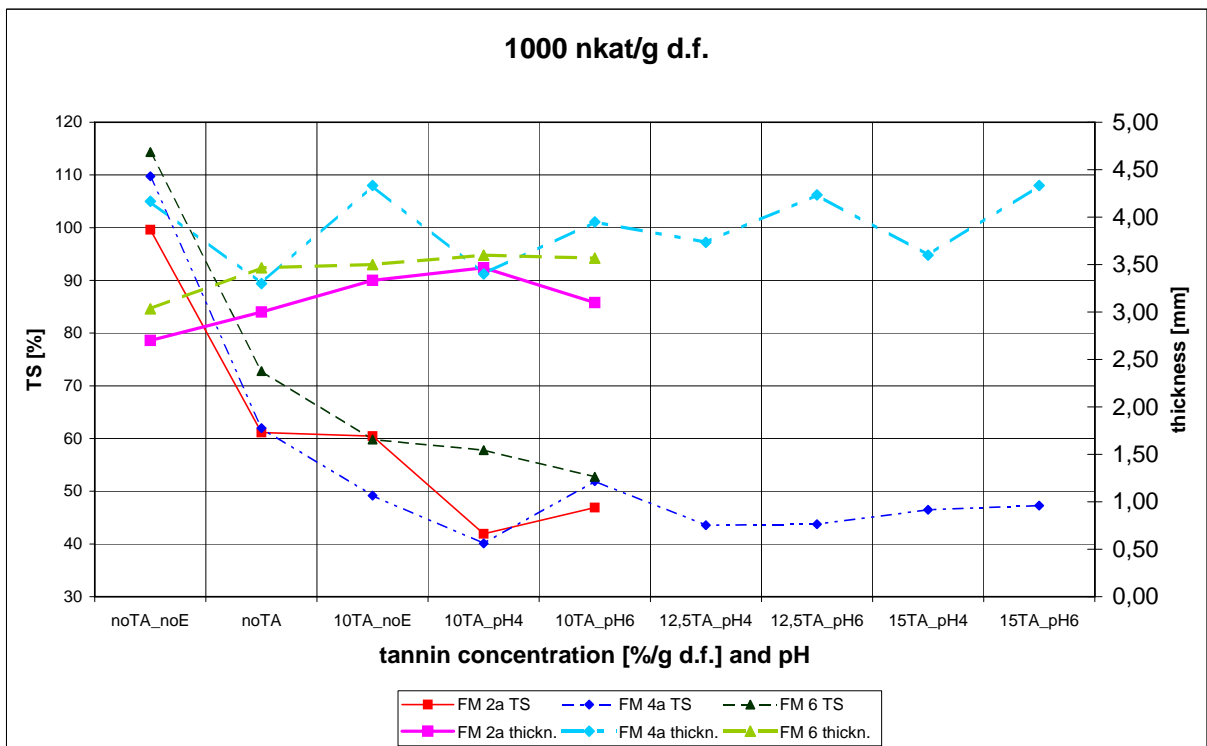
Figure 5.9: Thickness Swelling in corr. to diff. pH at 1000 nkat/g d.f.

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5.3   Effect of moisture content and density

The influence of the moisture content, after the drying process and before the pressing step, and the density was studied in boards made with different tannin concentrations and 500 nkat/g d.f. laccase. For each board at least two samples with the same production parameters were made. Figure 5.10 shows the IB strength in comparison to the moisture content and figure 5.11 the IB strength in comparison to the board density. In the first diagram a significant drop in moisture content (below 50%) induces a drop in IB strength as well. This is referable to an over-drying during the hot pressing step and a thereby generated thermal decay of the wood fibres and inter-fibre bonds. The bonds formed through radical coupling are cleaved again because of too high temperatures in the board. This effect is also seen in conventional made wet-process hardboards, where a minimum moisture content of 40% before pressing is stated.

The density in turn stands in direct relation to the IB strength, as a higher density is beneficial for higher IB values, but a drawback in terms of amount of fibre necessary to produce a board. This is not the case for boards made without any tannic acid and/or enzyme treatment, where the low self bonding ability of the mechanical defibrated fibres superposes the density-IB-relation.
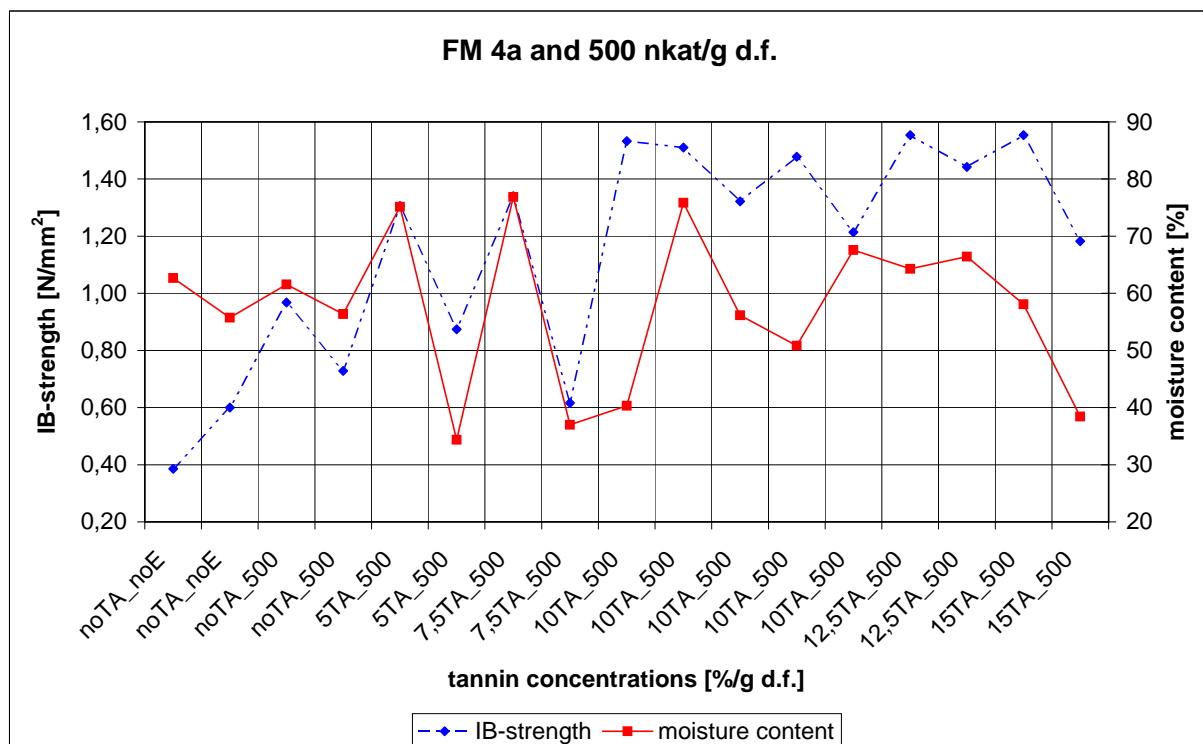
Figure 5.10: Relation - IB strength and moisture content
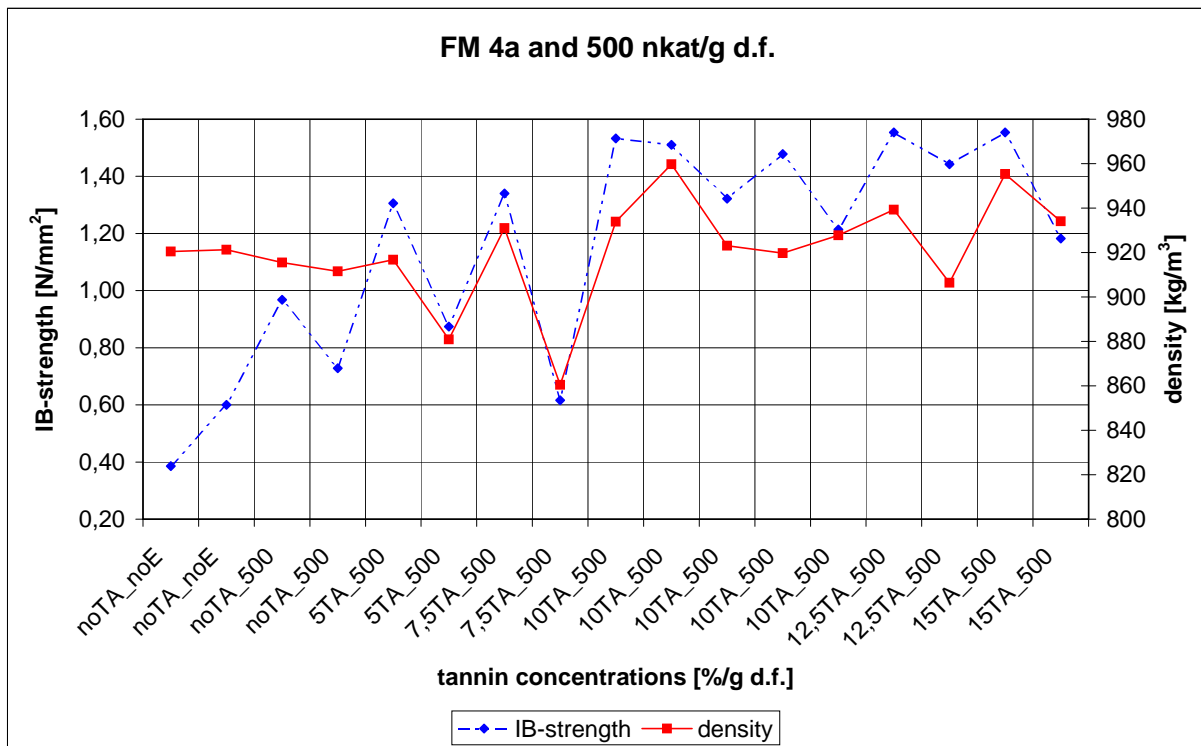
Figure 5.11: Relation - IB strength and board-density

5.4   Effect of hydrophobization additives

Here, boards with the same tannic acid concentration, but different amounts of hydropho-bization additives (Hydrowax) were compared. The tannic acid concentration was varied between 0 and 10% tannic acid per gram dry fibre. The enzyme dose was always 500 nkat/g dry fibre and the experiments were performed with fibre mixture 4a and partly with mixtures 2a and 6.

As in the other experiments, the IB strength, MOR, MOE and thickness swelling (TS) were used to make possible differences visible. Figure 5.12 shows the IB strength as a function of tannic acid concentration and different levels of Hydrowax addition. It is obvious that Hydrowax addition lowers the IB strength, although in some cases the IB strength increases with a higher amount of added Hydrowax (HW). This is due to the method which was used for HW addition. The Hydrowax was dispersed in water and this water/HW dispersion was poured over the fibre mat pre-impregnated with an enzyme solution. Thus, a system of two phases on top of the mat was developed, the non water-soluble Hydrowax swimming on top of the impregnation solution and thereby not all Hydrowax could penetrate into the fibre mat and coat the fibre surfaces. But this small amount was sufficient already to decrease the IB strength significantly. Two factors are responsible for this effect: the HW sealed surfaces are no longer accessible for the enzymes and the inter-fibre bonds

between the HW coated surfaces are limited to London-van der Waals attraction forces, which in turn are not very strong. The same is true for the modulus of rupture and the modulus of elasticity (figure 5.13). These two parameters decrease with increased HW concentration, even though not to the same extent compared to the IB strength. Figure 5.14 displays the thickness swelling (TS) and reveals a positive correlation between increased Hydrowax addition and TS. In respect of the fibre mixtures used, mixtures 2a and 4 have slightly better outcomes than mixture 6. This is an effect of the higher softwood content and therefore higher lignin concentrations.

The addition of HW has a positive influence on the dimensional stability of the fibre-boards, but negative impacts on the mechanical stability parameters.
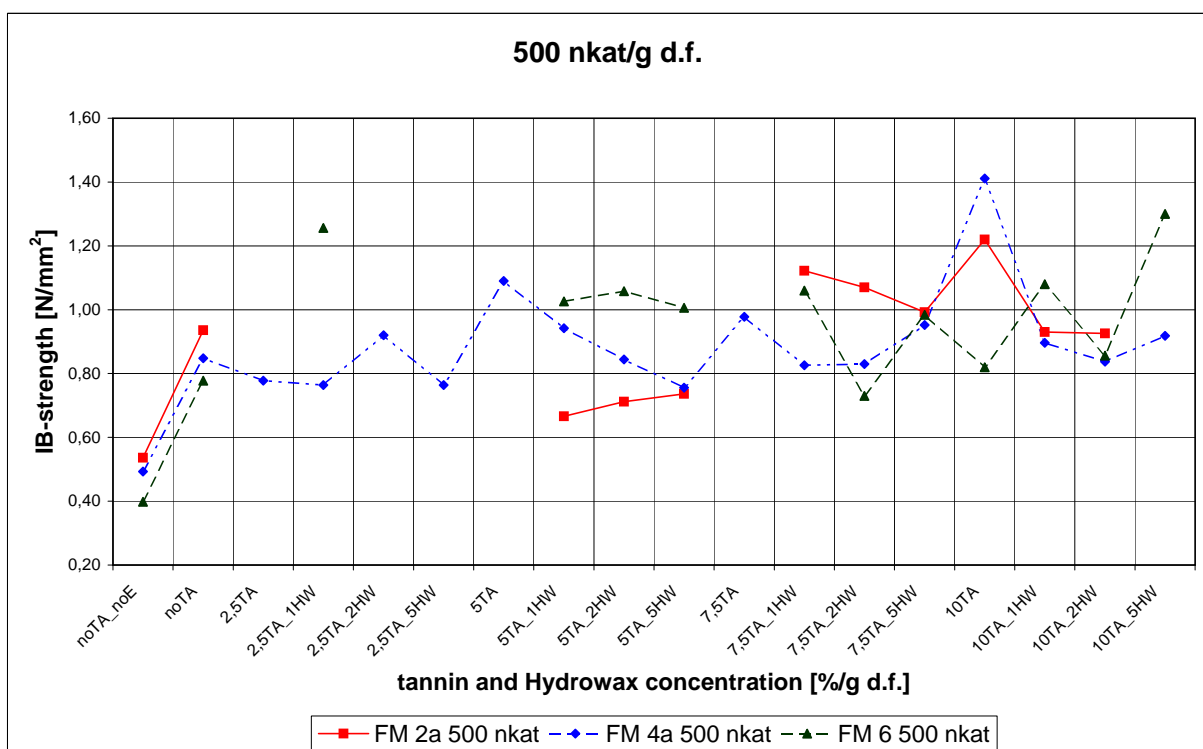
Figure 5.12: IB strength depending on tannin and Hydrowax concentration
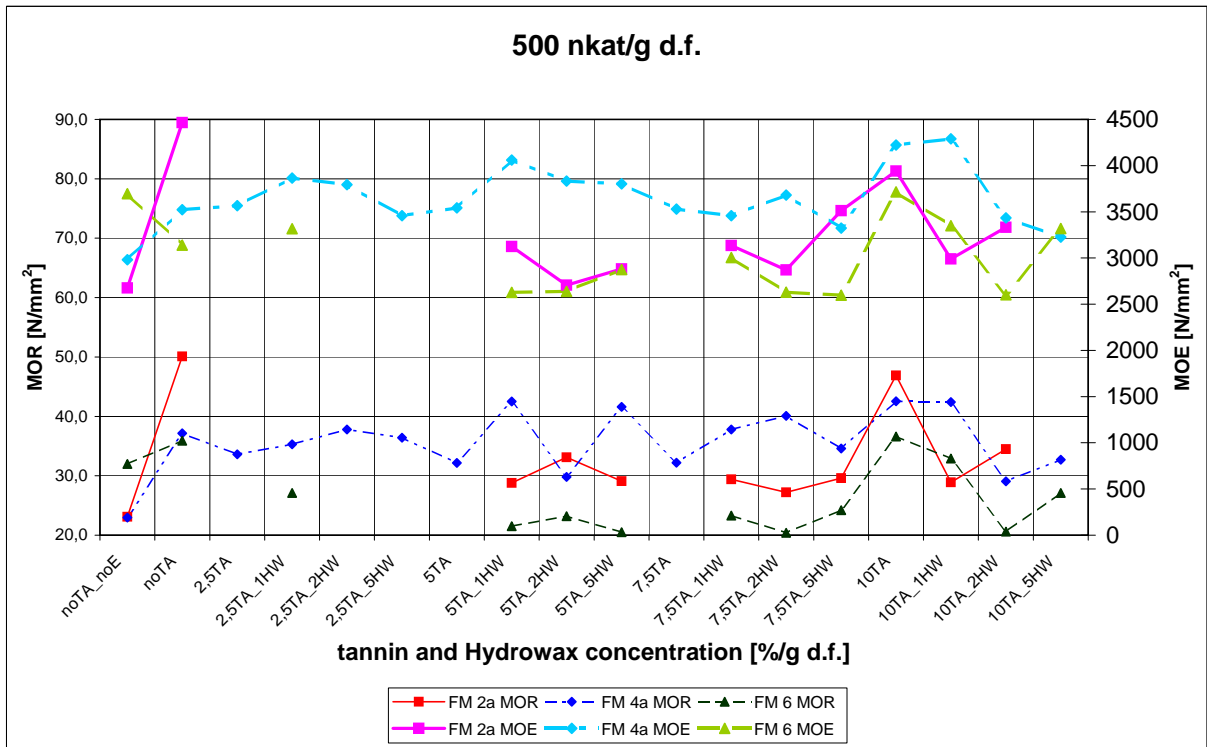
Figure 5.13: MOR and MOE depending on tannin and Hydrowax concentration
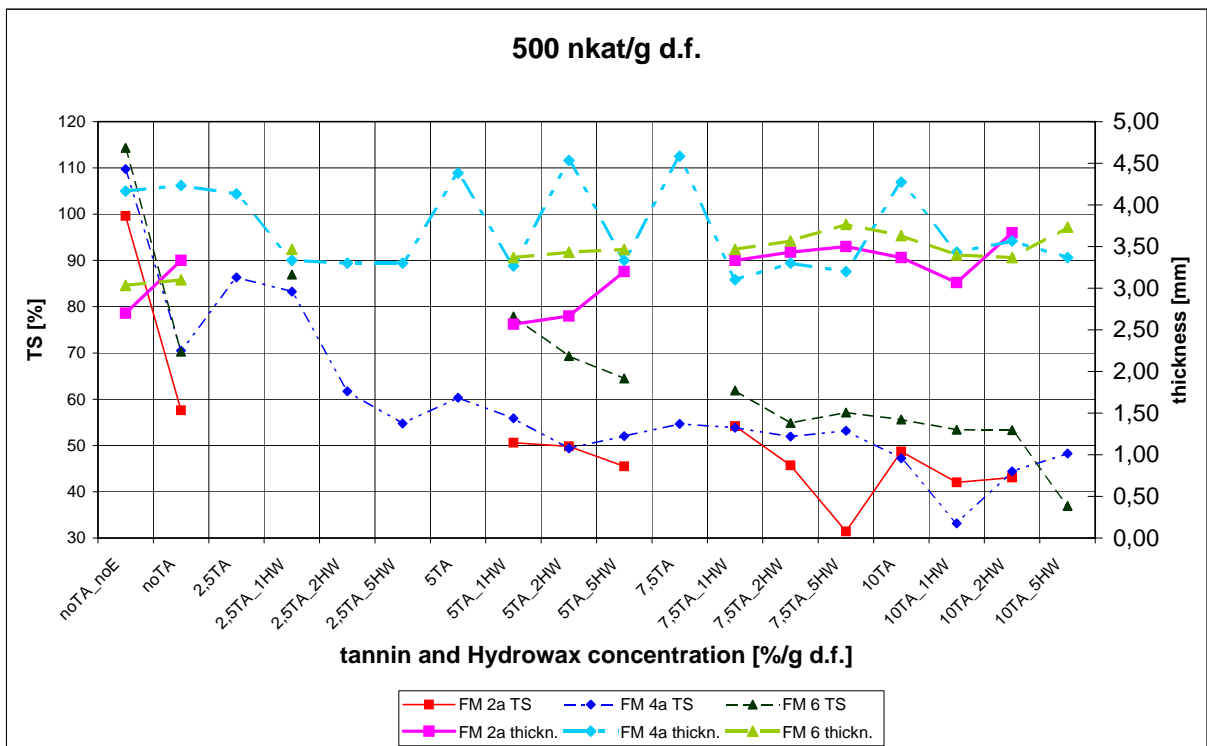
Figure 5.14: Thickness Swelling (TS) depending on tannin and Hydrowax concentration

5.5   Effect of press temperature

The effect of press temperature was studied with boards made with 10% tannic acid and 500 nkat per gram dry fibre. For reference, boards without tannin and/or enzyme treatment were made. Figure 5.15 shows the influence of different press temperatures and reveals the positive effect of enzyme treatment in comparison to sole tannic acid addition (noTA_P190, noE_P190). Boards pressed at 190°C reached maximum values both for IB strength and modulus of rupture (MOR), those made with 180°C had slightly lower or equal values but boards made at 200°C revealled a significant drop in IB strength and MOR. This is due to an overheating during hot-pressing (as discussed before) and a quicker inter-fibre bond-decay than formation.
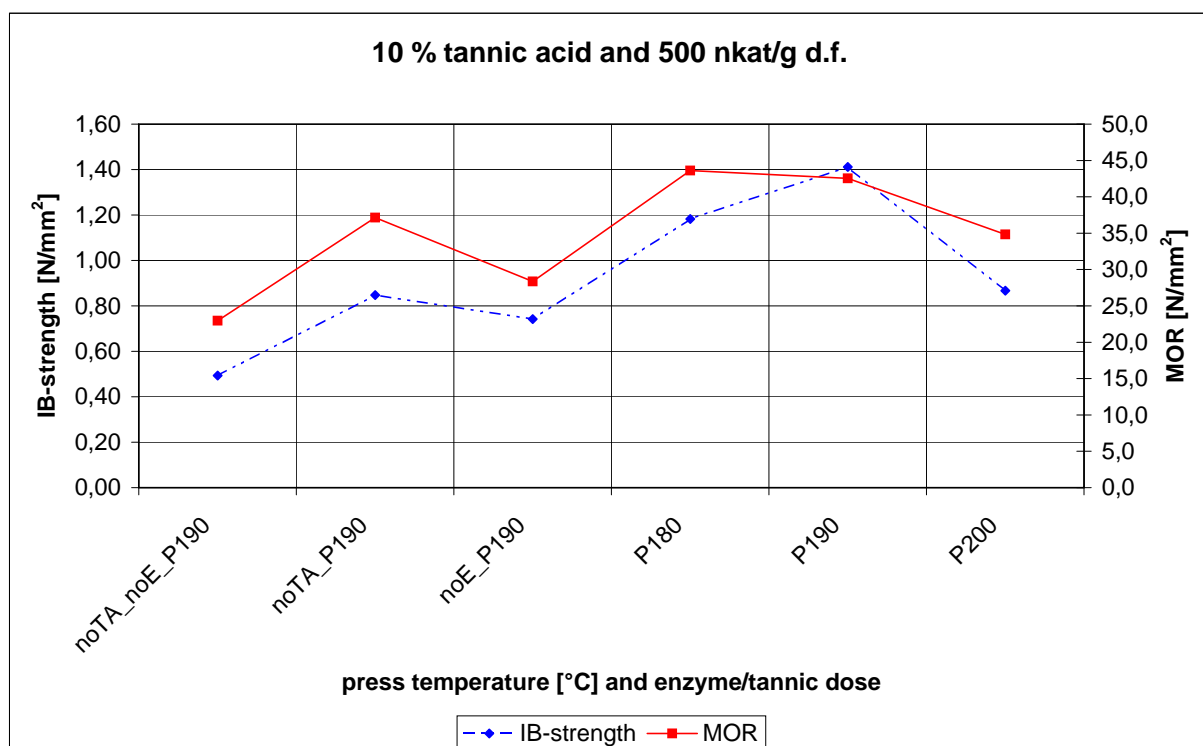
Figure 5.15: IB strength and MOE at different press temperatures

5.6   Effect of various fibre mixtures

In this section the influence of using different fibre mixtures to produce hardboards was studied. Internal bond strength (IB), modulus of rupture (MOR), modulus of elasticity (MOE) and thickness swelling (TS) were used as parameters for comparison. Boards made with 500 and 1000 nkat/g d.f., with 10% tannic acid per g d.f. and with or without laccase addition where compared.

Figure 5.16 shows the IB strength varying with the fibre mixture used. Mixtures 2a and 4a have higher IB-values whereas the values of mixture 6 are lower. This is due to the lower softwood content of mixture 6 and the so reduced lignin amount, available for radical formation through laccase. The same can be said for the MOR and MOE values (figure 5.17), where fibre mixture 2a shows the best values at MOR, and mixtures 4a and 2a have similar values at MOE. Also, in this experiment the values reached with mixture 6 are lower at MOR and slightly lower at MOE.

Thickness Swelling (figure 5.18) is worst with mixture 6 and similar for 2a and 4a, respectively. The slightly better values of 4a can be explained by the higher thickness values. The remaining ones are directly comparable for TS of 2a and 6, because of similar thickness ranges.

In summary it can be said, that mixtures 2a and 4a produce boards of similar quality, which is higher than the quality of boards made from mixture 6, due to the smaller softwood and lignin content. The lower lignin content is reflected in the worse outcome regarding dimensional and mechanical stability.
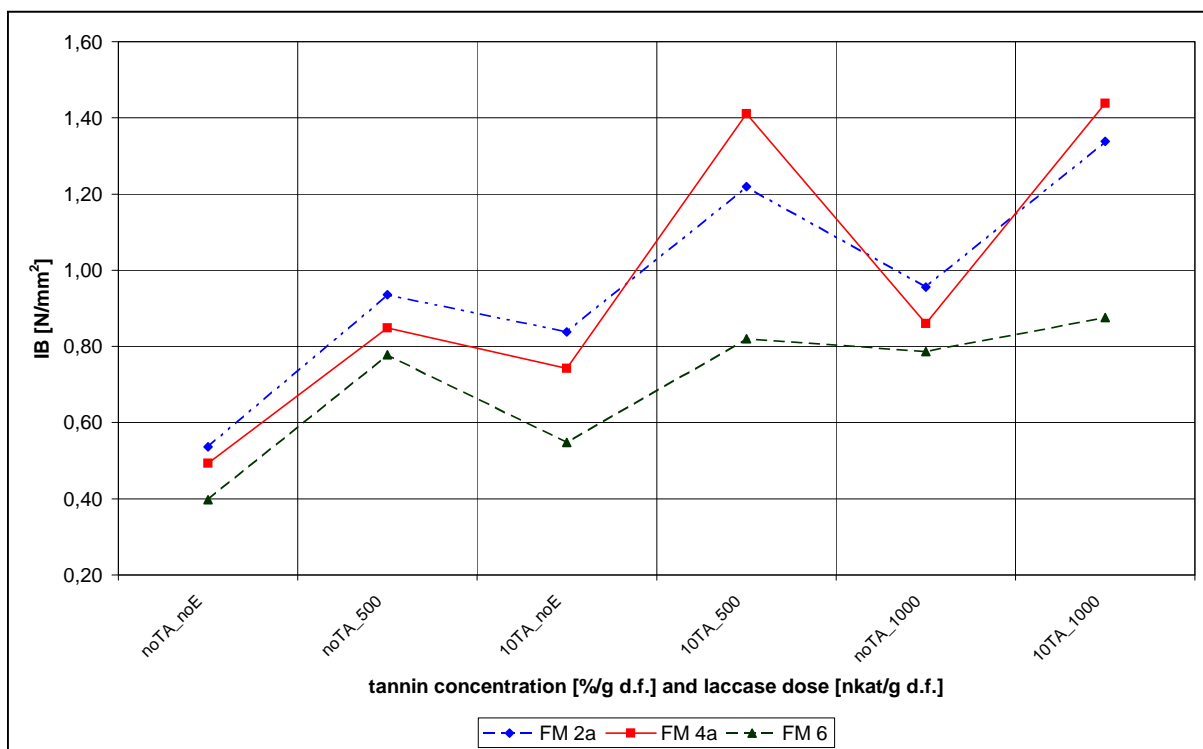
Figure 5.16: IB strength depending on fibre mixture
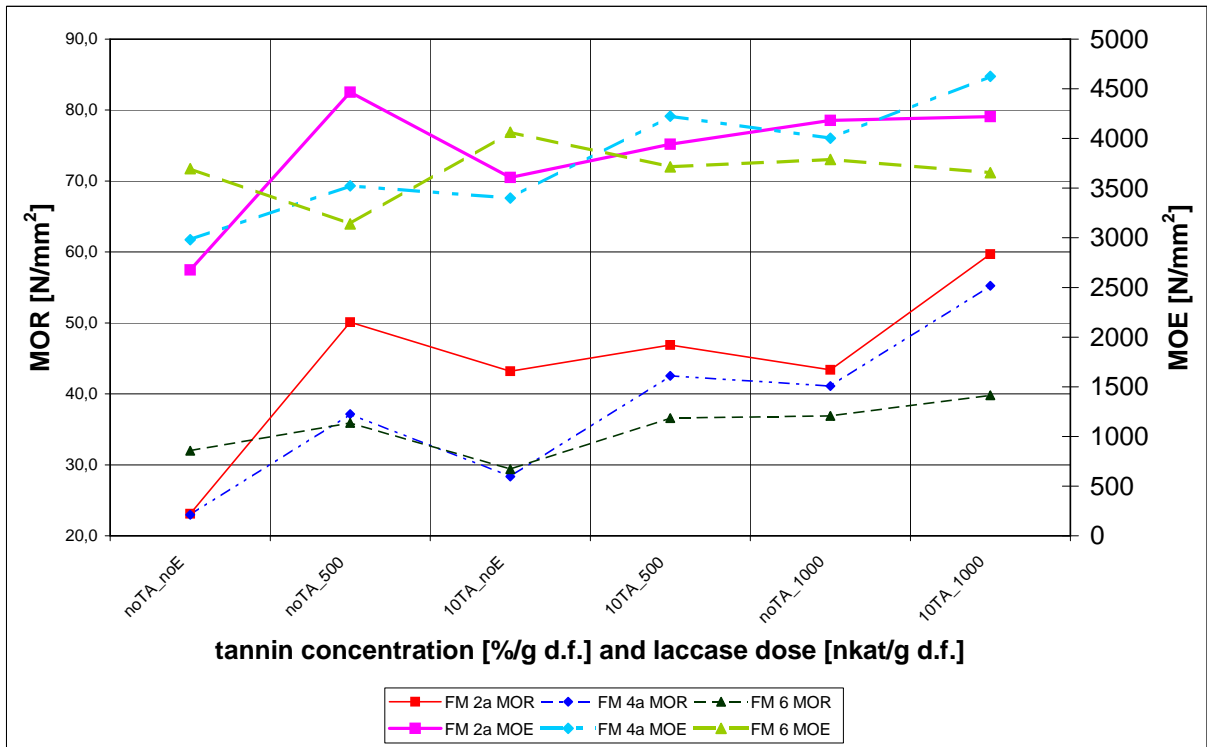
Figure 5.17: MOR and MOE depending on fibre mixture
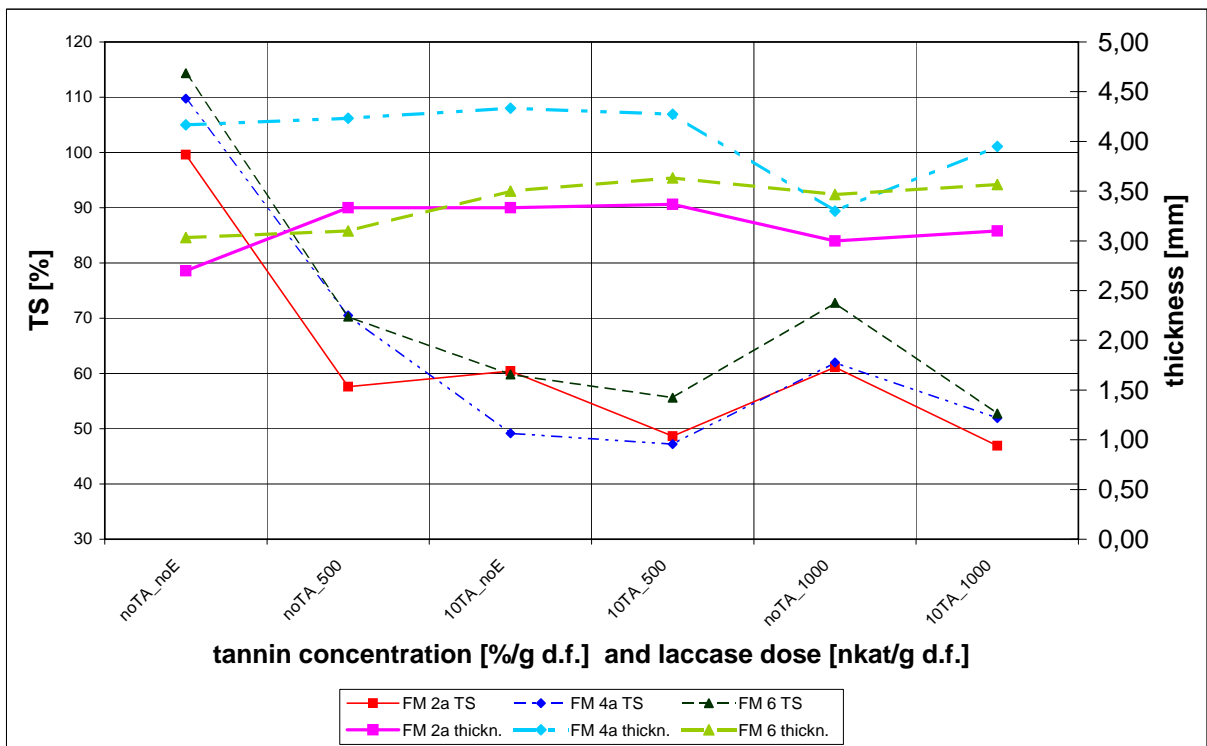
Figure 5.18: Thickness Swelling (TS) depending on fibre mixture

5.7 Differences between conventional and non-conventional method

In this section the differences in and effects of another board preparation method will be discussed. A detailed description of the two preparation methods is given in chapter 3, under 3.4 and 3.5, respectively.

Figure 5.19 shows the IB strength of boards made with equal tannic acid concentrations, enzyme doses and hydrophobization additives. The results are similar in terms of the IB strength trend, but the gathered absolute values are slightly better with the non-conventional method. This can be explained by the higher dilution of all added chemicals in the conventional way of preparation and the thereby higher loss of additives during the two pressing steps (mat-formation and board pressing step). But the trends are the same (except the sample 10TA_500_5CaCl$_2$). This difference may be a result of the better suspension of the chemical during the conventional method. The values for MOR and MOE (figure 5.20) correspond to the IB strength values and slightly better outcomes can be seen at the non-conventional method. Regarding thickness swelling (figure 5.21) the results are much better with the non-conventional method and with an increasing number of added chemicals a decrease in thickness swelling can be seen. Regarding the conventional method this observation cannot be approved because the TS values fluctuate much more. A correlation between IB strength and TS is also only visible at the non-conventional method. An adverse effect is shown at the sample 10TA_500_5CaCl$_2$.

At the end it can be said that the advantages of better suspension and higher water-to-dry-fibre proportion (consistency, beneficial for enzyme activity) at the conventional method are abolished by the high loss of added chemicals and enzymes during the two pressing steps (mat and board formation). The gathered results are slightly better at the non-conventional method.
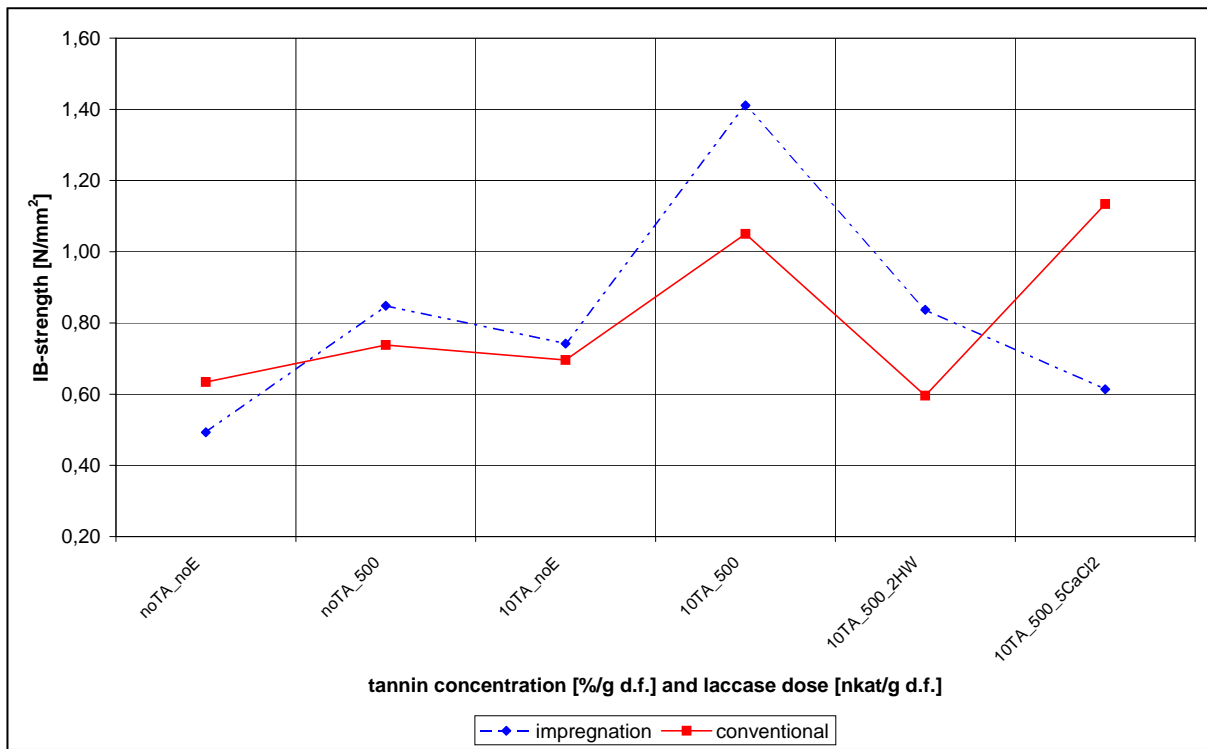
Figure 5.19: IB strength with impregnation and conventional method
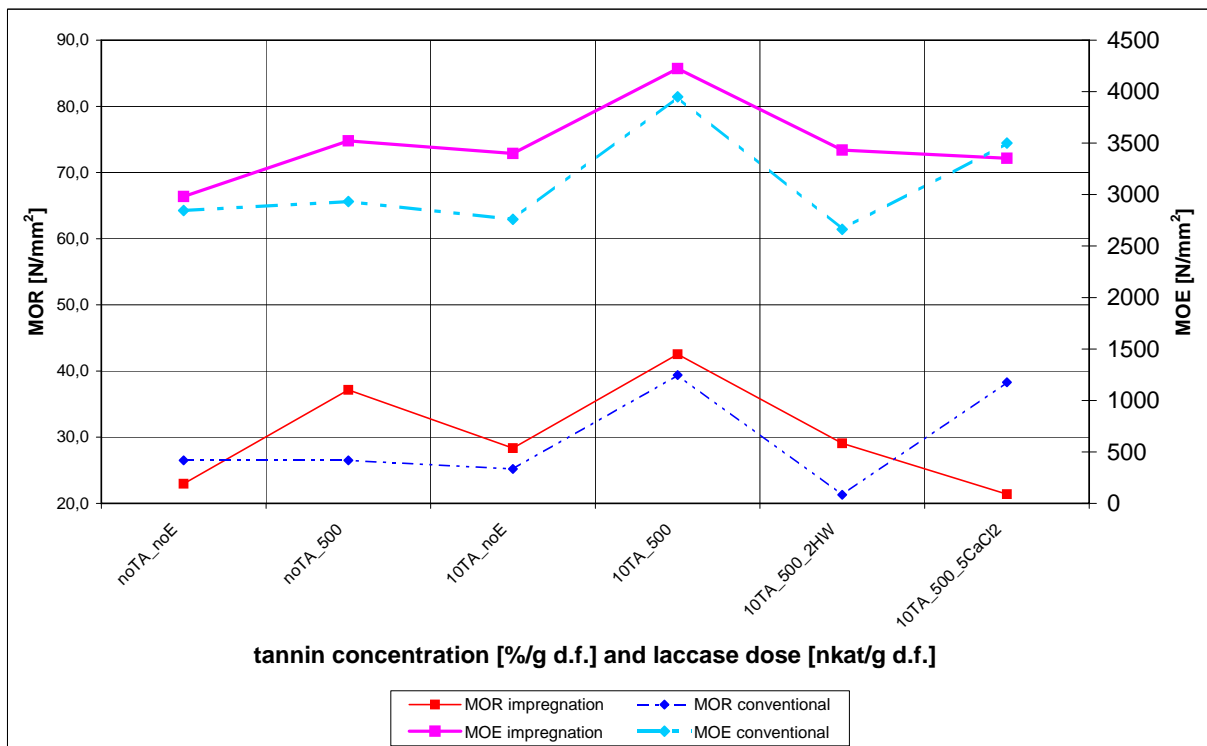
Figure 5.20: MOR and MOE with impregnation and conventional method
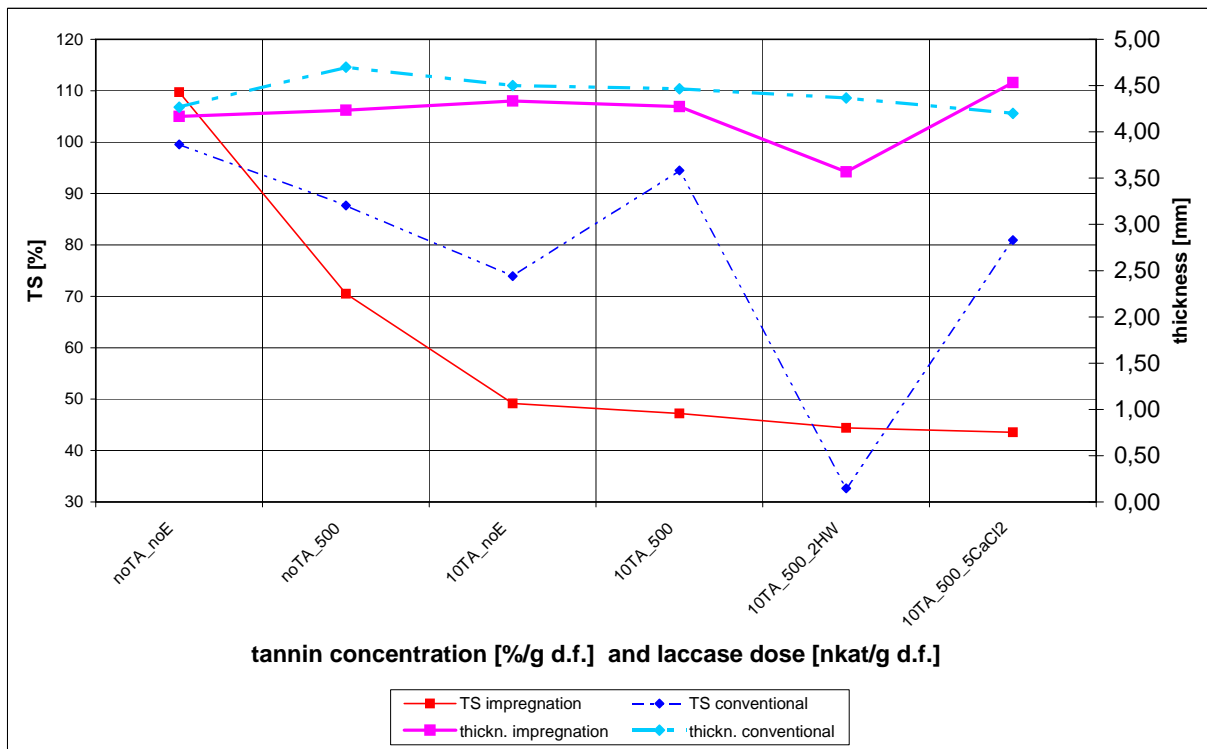
Figure 5.21: Thickness Swelling (TS) with impregnation and conventional method

Chapter 6

Conclusion

6.1 Summary

The hypothesis was to improve the mechanical properties and dimensional stability of hard-boards through impregnation with a laccase and/or tannic acid solution. Boards made with differing concentrations of laccase and/or tannic acid were prepared and the effects on the board parameters was studied. The assumption was to improve mechanical properties significantly and dimensional stability slightly. The European standards for load-bearing hardboards in dry-area according to EN 622-2 should be fulfilled. Beside the effects of process parameters like the pH of the impregnation solution, moisture content of fibremat before pressing or the press temperature were studied.

The study based on two different concentrations, 1000 and 500 nkat/g d.f. The tannic acid concentrations were raised in steps of 2,5% from 0-15%. It could be demonstrated that a raise in laccase dose to 1000 nkat/g d.f. and a tannic acid concentration above 10% does not produce better results. The IB strength level stagnates at 1,4-1,5 N/mm2 and the MOR and MOE at 50 N/mm2 and 4500 N/mm2, respectively. The same is true for the thickness swelling, and levels of around 45% could be reached.

The effect of pH was studied with boards made from three different fibre mixtures (2a, 4a and 6), impregnated with solutions of different pH (4, 5, 6 and 7) and with two different laccase doses (500 and 1000 nkat/g d.f.). The IB strength levels were highest at pH 6, at all tannic acid concentrations and laccase doses. The MOR and MOE levels were best at pH 4. In the case of thickness swelling the best result was observed at pH 4 and a TA concentration of 10%/g d.f., but a direct correlation between pH and TS could not be observed. A correlation between board thickness, tannic acid concentration and TS could be shown. A higher TA concentration and board thickness were beneficial for lower thickness swelling.

The effect of moisture content of the fibre mat after drying and before pressing was studied. The boards pressed were made up from fibre mixture 4a with a laccase dose of 500 nkat/g d.f. The IB strength dropped significantly when the fibre mat was dried to moisture contents below 50%. The density of the board stands in direct correlation to the IB strength and a raise in the first one entails a raise in the latter.

The boards were treated with different amounts of hydrophobization additives. The boards were made with tannic acid concentrations from 0-10%/g d.f. and 500 nkat/g d.f. laccase dose. An addition of Hydrowax had an adverse effect on the IB strength, MOR and MOE. Dimensional stability was increased through Hydowax addition, but standard values could not be reached.

The press temperature was set to 180, 190 and 200°C, respectively. The boards were made with 10% tannic acid per g d.f. and 500 nkat/g d.f. laccase dose. Temperatures of 180 and 190°C generated almost the same results, whereas a press temperature of 200°C led to a significant drop in IB and MOR values.

Hardboards of three different fibre mixtures (2a, 4a and 6) where produced in the same way and with same concentrations of enzymes and tannic acid. Fibre mxtures 2a and 4a showed higher IB strength, MOR and MOE values than mixture 6. The results with mixtures 2a and 4a were of equal value and differences are not dramatic. Thickness swelling values were similar at all three mixtures.

Boards with 10% tannic acid per g d.f., 500 nkat/g d.f. laccase and addition of Hydrowax or $CaCl_2$ were prepared and compared. IB strength, MOR and MOE values were better at the boards made with the non-conventional method, except the ones made with $CaCl_2$. TS decreased with the addition of enzymes, Hydrowax and $CaCl_2$ in the experiments made with the non-conventional method. In the conventional method, significant improvement in TS was only seen when Hydrowax was added.

Table 6.1 shows the comparison of achieved values and required properties for load-bearing hardboards in dry-area use according to EN 622-2.

Table 6.1: Comparison with European standard EN 622-2

	laccase treated	HB
IB [N/mm^2]	0,9-1,4	>0,6
MOR [N/mm^2]	40-50	>33
MOE [N/mm^2]	3500-4500	>2700
TS [%]	40-50	<35

The requirements for mechanical properties could be fulfilled but the dimensional stability is still a problem.

Appendix A

Sample plan and datasets

A.1 Sample plan

A.1.1 Boards made with a laccase dose of 500 nkat/g d.f.

Table A.1: Sample plan - Boards made with 500 nkat/g d.f.

Sample code	fibre mixture		
	6	4a	2a
noTA_noE	1	2	1
noTA_500	1	2	1
2,5TA_500	–	1	–
2,5TA_500_pH4	–	1	–
2,5TA_500_1HW_imp	–	1	–
2,5TA_500_2HW_imp	–	1	–
2,5TA_500_5HW_imp	–	1	–
5TA_500	–	2	–
5TA_500_1HW_imp	1	1	1
5TA_500_2HW_imp	1	1	1
5TA_500_5HW_imp	1	1	1
7,5TA_500	–	2	–
7,5TA_500_pH4	–	1	–
7,5TA_500_1HW_imp	1	1	1
7,5TA_500_2HW_imp	1	1	1
7,5TA_500_5HW_imp	1	1	1
7,5TA_500_pH4_D1402h	–	1	–
10TA_noE	1	2	1

Sample code	fibre mixture		
	6	4a	2a
10TA_500	1	5	1
10TA_500_pH4	1	1	1
10TA_500_pH5	–	2	–
10TA_500_pH7	–	2	–
10TA_500_1HW_imp	1	1	1
10TA_500_2HW_imp	1	4	1
10TA_500_5HW_imp	1	1	–
10TA_500_5CaCl2_imp	–	1	–
10TA_500_30min_preinc	–	1	–
10TA_500_60min_preinc	–	1	–
10TA_500_D1402h	2	2	1
10TA_500_pH4_D1402h	3	2	1
10TA_500_P180	–	2	–
10TA_500_P200	–	3	–
10TA_500_pH4_1HW_imp	1	1	1
10TA_500_pH4_2HW_imp	1	1	–
10TA_500_pH4_1HW_imp_D1402h	–	1	1
10TA_500_pH4_2HW_imp_D1402h	–	1	1
12,5TA_500	–	2	–
12,5TA_500_pH4	–	1	–
12,5TA_500_5CaCl2_imp	–	1	–
12,5TA_500_P200	–	1	–
15TA_500	–	2	–
15TA_500_pH4	–	1	–

A.1.2 Boards made with a laccase dose of 1000 nkat/g d.f.

Table A.2: Sample plan - Boards made with 1000 nkat/g d.f.

Sample code	fibre mixture		
	6	4a	2a
noTA_noE	1	2	1
noTA_1000	1	1	1
2,5TA_1000	–	1	–

Sample code	fibre mixture		
	6	4a	2a
5TA_1000	–	1	–
5TA_1000_2HW_imp	–	1	–
7,5TA_1000	–	1	–
7,5TA_1000_2HW_imp	–	1	–
7,5TA_1000_pH4_D1402h	–	1	–
10TA_1000	1	2	1
10TA_1000_pH4	1	1	1
10TA_1000_1HW_imp	–	1	1
10TA_1000_2HW_imp	–	1	1
10TA_1000_5HW_imp	–	1	–
10TA_1000_D1402h	2	2	1
10TA_1000_pH4_D1402h	3	1	1
12,5TA_1000	–	1	–
12,5TA_1000_pH4	–	1	–
15TA_1000	–	1	–
15TA_1000_pH4	–	1	–

A.1.3 Boards made from mats pre-treated with additives

Table A.3: Sample plan - Boards made from mats pre-treated with additives

Sample code	fibre mixture		
	6	4a	2a
7,5TA_1000_1,5HW_pre	–	1	–
7,5TA_1000_2HW_pre	–	1	–
7,5TA_1000_5CaCl2_pre	–	1	–
10TA_500_1HW_pre	–	1	–
10TA_500_1,5HW_pre	–	1	–
10TA_500_2HW_pre	–	1	–
10TA_500_5CaCl2_pre	–	1	–
10TA_500_1HW_pre_2h104pre	–	1	–
10TA_500_1,5HW_pre_2h104pre	–	1	–
10TA_500_2HW_pre_2h104pre	–	1	–
10TA_1000_1HW_pre	–	1	–

Sample code	fibre mixture		
	6	4a	2a
10TA_1000_1,5HW_pre	–	1	–
10TA_1000_2HW_pre	–	1	–
10TA_1000_5CaCl2_pre	–	1	–

A.1.4 Boards made with the conventional method

Table A.4: Sample plan - Boards made with the conventional method

Sample code	fibre mixture		
	6	4a	2a
noTA_noE_conv	–	1	–
noTA_500_conv	–	1	–
10TA_noE_conv	–	1	–
10TA_500_1,5HW_conv	–	1	–
10TA_500_2HW_conv	–	1	–
10TA_500_5CaCl2_conv	–	1	–
10TA_500_conv	–	1	–

A.2 Datasets

A.2.1 Effect of different laccase dose and tannin concentration

Table A.5: Data - Effect of different laccase dose and tannin concentration - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_500	0,97	37,3	3537	77	915	62	4,27
2,5TA_500	0,78	33,6	3566	86	917	74	4,13
5TA_500	1,09	32,2	3543	60	899	55	4,38

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
7,5TA_500	0,98	32,2	3529	55	896	57	4,58
10TA_500	1,41	42,5	4223	47	933	58	4,27
12,5TA_500	1,50	43,3	4059	41	923	65	4,43
15TA_500	1,37	54,6	4868	43	945	48	4,50
noTA_1000	0,60	22,0	2779	113	921	56	4,10
2,5TA_1000	0,71	34,0	3432	83	908	72	4,20
5TA_1000	0,79	37,0	3561	61	919	77	4,17
7,5TA_1000	0,93	43,3	4384	60	928	79	4,30
10TA_1000	1,44	55,3	4625	52	939	65	3,95
12,5TA_1000	1,06	49,5	4690	44	926	76	4,23
15TA_1000	1,28	40,3	3883	47	939	75	4,33

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, **u** moisture content fibre mat, **d** board-thickness

A.2.2   Effect of different pH

Table A.6: Data - Effect of different pH - FM 2a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,54	23,1	2676	100	891	79	2,70
noTA_500	0,94	50,1	4466	58	918	81	3,33
10TA_noE	0,84	43,2	3608	60	947	78	3,33
10TA_500_pH4	1,13	58,3	4684	55	980	81	3,37
10TA_500	1,22	46,9	3941	49	946	78	3,37
noTA_noE	0,54	23,1	2676	100	891	79	2,70
noTA_1000	0,96	43,4	4182	61	933	82	3,00
10TA_noE	0,84	43,2	3608	60	947	78	3,33
10TA_1000_pH4	1,00	60,3	5048	42	953	82	3,47
10TA_1000	1,34	59,7	4220	47	969	75	3,10

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, **u** moisture content fibre mat, **d** board-thickness

Table A.7: Data - Effect of different pH - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_500	0,85	37,2	3522	70	914	59	4,23
2,5TA_500_pH4	0,82	43,1	3943	67	886	73	3,47
2,5TA_500	0,78	33,6	3566	86	917	74	4,13
7,5TA_500_pH4	1,15	49,5	3062	50	929	77	3,27
7,5TA_500	0,98	32,2	3529	55	896	57	4,58
10TA_noE	0,74	28,4	3400	49	930	44	4,33
10TA_500_pH4	1,14	49,0	4629	35	970	61	4,20
10TA_500	1,41	42,5	4223	47	933	58	4,27
10TA_500_pH7	0,79	35,2	4182	62	944	53	4,83
12,5TA_500_pH4	1,00	54,4	4652	50	907	70	3,80
12,5TA_500	1,50	43,3	4059	41	923	65	4,43
15TA_500_pH4	1,01	56,4	4526	46	914	60	3,63
15TA_500	1,37	54,6	4868	43	945	48	4,50
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_1000	0,86	41,1	4002	62	879	72	3,30
10TA_noE	0,74	28,4	3400	49	930	44	4,33
10TA_1000_pH4	1,16	64,4	5359	40	949	82	3,40
10TA_1000	1,44	55,3	4625	52	939	65	3,95
12,5TA_1000_pH4	1,12	46,9	4011	44	890	62	3,73
12,5TA_1000	1,06	49,5	4690	44	926	76	4,23
15TA_1000_pH4	1,23	48,2	4417	46	959	69	3,60
15TA_1000	1,28	40,3	3883	47	939	75	4,33

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Table A.8: Data - Effect of different pH - FM 6

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,40	32,0	3697	114	870	73	3,03

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_500	0,78	35,9	3140	70	892	72	3,10
10TA_noE	0,55	29,4	4063	60	920	63	3,50
10TA_500_pH4	0,88	32,7	3360	62	932	76	3,80
10TA_500	0,82	36,6	3715	56	916	75	3,63
noTA_noE	0,40	32,0	3697	114	870	73	3,03
noTA_1000	0,79	36,9	3789	73	888	66	3,47
10TA_noE	0,55	29,4	4063	60	920	63	3,50
10TA_1000_pH4	0,90	35,0	3497	58	902	76	3,60
10TA_1000	0,88	39,8	3656	53	915	75	3,57

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

A.2.3 Effect of moisture content and density

Table A.9: Data - Effect of moisture content and density - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,39	23,9	3184	107	920	63	4,23
noTA_noE	0,60	22,0	2779	113	921	56	4,10
noTA_500	0,97	37,3	3537	77	915	62	4,27
noTA_500	0,73	37,0	3507	64	912	56	4,20
5TA_500	1,31	35,7	3717	54	917	75	4,27
5TA_500	0,87	28,6	3368	67	881	34	4,50
7,5TA_500	1,34	37,2	3758	50	931	77	4,23
7,5TA_500	0,62	27,2	3300	60	860	37	4,93
10TA_500	1,53	37,1	4183	48	934	40	4,40
10TA_500	1,51	54,7	4361	56	960	76	3,47
10TA_500	1,32	40,6	4532	42	923	56	4,37
10TA_500	1,48	42,8	3864	42	920	51	4,43
10TA_500	1,21	37,5	4176	48	928	68	4,70
12,5TA_500	1,55	51,2	4562	40	939	64	4,23

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
12,5TA_500	1,44	35,3	3555	42	906	66	4,63
15TA_500	1,55	57,5	4841	44	955	58	4,33
15TA_500	1,18	51,7	4895	41	934	38	4,67

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

A.2.4 Effect of hydrophobization additives

Table A.10: Data - Effect of hydrophobization additives - FM 2a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,54	23,1	2676	100	891	79	2,70
noTA_500	0,94	50,1	4466	58	918	81	3,33
5TA_500_1HW_imp	0,67	28,8	3124	51	922	60	2,57
5TA_500_2HW_imp	0,71	33,1	2707	50	907	60	2,67
5TA_500_5HW_imp	0,74	29,1	2882	45	979	86	3,20
7,5TA_500_1HW_imp	1,12	29,4	3136	54	952	84	3,33
7,5TA_500_2HW_imp	1,07	27,2	2870	46	955	82	3,43
7,5TA_500_5HW_imp	0,99	29,6	3512	31	960	82	3,50
10TA_500	1,22	46,9	3941	49	946	78	3,37
10TA_500_1HW_imp	0,93	28,9	2990	42	905	75	3,07
10TA_500_2HW_imp	0,93	34,5	3333	43	942	72	3,67

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Table A.11: Data - Effect of hydrophobization additives - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_500	0,85	37,2	3522	70	914	59	4,23
2,5TA_500	0,78	33,6	3566	86	917	74	4,13
2,5TA_500_1HW_imp	0,76	35,3	3866	83	911	84	3,33
2,5TA_500_2HW_imp	0,92	37,8	3793	62	923	79	3,30
2,5TA_500_5HW_imp	0,76	36,4	3458	55	921	80	3,30
5TA_500	1,09	32,2	3543	60	899	55	4,38
5TA_500_1HW_imp	0,94	42,5	4061	56	951	73	3,27
5TA_500_2HW_imp	0,84	29,8	3833	49	921	53	4,53
5TA_500_5HW_imp	0,76	41,6	3802	52	901	77	3,33
7,5TA_500	0,98	32,2	3529	55	896	57	4,58
7,5TA_500_1HW_imp	0,83	37,8	3458	54	923	81	3,10
7,5TA_500_2HW_imp	0,83	40,1	3682	52	945	82	3,30
7,5TA_500_5HW_imp	0,95	34,6	3323	53	952	59	3,20
10TA_500	1,41	42,5	4223	47	933	58	4,27
10TA_500_1HW_imp	0,90	42,4	4290	33	943	80	3,43
10TA_500_2HW_imp	0,84	29,1	3433	44	943	59	3,57
10TA_500_5HW_imp	0,92	32,7	3227	48	917	58	3,37

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Table A.12: Data - Effect of hydrophobization additives - FM 6

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,40	32,0	3697	114	870	73	3,03
noTA_500	0,78	35,9	3140	70	892	72	3,10
2,5TA_500_1HW_imp	1,26	27,1	3316	87	906	81	3,47
5TA_500_1HW_imp	1,03	21,5	2629	78	890	82	3,37
5TA_500_2HW_imp	1,06	23,2	2639	69	907	80	3,43
5TA_500_5HW_imp	1,01	20,5	2876	65	889	76	3,47

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
7,5TA_500_1HW_imp	1,06	23,3	3006	62	894	77	3,47
7,5TA_500_2HW_imp	0,73	20,4	2630	55	855	68	3,57
7,5TA_500_5HW_imp	0,98	24,2	2597	57	879	69	3,77
10TA_500	0,82	36,6	3715	56	916	75	3,63
10TA_500_1HW_imp	1,08	32,9	3349	53	918	76	3,40
10TA_500_2HW_imp	0,86	20,6	2601	53	874	76	3,37
10TA_500_5HW_imp	1,30	27,1	3320	37	901	79	3,73

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

A.2.5 Effect of press temperature

Table A.13: Data - Effect of press temperature - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_500	0,85	37,2	3522	70	914	59	4,23
10TA_noE	0,74	28,4	3400	49	930	44	4,33
10TA_500_P180	1,18	43,6	4285	54	949	66	4,37
10TA_500	1,41	42,5	4223	47	933	58	4,27
10TA_500_P200	0,87	34,8	3619	52	922	56	4,70

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

A.2.6 Effect of various fibre mixtures

Table A.14: Data - Effect of various fibre mixtures - FM 2a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,54	23,1	2676	100	891	79	2,70
noTA_500	0,94	50,1	4466	58	918	81	3,33
10TA_noE	0,84	43,2	3608	60	947	78	3,33
10TA_500	1,22	46,9	3941	49	946	78	3,37
noTA_1000	0,96	43,4	4182	61	933	82	3,00
10TA_1000	1,34	59,7	4220	47	969	75	3,10

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Table A.15: Data - Effect of various fibre mixtures - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_500	0,85	37,2	3522	70	914	59	4,23
10TA_noE	0,74	28,4	3400	49	930	44	4,33
10TA_500	1,41	42,5	4223	47	933	58	4,27
noTA_1000	0,86	41,1	4002	62	879	72	3,30
10TA_1000	1,44	55,3	4625	52	939	65	3,95

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Table A.16: Data - Effect of various fibre mixtures - FM 6

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,40	32,0	3697	114	870	73	3,03

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_500	0,71	35,9	3140	70	892	72	3,10
10TA_noE	0,55	29,4	4063	60	920	63	3,50
10TA_500	0,82	36,6	3715	56	916	75	3,63
noTA_1000	0,79	36,9	3789	73	888	66	3,47
10TA_1000	0,88	39,8	3656	53	915	75	3,57

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

A.2.7 Differences between non-conventional and conventional method - FM 4a

Table A.17: Data - Non-conventional method - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE	0,49	23,0	2982	110	921	59	4,17
noTA_500	0,85	37,2	3522	70	914	59	4,23
10TA_noE	0,74	28,4	3400	49	930	44	4,33
10TA_500	1,41	42,5	4223	47	933	58	4,27
10TA_500_2HW_imp	0,84	29,1	3433	44	943	59	3,57
10TA_500_5CaCl2_imp	0,61	21,4	3353	44	954	41	4,53

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Table A.18: Data - Conventional method - FM 4a

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
noTA_noE_conv	0,63	26,5	2846	100	904	–	4,27
noTA_500_conv	0,74	26,5	2932	88	904	–	4,70

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, u moisture content fibre mat, **d** board-thickness

Sample code	IB [N/mm^2]	MOR [N/mm^2]	MOE [N/mm^2]	TS [%]	ρ [kg/m^3]	u [%]	d [mm]
10TA_noE_conv	0,70	25,2	2759	74	923	–	4,50
10TA_500_conv	1,05	39,4	3949	95	931	–	4,47
10TA_500_2HW_conv	0,60	21,3	2663	33	925	–	4,37
10TA_500_5CaCl2_conv	1,13	38,3	3501	81	903	–	4,20

Abbreviations: IB internal bond strength, **MOR** modulus of rupture, **MOE** modulus of elasticity, **TS** thickness swelling, ρ board-density, **u** moisture content fibre mat, **d** board-thickness

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