Department of Forest Products Technology

Surface modification of solid wood using different techniques

Lauri Rautkari

Aalto University

DOCTORAL DISSERTATIONS

Aalto University publication series
DOCTORAL DISSERTATIONS 4/2012

Surface modification of solid wood using different techniques

Lauri Rautkari

Doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the School of Chemical Technology for public examination and debate in Auditorium Puu2 at the Aalto University School of Chemical Technology (Espoo, Finland) on the 24th of February 2012 at 12 noon.

Aalto University
School of Chemical Technology
Department of Forest Products Technology

Supervisor
Professor Mark Hughes, Aalto University, Finland

Instructors
Professor Mark Hughes, Aalto University, Finland
Professor Frederick Kamke, Oregon State University, USA

Preliminary examiners
Prof. Peer Haller, Technische Universität Dresden, Germany
Prof. Milan Šernek, University of Ljubljana, Slovenia

Opponent
Dr. Heiko Thömen, Bern University of Applied Sciences, Switzerland

Aalto University publication series
DOCTORAL DISSERTATIONS 4/2012

ISBN 978-952-60-4464-4 (printed)
ISBN 978-952-60-4465-1 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

Unigrafia Oy
Helsinki 2012

Finland

The dissertation can be read at http://lib.tkk.fi/Diss/

441 697
Printed matter

Aalto University

Abstract

Aalto University, P.O. Box 11000, FI-00076 Aalto www.aalto.fi

Author
Lauri Rautkari

Name of the doctoral dissertation
Surface modification of solid wood using different tecniques

Publisher School of Chemical Technology

Unit Department of Forest Products Technology

Series Aalto University publication series DOCTORAL DISSERTATIONS 4/2012

Field of research Wood Material Technology

Manuscript submitted 4 October 2011 **Manuscript revised** 13 December 2011

Date of the defence 24 February 2012 **Language** English

☐ **Monograph** ☒ **Article dissertation (summary + original articles)**

The rising demand for consistent, high quality, as well as high density wood species has raised interest in different wood modification techniques. One modification method is wood densification, where solid bulk wood can be compressed, following softening, until its density reaches that of the cell wall (1.50 g/cm^3). It is well known that many of the properties of solid wood correlate with its density and as such can be enhanced by increasing the density. By targeting the compression to the surface of solid wood only, the surface properties can be enhanced.

The main aim of this thesis was to evaluate the effect of different wood surface densification methods on surface properties. Three methods were evaluated; (i) a lamination technique, where low density wood was laminated to a high density compressed wood surface, (ii) surface modification where densification was accomplished using a single sided heated press and (iii) with a single sided heated press assisted by frictional heating. With the lamination technique, it proved easy to generate the desired hard surface, but an adhesive is needed. The difference between compression with and without friction is that when using friction the process temperature is rather difficult to control, but an even layer of extractives are formed on the surface. Without friction, however, extractive spots are seen on the surface.

The results show that the process parameters used in surface densification have a significant influence on the vertical density profiles, which in turn have an influence on surface hardness. On the other hand hardness correlates with the degree of densification and the thickness of the densified surface. Moreover, wettability decreased significantly, caused by the closure of lumens, a smooth surface and an extractive layer on the surface. The extractives on the surface were analysed by FTIR-ATR spectroscopy and X-ray photoelectron spectroscopy. Using FTIR-ATR spectroscopy there was no trace of extractives, but with X-ray photoelectron spectroscopy an extractive layer was identified, this was most probably due to the penetration depth of the IR-beam, which is rather high, compared to X-ray photoelectron spectroscopy, which is highly surface sensitive. The extractive layer could provide a natural coating and reduce the need for further coating. Furthermore, a potential measure error was found when measuring the vertical density profile of composites with large differences in densities, caused by the calibration process.

Keywords densification, surface densification, surface modification, wood modification

ISBN (printed) 978-952-60-4464-4 **ISBN (pdf)** 978-952-60-4465-1

ISSN-L 1799-4934 **ISSN (printed)** 1799-4934 **ISSN (pdf)** 1799-4942

Location of publisher Espoo **Location of printing** Helsinki **Year** 2012

Pages 126 **The dissertation can be read at** http://lib.tkk.fi/Diss/

A! Aalto-yliopisto

Tiivistelmä

Aalto-yliopisto, PL 11000, 00076 Aalto www.aalto.fi

Tekijä
Lauri Rautkari

Väitöskirjan nimi
Massiivipuun pinnan modifiointi eri tekniikoilla

Julkaisija Kemian tekniikan korkeakoulu

Yksikkö Puunjalostustekniikan laitos

Sarja Aalto University publication series DOCTORAL DISSERTATIONS 4/2012

Tutkimusala Puun materiaalitekniikka

Käsikirjoituksen pvm 04.10.2011 **Korjatun käsikirjoituksen pvm** 13.12.2011

Väitöspäivä 24.02.2012 **Kieli** Englanti

☐ **Monografia** ☒ **Yhdistelmäväitöskirja (yhteenveto-osa + erillisartikkelit)**

Tiivistelmä

Tasa- ja korkealaatuisen sekä tiheän puumateriaalin kasvava kysyntä on lisännyt kiinnostusta puun eri modifiointitekniikoihin. Eräs modifiointimenetelmistä on puun puristaminen, jossa pehmennettyä massiivipuuta voidaan puristaa kasaan kunnes soluseinän tiheys (1.50 g/cm^3) on saavutettu. Monet massiivipuun ominaisuudet ovat yhteydessä tiheyteen ja siksi niitä voidaan parantaa kasvattamalla tiheyttä. Kohdentamalla puristus vain massiivipuun pintakerrokseen voidaan pinnan ominaisuuksia parantaa.

Työn päätavoitteena oli arvioida erilaisia puun pinnan puristusmenetelmiä ja niiden vaikutuksia pinnan ominaisuuksiin. Kolme eri menetelmää arvioitiin: (i) laminointitekniikka, jossa puristettu puu laminoitiin alhaisen tiheyden omaavan puun pinnalle, (ii) pinnan modifiointi yhdeltä puolelta lämmitetyllä puristimella ja (iii) yhdeltä puolelta lämmitetyn puristimen ja kitkan avulla. Laminointitekniikalla saatiin halutunlainen kova pinta, mutta liimaa tarvitaan. Kitkan käyttö puristuksessa eroaa siten, että kitkaa käytettäessä prosessilämpötilaa on melko vaikea hallita, mutta pinnalle muodostuu tasainen uuteainekerros. Puristettaessa ilman kitkaa pinnalla näkyy uuteainetäpliä.

Tulokset osoittavat, että pintapuristuksessa prosessiparametreilla on merkittävä vaikutus tiheysprofiiliin, joka taas vaikuttaa pinnan kovuuteen. Toisaalta kovuus korreloi puristusasteen ja tiivistetyn pinnan paksuuden kanssa. Lisäksi pinnan kostuvuus vähentyi merkittävästi, johtuen suljetuista soluonteloista, sileästä pinnasta ja pinnalle muodostuneesta uuteainekerroksesta. Uuteainekerrosta analysoitiin FTIR-ATR spektroskopialla ja röntgenfotoelektronispektroskopialla. FTIR-ATR spektroskopialla ei havaittu uuteaineita, mutta röntgenfotoelektronispektroskopialla uuteainekerros havaittiin, mikä hyvin todennäköisesti johtui IR-säteen mittaussyvyydestä, joka on melko korkea verrattuna erittäin pintaherkkään röntgenfotoelektronispektroskopiaan. Muodostunut uuteainekerros voisi tarjota luonnollisen pinnoitteen, joten muuta pintakäsittelyä voisi vähentää. Lisäksi havaittiin mahdollinen laitteen kalibroinnista johtuva mittausvirhe, kun mitattiin tiheysprofiilia korkeita tiheyseroja omaavasta komposiitista.

Avainsanat puun modifiointi, pinnan modifiointi, puun puristaminen

ISBN (painettu) 978-952-60-4464-4 **ISBN (pdf)** 978-952-60-4465-1

ISSN-L 1799-4934 **ISSN (painettu)** 1799-4934 **ISSN (pdf)** 1799-4942

Julkaisupaikka Espoo **Painopaikka** Helsinki **Vuosi** 2012

Sivumäärä 126 **Luettavissa verkossa osoitteessa** http://lib.tkk.fi/Diss/

PREFACE

This study was mainly carried out at the Department of Forest Products Technology at Aalto University (Finland), Department of Wood Science & Engineering at Oregon State University (USA) and Department of Architecture, Wood and Civil Engineering at Bern University of Applied Sciences (Switzerland), but also partly in BioComposites Centre at Bangor University (UK) during 2007 – 2011.

The work was mainly funded by National Graduate School of Timber Construction and Design and a project in Bern University of Applied Sciences, some travel and other expenses were covered by USDA Special Grant for Wood Utilization Research, Oregon State University. In addition several other sources financed the work and I would like to thank following foundations and associations: the Association of Finnish Sawmillmen, the Emil Aaltonen Foundation, the Finnish Association of Civil Engineers, the Finnish Cultural Foundation, the Finnish Woodworking Engineers Association, the Foundation of Professor Eero Kivimaa, Puumiesten Ammattikasvatussäätiö, the Research Foundation of Helsinki University of Technology, Tekniikan edistämissäätiö and Veljekset Saarelaisen säätiö. I would like to thank Stora Enso Wood Products Oy Ltd for providing some of the wood materials used in the study.

First of all, I wish to express my deepest gratitude to my supervisor and instructor professor Mark Hughes for his guidance and encouragement during the study. He was always ready to help me, no matter which kind of problem I had. Even if I was overseas in Oregon, his phone service was in operation. Furthermore, I am most grateful to my second instructor professor Fred Kamke for his support and the opportunity to work in Oregon State University.

Besides the official instructors, I would thank my co-authors Frédéric Pichelin and Milena Properzi, who were responsible that I started my thesis in the first place by offering work in Switzerland. I would also like to thank my co-authors Nick Laflin, Leena-Sisko Johansson and especially Tuomas Hänninen for introducing wood chemistry to me and Kristiina Laine who is continuing this study further.

I would like to thank all my colleagues and friends in Switzerland, who helped me with all practical issues from language problems to car purchase. Especially I wish to thank for Ingo, Christelle and Sebastian in our lab.

Special thanks go to all my colleagues and friends in USA, especially Andreja, Guenther, Milo and Vardan in the lab. The life in Corvallis would not have been so special without all foreign and national friends that I met and lived with in the dormitory. I really miss our scrappy minivan and road trips in the west coast!

I would like to thank doctoral program planning officer Sirje Liukko and professors Matti Kairi and Stefan Winter for valuable comments during the study. I would also like to thank to my current and former colleagues and friends in the wood product lab in Finland: Akio, Annika, Anti, Appu, Arto, Atsushi, Ditta, Eeva, Eki, Heidi, Janne, Jonna, Jukka, Jussi x2, Katja, Kari, Kimmo, Lauri, Michael, Mindaugas, Olli, Pekka, Pertti, Pia, Ulla, Tero x2, Tiina, Timo, and Toni. Thanks go also to those numerous students who have worked in our lab during summers and those who have contributed their master thesis.

Finally, I would like to express my gratitude to my family; my parents Olli and Sirkka for their support, and my brother Tapsa for providing me a 24/7 IT service desk. I would also like to thank Sanna and Jiri for all your support and patience with my weird hobbies at home, such as reading dissertations in bed before going to sleep. A special thanks goes to Miisa, our biological alarm clock.

Espoo, 22nd December 2011

Lauri Rautkari

LIST OF PUBLICATIONS

The thesis is mainly based on the following scientific papers, which are referred to in the text by their Roman numerals:

I Rautkari L, Kamke FA, Hughes M (2011) Density profile relation to hardness of viscoelastic thermal compressed (VTC) wood composite. Wood Sci Technol 45: 693-705

II Rautkari L, Kamke FA, Hughes M (2011) Potential error in density profile measurements for wood composites. Eur J Wood Prod 69: 167-169

III Rautkari L, Laine K, Laflin N, Hughes M (2011) Surface modification of Scots pine: the effect of process parameters on the through thickness density profile. J Mater Sci 46: 4780-4786

IV Rautkari L, Properzi M, Pichelin F, Hughes M (2009) Surface modification of wood using friction. Wood Sci Technol 43: 291-299

V Rautkari L, Properzi M, Pichelin F, Hughes M (2010) Properties and set-recovery of surface densified Norway spruce and European beech. Wood Sci Technol 44: 679-691

VI Rautkari L, Hänninen T, Johansson L-S, Hughes M (2012) A study by X-ray photoelectron spectroscopy (XPS) of the chemistry of the surface of Scots pine (*Pinus sylvestris* L.) modified by friction. Holzforschung 66: 93-96

AUTHOR'S CONTRIBUTION

I, II Defined the research plan with input from co-authors, was responsible for the experimental work and analysis and wrote first draft of the manuscript.

III Defined the research plan with input from co-authors, supervised the experiments and analysis and wrote first draft of the manuscript.

IV, V Defined the research plan with input from co-authors, was responsible for the experimental work and analysis and wrote first draft of the manuscript.

VI Defined the research plan with input from co-authors, was responsible for the experimental work and analysis and wrote first draft of the manuscript, except all work related to XPS.

LIST OF ABBREVIATIONS

ATR	attenuated total reflection
DCA	dynamic contact angle
FTIR	Fourier transform infra-red
H_B	Brinell hardness
IS	irreversible swelling
mc	moisture content
MDF	medium density fibreboard
MOE	modulus of elasticity
MOR	modulus of rupture
OSB	oriented strand board
RH	relative humidity
S_r	set-recovery
T_g	glass transition temperature
TM	thermo-mechanical
THM	thermo-hydro-mechanical
VDP	vertical density profile
VTC	viscoelastic thermal compression
XPS	X-ray photoelectron spectroscopy

TABLE OF CONTENTS

1 INTRODUCTION

1.1 Background

Wood can be obtained in many diverse species that vary in density, strength and durability, which can be located in endangered rainforest. However, rising demand for consistent, high quality material as well as high density wood species has increased interest in different wood modification techniques. Hill (2006) explains that wood can be modified chemically, biologically or physically, which results in an increase in certain properties during its service life. Moreover, modified wood should not be toxic under service conditions and there should be no release of any toxic substances either during service or at the end of the service life. This implies that it is possible to use, for example, hazardous chemicals during the modification process, but that they should not remain in the wood once the modification process is complete. Wood modification methods can be broken down into chemical, thermal, surface or impregnation processes or, alternatively, combinations thereof. The aim of all methods is to improve one or more of the properties of wood, such as mechanical properties, dimensional stability or resistance to biological degradation.

One modification method is wood densification. It is well known that many of the properties of solid wood are correlated with its density, thus the mechanical properties of wood can be enhanced by increasing the density. Since wood is a porous cellular material, an increase in its density can readily be achieved either by compressing it or by impregnating it with resins. It is also commonly known that solid wood can be compressed in perpendicular to the grain direction under certain conditions of heat and moisture without causing damage to the cell wall. One negative effect of compressing the whole wood is, however, the loss in volume and consequently a reduction in beam loading capacity, albeit the material properties may

be enhanced. To circumvent this issue, an alternative approach is to bulk compress thin boards and laminate these to either side of uncompressed wood using an adhesive (Kutnar et al. 2008b). Alternatively, it may be possible to compress only the surfaces of solid wood by 1-5 mm or only few cell layers; in this way it is mainly the surface properties that are improved. In order to achieve such a 'targeted' compression, it is necessary to first soften the part of wood which is to be compressed, but not the remaining part. This can be achieved e.g. using a press with only one heated platen and therefore only one surface is softened and can be compressed, but the other side and core remain uncompressed. One of the main issues to be addressed when compressing wood is its tendency to spring back, particularly in humid or wet conditions. This problem can, however, be solved by impregnating the wood with resin before compression or by using certain thermal treatments after the densification process has been completed.

1.2 Aims of the study

Many different techniques to bulk compress wood are known. However, surface densification techniques have not been widely studied. The main objective of this study was to evaluate different wood surface densification methods and their effect on surface properties, especially surface hardness. The techniques investigated were:

I. Surface densification by a lamination technique, where thin compressed lamellae were bonded to untreated wood using an adhesive, thereby creating a composite with an irregular density profile. Using this technique, a high density surface was achieved, whilst the remainder of the composite remained rather low density. Density profile and hardness were determined (Papers I-II).

II. Surface densification using a heated plate and pressure, where one side of solid wood is heated during compression and therefore one side is softened and compressed. Compression was controlled with a universal testing machine. The process parameters were easily controlled using this surface densification technique. The effect of processing parameters on the density profile was determined (Paper III).

III. Surface densification by friction, where one side of solid wood is heated with the assistance of motion. This technique allowed smoothing of the surface during compression. Hardness, surface properties and surface chemistry were determined (Papers IV-VI).

This thesis is divided to several chapters, where the background of solid wood densification and surface densification are introduced and earlier studies are presented. The main methodologies are presented shortly and the key results of Papers I-VI are summarised and discussed. The overall target of solid wood surface densification processes are to improve surface properties, which are important, when solid wood is used e.g. as flooring or where high resistance to wear are needed.

2 WOOD DENSIFICATION

It is well known that wood density correlates with its mechanical properties and that when above its glass transition temperature wood can be compressed without rupturing the cell walls. Wood is a porous material and, in theory, can be rather easily compressed until the density reaches that of the cell wall material, which is approximately 1.50 g/cm³ (Wilfong 1966; Kellog and Wangaard 1969). Wood can, of course, be impregnated with resins or plastics without compression and an increase in density, and therefore enhanced mechanical properties, be obtained (Gindl et al. 2004; Zhang et al. 2006).

Several studies to achieve solid wood compression have been reported (Inoue et al. 1993a; Ito et al. 1998a,b; Navi and Girardet 2000; Kamke 2006). All these methods, however, have the same main phases - wood softening and wood compression. Furthermore, the methods usually include a post-treatment phase and a cooling phase. The post-treatment phase often involves a heat-treatment process, which decreases irreversible thickness swelling (set-recovery), when the compressed wood is exposed to humid or wet conditions.

2.1 Theory of wood softening

Solid wood can be regarded as a complex polymeric cellular composite. It consists of amorphous polymers; lignin, hemicelluloses and disordered cellulose, which are all hygroscopic and which soften under certain conditions, as well as crystalline cellulose. The viscoelastic behaviour of these compounds has been widely studied (Goring 1963; Hillis and Rozsa 1978; Back and Salmén 1982; Salmén 1984; Salmén et al. 1986; Irvine 1984; Kelley et al. 1987; Salmén 1990). In these polymers, the transition between the glassy and rubbery state is defined as the glass transition

temperature (T_g). Many of the properties of a polymer, for example its elastic modulus (Fig. 1), change dramatically when this softening point has been passed.

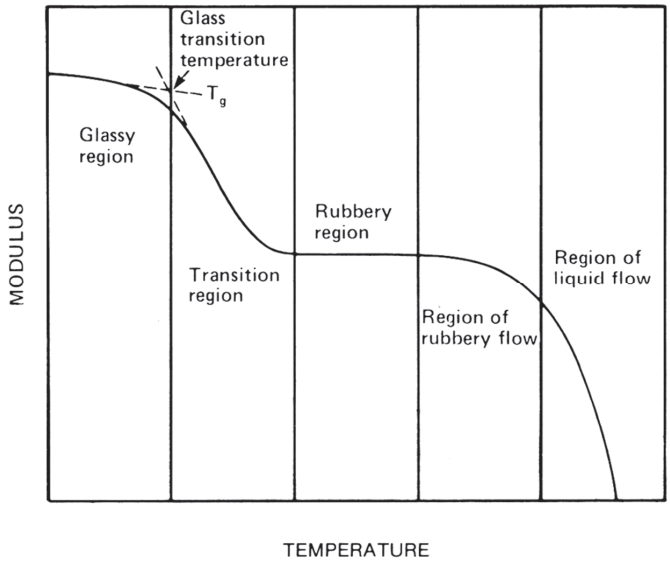

Fig. 1 Schematic illustration of the elastic behaviour of an amorphous non cross-linked polymer (Source: Irvine 1984, reproduced with permission from TAPPI).

Wood softens when it is heated and the components (lignin, hemicellulose and disordered cellulose) soften at different points depending on temperature and moisture content. Thus amorphous cellulose is more hygroscopic than crystalline cellulose, therefore crystallinity of cellulose has an effect on glass transition temperature of cellulose. Higher the crystallinity is, less the moisture content effects on softening (Back and Salmén 1982). It has been reported that the content of wood extractives is negatively correlated with equilibrium moisture content of wood (Nzokou and Kamden 2004). Therefore the extractives content also has an effect on wood softening behaviour. Figs. 2 and 3 show the effect of temperature and moisture on the softening behaviour of different wood compounds. The total lignin content in softwoods is approximated to be 28% by Salmén (1984) and Dinwoodie (2000) and its function is that of a matrix, maintaining the form of wood. Thus, the properties of lignin are particularly critical when it comes to the softening behaviour of wood. Moreover, it has been reported that moisture changes in wood under load cause the mechano-sorption effect, which reduces the elastic modulus (Grossman 1976; Hoffmeyer and Davidson 1989; Navi et al. 2002). Therefore mechano-sorption effect could assist wood softening and therefore also the wood compression.

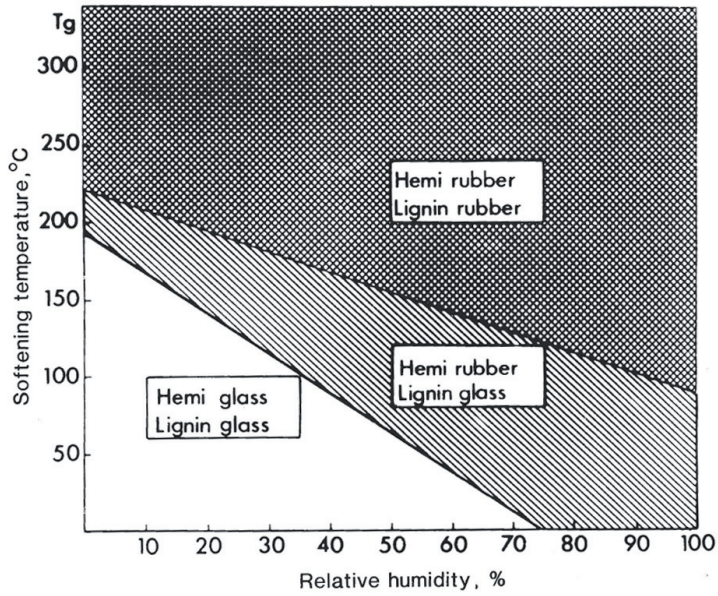

Fig. 2 The effect of relative humidity on the softening temperature of lignin and hemicellulose, showing the glassy and rubbery regions (Source: Salmén et al. 1986, reproduced with permission from Elsevier Ltd).

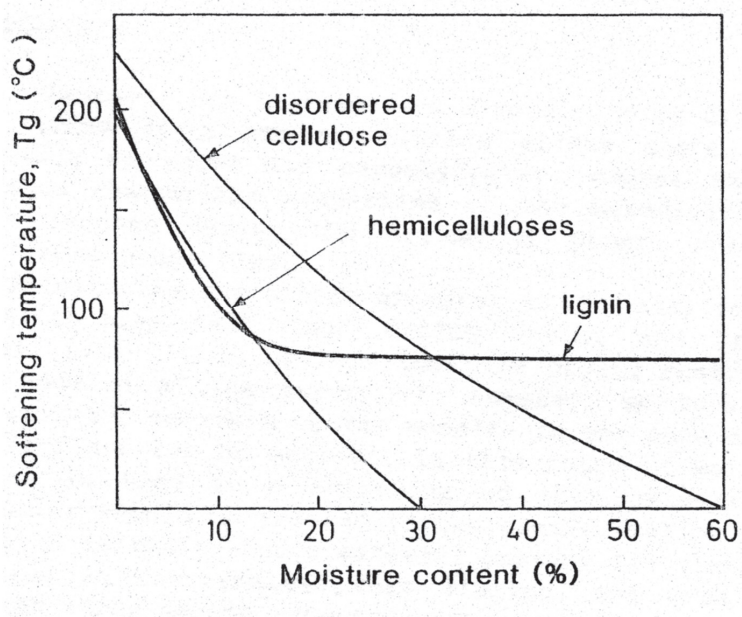

Fig. 3 A schematic illustration of the dependency of the softening temperatures of lignin, hemicelluloses and amorphous cellulose on moisture content (Source: Salmén 1990, reproduced with permission from Cambridge University Press).

2.2 Wood densification

Earlier studies by Viitaniemi and Kontinen (1994) and Heräjärvi (2009) have shown that solid wood can by dried using a contact drier, where the wood material is dried between hot plates and water can be removed faster than is typical of a convective kiln dryer. The more rapid removal of water in contact drying is partly the result of the more effective conductive heat transfer between the hot plate and wood and partly due to the removal of water by mechanical compression. The compression can deform the wood material with the result that twisting and warping are reduced (Heräjärvi 2009) and the wood material is compressed into a more dense form. It has also been shown that rotary cut veneer can be dried using a compression drying technique employing either hot plates or a roller press (Adachi et al. 2004; Bekhta et al. 2009) resulting in smoother surfaces (Candan et al. 2010; Diouf et al. 2011). It may be concluded, therefore, that drying using compression is quicker than kiln drying and at the same time certain properties such as surface smoothness, straightness and mechanical properties can be improved.

With some limitations, compression of solid wood can be compared to the manufacture of wood-based panels such as particleboard and medium density fibreboard (MDF). In wood-based panel manufacture, the wood material is often in fibre or in particle form and adhesive and other additives are frequently used to combine the product and enhance certain properties. Heat and moisture transfer during the hot pressing of wood-based panels can be compared to that of the transfer processes occurring during solid wood compression. The heat and moisture transfer during compression are essential in forming the vertical density profile (VDP) and it has a great influence on the properties of wood based panels (Wong et al. 1998; Wong et al. 1999; Wang et al. 2001). It should, therefore, most probably have an influence on the properties of compressed solid wood.

Solid wood compression (i.e. bulk densification) methods can be divided into two categories – open and closed systems. Open systems consist of apparatus capable of applying a compressive force to the wood, but that are not enclosed and thus the compression itself is carried out under ambient conditions. Relative humidity cannot, therefore, be accurately controlled during the compression process. This type of open process has also been referred to by Navi and Girardet (2000) and Heger et al. (2004) as a thermo-mechanical (TM) process. On the other hand, closed systems consist of

apparatus for compressing wood that are enclosed and so the relative humidity can be controlled during the compression operation using saturated steam. This type of process has been described by Navi and Girardet (2000) and by Navi and Heger (2004) as a thermo-hydro-mechanical (THM) process. As discussed previously, relative humidity will be an important consideration during the softening phase of the compression process. Therefore, when using open systems, the wood material has to have a high enough moisture content before compression to ensure that the softening stage is completed successfully. A variation of the open system uses a steam injection press (Geimer 1982; Fang et al. 2011) to give some control over the moisture content during pressing. The softening stage during pressing can be accomplished relatively easily; however, a more important issue is to keep the wood moist during the post-treatment phase, where temperature (Navi and Heger 2004) and relative humidity (Navi et al. 2007) correlate exponentially with the treatment time needed for elimination of set-recovery.

Wood densification increases several wood properties and these are largely dependent on the degree of densification and the densification technique that is used. If the compressed wood is post-treated with a heat-treatment process the properties can, to some extent, be compared to those of heat-treated wood where the densities are similar. The properties of compressed wood produced using different methods are not always comparable, even if the densities are the same, because the processes can vary widely. It has been reported that mechanical properties such as modulus of rupture and modulus of elasticity (Kamke and Rautkari 2009), hardness (Navi and Girardet 2000) and shear strength (Navi and Girardet 2000) can be increased through wood densification. Moreover, fungal degradation (Schwarze and Spycher 2005; Skyba et al. 2008) and wettability (Kutnar et al. 2008a) can be decreased. Even though modulus of rupture (MOR) and modulus of elasticity (MOE) are enhanced by increasing density, the total bending capacity can be decreased because of the loss in volume of the wood material. Therefore there is a strong case for a densification process where only the surface of solid wood is compressed.

2.3 Surface densification

Surface densification can be achieved either by bonding higher density wood to a lower density core using adhesives, or by compressing the wood in the transverse

sense from one or both sides so that the density of only a few millimetres of the top most layer of the wood is increased. In this way the loss of volume is minimised and the surface properties are improved. It is logical that surface densification is performed on wood material that already has a relatively low density. The surface densification processes have the same phases as in bulk densification namely the surface of the wood has to be first softened and then compressed, but often it also has a cooling phase. It is essential to soften only the surface otherwise, of course, the wood material will be compressed throughout. This is why the surface densification process time has to be rather short, so that there is no time for the heat to transfer to the core. Therefore, the initial moisture content also has to be rather low, since when the mechanical compression is released, the wood material should be below the T_g to avoid immediately spring back, caused by generated inner stresses and also partly steam pressure generated in the process as seen in MDF process (Cai et al. 2006). For this reason moisture content and temperature play an important role.

Spring back can be avoided by applying a cooling phase before releasing the mechanical compression. Whereas the bulk densification of solid wood is rather easily accomplished, surface densification process by compression is more complicated. The most essential aspect is to produce a vertical density profile such that the peak density is as near as possible to the surface and also that the density peak should be broad enough to ensure that the properties are modified sufficiently for a particular application. The density profile is generated during the compression process (Gong et al. 2010; Laine et al. 2011; Rautkari and Hughes 2010a) and many variables influence its development. These include pressing temperature, ambient conditions, press closing time and press holding time. Moreover, wood species, chemical composition, the direction of pressing (i.e. radial, tangential or other), initial density and wood moisture content also have a significant role. Earlier studies have shown (Pizzi et al. 2005; Lamason and Gong 2007; Rautkari et al. 2008; Gong et al. 2010) that relatively dry wood (approximately mc 12%) should be used in surface densification processes. As a result, the densification process is relatively fast; only some minutes or even seconds (Pizzi et al. 2005; Rautkari et al. 2008) and so processing time is also dependent on the initial moisture content.

There are several methods of densifying only the surface of solid wood. One way is batchwise compression, where one side of wood is compressed using a press with only one heated platen (Inoue et al. 1990; Lamason and Gong 2007; Gong et al. 2010; Laine et al. 2011). Alternatively surface densification can be carried out with the assistance of motion in a continuous press (Tarkow and Seborg 1968), by using a heated roller and friction (Rehm and Raatz 2005; Fuchs et al. 2007a,b) or by using a linear friction technique with wood against wood (Pizzi et al. 2005) or with a heated steel plate (Rautkari et al. 2008). Fig. 4 shows the surface of a Norway spruce specimen densified using friction technology, where it can be seen that only one or two cell layers are compressed. Greater surface deformation can be seen in the Scots pine specimen shown in Fig. 5 produced by compressing with a heated platen. As can be seen several growth rings have been deformed and, with higher magnification, it can be seen that the compression is restricted mainly to earlywood.

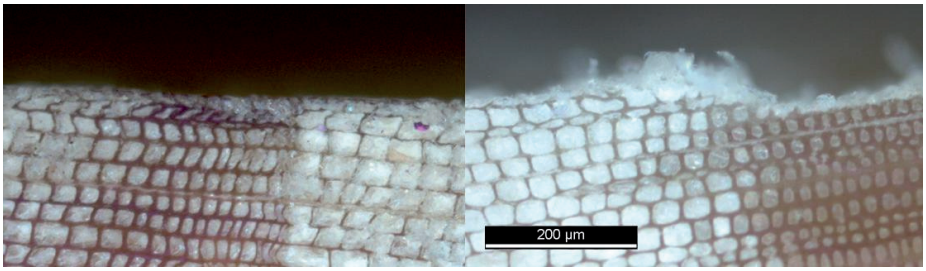

Fig. 4 Surface densified spruce on left side and right side surface after table saw preparation (Paper IV).

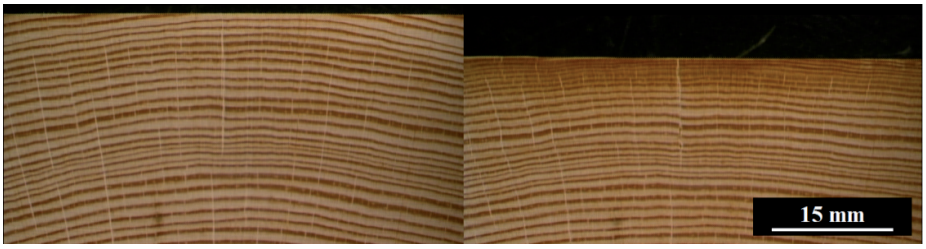

Fig. 5 Surface densified Scots pine using a single side heated press on right side and left side surface is planed.

However, earlier studies on surface densified wood have shown that the mechanical properties such as hardness are correlated with the degree of compression (Lamason and Gong 2007; Rautkari et al. 2008), but modulus of elasticity and rupture on the other hand did not exhibit any significant increase (Lamason and Gong 2007). It has also been reported that surface densification reduces the water wetting properties. As a result, the water penetration on surface densified wood rate is significantly slower

than on the surface of untreated wood (Pizzi et al. 2005; Rautkari et al. 2010b). Moreover, the glossiness of surface densified solid wood has been reported to be increased by up to 700% (Rautkari et al. 2008), compared to untreated wood, which indicates a smooth surface. Surface roughness has also been shown to be significantly reduced on the edge of surface densified MDF (Rehm and Raatz 2005; Fuchs et al. 2007b). It has also been reported (Subyakto et al. 1998) that surface densification improves fire retardant properties of solid wood somewhat. All the results depend on the surface densification process and the intensity of the process.

2.4 Summary

The phenomena's of wood softening, bulk wood densification and wood surface densification are presented in the section above (2. Wood densification). Many of the properties can be enhanced by compression, but the surface densification techniques are not widely studied. Main target of surface densification is to increase the surface properties of the solid wood. The materials and methods used in in this study are presented in the following section, where different properties such as hardness, wettability and surface chemistry were evaluated.

3 MATERIALS AND METHODS

3.1 Wood material

Various hardwood and softwood species were used in the studies. The wood species were hybrid poplar (*Populus deltoides* x *Populus trichocarpa* L.) (Papers I and II), Douglas-fir (*Pseudotsuga menziesii* L.) (Paper II), Scots pine (*Pinus sylvestris* L.) (Papers III and VI), Norway spruce (*Picea abies* L.) (Papers IV and V) and European beech (*Fagus sylvatica* L.) (Paper V). The wood species were selected for the different modification methods depending on the focus of a particular project. More detailed information about the wood material used in each study is presented in the original papers.

3.2 Densification processes

3.2.1 Surface modification by lamination

Papers I and II focus on the whole wood densification of thin lamellae which are then laminated, using an adhesive, to untreated wood thereby creating a composite. The method used for whole wood densification was a Viscoelastic Thermal Compression (VTC) process that had been developed in the USA (Kamke and Sizemore 2008). Wood densification was carried out in a reaction vessel in which pressurized steam was delivered from a steam generator. The reactor incorporated separately heated platens with mechanical stops and a water cooling system. The VTC process has several phases: i) wood softening, ii) first-stage compression, iii) venting, iv) second-stage compression, v) heat-treatment and vi) cooling. More details about the process are given in Papers I and II and have also been reported by Kutnar et al. (2009) and Kamke and Rathi (2010).

3.2.2 Surface modification using a heated plate

Surface densification was carried out using a specially designed heated press tool fitted to a material testing machine. The surface of the wood was softened by an electrically heated plate incorporated into the press tool. The tool was also equipped with a water cooling system. Mechanical stops ensured that the specimens would be compressed to the same final thickness. The press was then set to close in a specified time ("closing time"). Once the unheated loading plate had contacted with the stops, the press remained closed with the heat being applied for a specified holding time. After the desired holding period, the cooling system was turned on and the load maintained until the temperature was below 100ºC. More details about the process are found in Paper III.

3.2.3 Surface modification using friction technique

Linear vibration friction technology is widely used in the plastics and automotive industries and has been investigated as a means of bonding wood without adhesives (Gfeller et al. 2003 and 2004), but also for surface densification (Pizzi et al. 2005; Rautkari et al. 2008). Surface modification by frictional densification was carried out using a modified Branson 2700 linear vibration welding machine (Dietzenbach, Germany). Densification was carried out at a frequency of 100 Hz and amplitude of 3 mm. The surface of the lower platen, where the friction was produced, was smooth, polished steel and it was pre-heated to 100ºC for a more stable process temperature. After frictional heating and compression, pressure was maintained until the surface temperature had cooled down to 60°C, when it was assumed that the wood material in the vicinity of the surface had solidified. Further details about this process are to be found in Papers IV, V and VI.

3.3 Microscopy

Microscopy studies were conducted with various optical microscopes, depending upon where the experiments were carried out. Anatomical changes to the modified specimens (Papers IV and V) were examined using both a Leica DMLM 25-5009 epi-illumination microscope equipped with a Leica DFC 320 video camera and a Leica MZ16 7.1-11.59 stereomicroscope equipped with a Leica DFC 300 video camera. All the measurements were processed using Leica IM 1000 software. Anatomical changes to the modified specimens (Papers III and VI) were examined

using a Leica WILD MZ 8 microscope and a Nikon Optiphot-2 microscope, both equipped with a JVC 3-CCD 320 video camera for image capture.

3.4 Hardness

Brinell hardness was measured on surface densified Norway spruce wood (Paper IV) and on the surface of densified hybrid poplar and Douglas fir wood that had been laminated with untreated wood (Paper I). The Brinell hardness method employed was adapted from the EN 1534 (2000) and JIS Z 2101 (1994) standards. In the EN 1534 (2000) standard, the load is constant and the diameter of the indentation is measured. In the JIS Z 2101 (1994) standard, the indentation depth is constant and the load is measured. In this study, the load was constant and the indentation depth was measured. Moreover different forces were applied to investigate the influence of the penetration depth of the indenter. The Brinell hardness H_B (N/mm²) was calculated using Eq. 1.

$$H_B = \frac{F}{\pi * D * h} \tag{1}$$

where D (mm) is the diameter of the indenter, h (mm) the maximum depth of the indentation, and F (N) the applied load. Maximum load was reached in 15 s, maintained for 25 seconds and then removed over a period of 15 s. The maximum depth h_{max} of the indentation and the elastic deformation, h_ε, of the indentation were measured. The elastic deformation is the "immediate" recovery of the indentation when the load is removed. The value h_ε is measured when the load reaches zero during unloading. The surface elasticity ε_ε was calculated using Eq. 2.

$$\varepsilon_e = \frac{h_{max} - h_e}{h_{max}} \tag{2}$$

3.5 Vertical density profile

Vertical density profiles were measured using an X-ray densitometer (QMS, Model QDP-01) (Papers I and II) and densitometer based on a gamma ray source (ATR Density Profilometer DPM201) (Paper III). The X-ray / gamma ray beam was projected through the width of the specimen (tangential direction), meaning that the

vertical density profile was measured with respect to the specimen thickness. The density was measured at intervals of 0.02 mm (Paper I), 0.04 mm (Paper II) and 0.1 mm (Paper III) through the thickness of the specimens.

3.6 Contact angle

Contact angles were measured on surface densified Norway spruce and European beech. Contact angle measurements were performed with a Krüss DSA 10 contact angle measuring instrument and analysed by a drop shape analysis program (Krüss DSA v1.80). Distilled water was used for the drop. More details are given in Paper V.

3.7 FTIR-ATR spectroscopy

Untreated and surface densified Norway spruce and European beech and their chemical changes during densification process were evaluated with FTIR (Fourier transform infrared). IR spectra were obtained using a Perkin–Elmer Spectrum 100 FT-IR instrument with a universal ATR (attenuated total reflection) diamond crystal. The spectra were recorded in the wavenumber range of 800–4000 cm^{-1} at resolution of 8 cm^{-1}. The analysis depth was 0.2–2 μm, depending on the wavenumber. The spectra were ATR-corrected before the analyses. Moreover, the IR spectra of spruce canal resin were obtained for verifying the absorption peak in the carbonyl region.

3.8 X-ray photoelectron spectroscopy

Differences between the surface chemistry of friction densified Scots pine and the same material compressed in a heated press without motion were evaluated by means of XPS (X-ray photoelectron spectroscopy). Both sapwood and heartwood were analysed with and without extraction. XPS analyses were carried out using an AXIS 165 electron spectrometer (Manchester, UK) and monochromatic Al K_α irradiation at 100W. For elemental composition, low resolution wide spectra were recorded, using 80 eV pass energy and 1 eV step. For more detailed chemical information, carbon and oxygen were also recorded in high resolution mode, using 20 eV pass energy and 0.1 eV step. More details are provided in Paper VI.

3.9 Set-recovery

The set-recovery of surface densified wood (Paper V) and densified whole wood (Paper I) was measured after humid-dry cycles and wet-dry cycles, respectively. The set-recovery (S_r) of surface densified wood was calculated using Eq. 3 (Paper V).

$$S_r = \frac{T_r - T_c}{T_0 - T_c}, \text{ when } T_r \geq T_c \text{ and } T_0 > T_c \quad (3)$$

where T_r is the thickness of the specimen (RH 65%, 20ºC) after 5 humid-dry cycles, T_c is the thickness of the compressed specimen and T_0 is the initial thickness of the specimen (RH 65%, 20ºC). The set-recovery, also referred to as irreversible swelling (*IS)*, of densified whole wood was calculated using Eq. 4 (Paper I).

$$IS = \frac{(T_s - T_0)}{T_0} \quad (4)$$

where T_s is oven dry thickness after water soaking and T_0 is oven dry thickness before soaking.

4 RESULTS AND DISCUSSION

4.1 Wood surface densification

In order to improve solid wood surface properties, three densification types were evaluated. In Papers I-II high density solid wood (densified using a VTC process) was laminated to low density wood. This certainly increases surface density, but an adhesive is needed. Untreated hybrid poplar and VTC hybrid poplar specimens are shown in Fig. 6. In Table 1 the initial density and density after densification are presented.

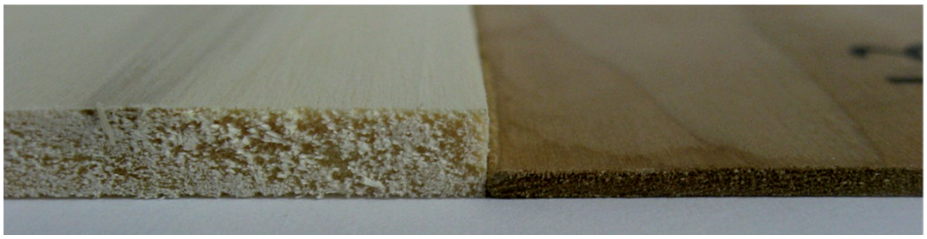

Fig. 6 Untreated hybrid poplar specimen (left) and VTC processed specimen (right).

Table 1 Initial densities and VTC wood densities (Paper I).

Material	Initial density g/cm³	Density after compression g/cm³	Degree of densification %
Hybrid poplar	0.37	1.22	236
Douglas-fir	0.46	1.14	148

Earlier studies (Inoue et al. 1990; Lamason and Gong 2007; Gong et al. 2010) showed that only the surface of solid wood can be compressed. Paper III describes how process parameters such as temperature, moisture content, press closing time and press holding time affect the density profile generated when solid wood is

compressed. It is important that the densification occurs only on the surface, if it is the surface properties that are to be enhanced. Surface densification using a heated plate combined with motion on the surface is presented in Papers IV-VI. Earlier studies have shown that motion reduces the surface roughness (Rehm and Raatz 2005; Fuchs et al. 2007b).

4.2 Hardness

The main target of surface densification is to increase the hardness of the surface. It is known that hardness of wood is depending on the density (Dumail et al. 1998; Holmberg 2000; Heräjärvi 2004). Generated hardness results are more complex within material with inhomogeneous density, such as surface densified solid wood and wood-based panels e.g. MDF or particleboard, which all have certain irregular vertical density profile, where surfaces are denser than the core. Within inhomogeneous wooden products, the hardness is resulted from combination of the density of the surface and core, but also the thickness relation of surface and core. In other words, if surface has high density, but it is rather thin and at the same time core has low density the hardness value that is measured is more a result from the core. This phenomenon is demonstrated in Fig. 7, where are two types of penetrations presented on a cross section of hybrid poplar wood which was laminated with high density densified wood. In a typical hardness test, where diameter of 10 mm steel ball has penetrated during the experiment with low force and high force. On left side, there is only small penetration and on right side deeper penetration. It is clear that when thin high density lamella has ruptured, the core begins to support more of the load.

Fig. 7 Low density hybrid poplar laminated with high density VTC wood. Two different types of penetrations presented, using low (left side) and high (right side) forces.

The hardness of a solid material is generally measured by the ability of an indenter to penetrate the surface. In the various standards for different materials the procedure differs in each. In principle, either load or indentation size is measured, with the other being kept constant. The tip shape of the indenter varies depending on which standard is used. One such hardness method is the Brinell hardness method, which was proposed by Johan August Brinell in 1900 originally for metallic materials. Nowadays the Brinell hardness method is widely used to measure the hardness of both metals (EN-ISO 6506-1 2005) and wood and wooden products (EN 1534 2000). The Brinell hardness test procedure is more accurately defined in EN ISO 6506-1 (2005) than in EN 1534 (2000). This is explained in Paper I. Moreover, the JIS Z 2101 (1994) standard has also been referred to as a "Brinell" method by Inoue et al. (1993a), Hirata et al. (2001), Fukuta et al. (2007) and Teranishi et al. (2008). Another common method used to measure the hardness of wood materials is the so-called Janka method, which is explained in both the ISO 3350 (1975) and ASTM D 143 (1997) standards. Hardness measured by the Janka method correlates rather well with Brinell hardness (Kontinen and Nyman 1977; Bektas et al. 2001). All these methods have slightly different approaches to evaluating hardness and this is explained in Paper I and in more detail by Doyle and Walker (1985). The methods measure either the hardness properties of the material or the hardness properties of the surface and it is not always obvious which properties are being measured. Generally it depends on how deep the indenter penetrates; with deeper penetration, it is the materials properties that are being measured rather than the surface properties. Nevertheless, depending upon which method is chosen, the measured properties will differ significantly.

According to EN-1534 (2000), Brinell hardness is, in essence, calculated from the surface area which a 10 mm diameter metal ball indenter creates on the wood when the applied force is constant. Brinell hardness is calculated from Eq. 5.

$$H_B = \frac{2F}{\pi * D * (D - \sqrt{D^2 - d^2})} \tag{5}$$

where F is the applied nominal force, D is the diameter of the indenter and d is the diameter of the indentation (taken as the average of the along the grain diameter and

the across the grain diameter). The unit of the results is kp/mm². According to EN-1534 (2000) the unit can be changed using Eq. (6), when the unit is N/mm².

$$H_B = \frac{2F}{g * \pi * D * (D - \sqrt{D^2 - d^2})} \quad (6)$$

Both Eqs. 5 and 6 are referred to as Brinell hardness, Eq. 5 has not a constant *g* (acceleration of gravity) which can confuse the results, especially customers. Moreover, when the diameter of the indentation is measured, the measurements are rather subjective, at least when measured on solid wood, because the indentations are often unclear. Solid wood hardness values vary greatly, even within the same wood specimen, therefore many indentations are needed to give reliable results and this makes the measurements rather laborious. Therefore, Brinell hardness can be measured according to JIS Z 2101 (1994), where the indentation depth is measured using an accurate testing machine. Then, Brinell hardness is calculated using Eq. 1. It has been reported that the manually measured diameters of indentations, and automatically measured penetration depths, correlate well (Heräjärvi 2004).

The hardness of modified and unmodified solid wood surfaces (Paper I and Paper IV) was measured by a modified Brinell hardness method using constant load (Paper IV) and several different loads (Paper I). The results were calculated according to Eq. 1. In Paper I, unmodified wood (hybrid poplar) was laminated with a thin layer of densified wood (hybrid poplar) and the influence of the lamination thickness and the applied load were investigated. The results (Fig. 8) show that surface hardness was increased by up to 380% with lamination compared to untreated wood, even though the hardness of untreated wood was extremely low. The hardness values were strongly dependent upon the force applied to the wood composites; the deeper the indenter penetrated, the more the values were influenced by the properties of the untreated core wood. This phenomenon has also been reported by Kontinen and Nyman (1977) and by Niemz and Stübi (2000). Thus, the applied force has a significant effect on the hardness of an inhomogeneous wood composite. According to EN 1534 (2000), the applied force should be 1000 N, but it is often changed to a lower force (Kontinen and Nyman 1977; Schwab 1990; Holmberg 2000; Niemz and Stübi 2000; Bektas et al. 2001; Hirata et al., 2001; Gindl et al. 2004; Pizzi et al.

2005; Rautkari et al. 2008). This means that it is possible to obtain higher hardness values by choosing a lower applied force. More details are explained in Paper I.

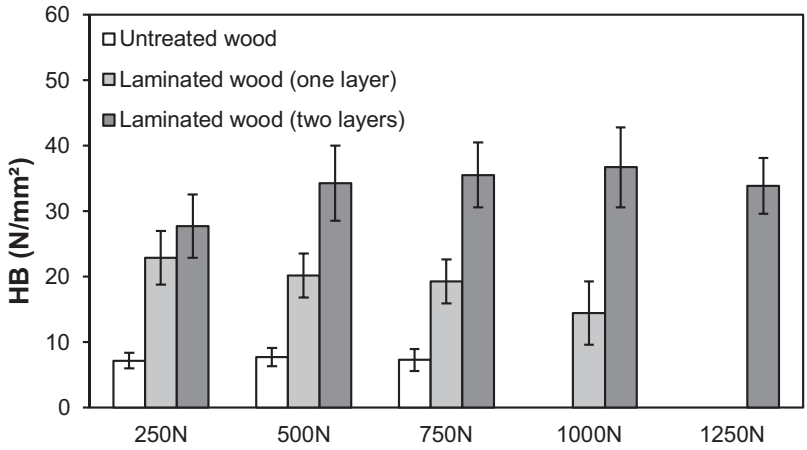

Fig. 8 The hardness of laminated hybrid poplar with 1 or 2 layers of VTC wood (Paper I).

Earlier studies (Kontinen and Nyman 1977; Wang and Wang 1999; Yu et al. 2011) have shown that the moisture content of wood negatively correlates with hardness. This means that if wood is heat-treated after compression, to avoid set-recovery, the material will have a different moisture content (Stamm and Hansen 1937; Bekhta and Niemz 2003) to that of unmodified wood, due to a decrease in its hygroscopicity. This phenomenon will have influenced the results in Paper I at least.

The surface of solid Norway spruce was friction densified (Paper IV) and the hardness measured using Eq. 1 and a constant load (300 N). The average Brinell hardness of unmodified Norway spruce was found to be 12 N/mm² on the radial surface and 9 N/mm² on the tangential surface. Brinell hardness was found to increase with an increasing densification ratio (Fig. 9). Each point is the average of 4 measurements from the same specimen. It is clear that by compressing the wood material the density increases and thus the hardness increases. However, even if the wood is compressed by less than 1 mm, hardness is still enhanced. This indicates that the surface has a significant effect on hardness, but that the rather low load used to measure hardness may have played a significant role. The red dot is the hardness value for untreated reference for Norway spruce on the tangential surface. The force used in this study was relatively low and therefore it has a positive effect on the results as described in Paper I. The variation in the results presented in Fig. 9 is

probably caused by the different process parameters used in the study, which could have led to the densification occurring beneath the surface that could have affected the results. Unfortunately, the VDPs were not measured.

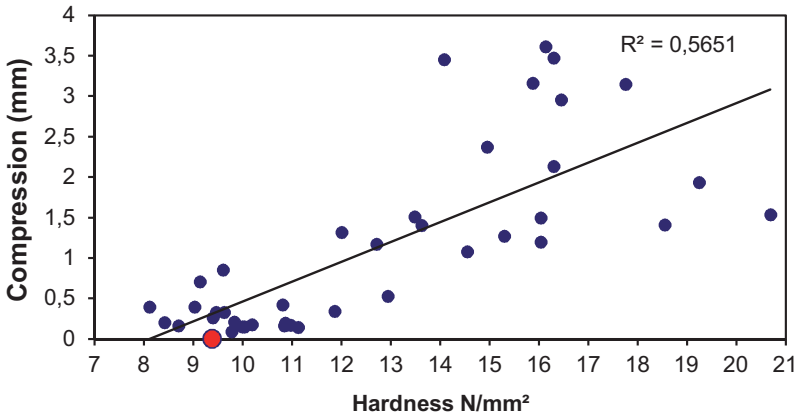

Fig. 9 The influence of compression rate on hardness of surface densified spruce in radial direction (Paper IV).

4.3 Elastic-recovery

The hardness of wood is an important value to estimate wearing properties. Furthermore, the elastic properties of the surfaces are important as well. If hardness is evaluated from the maximum depth of the penetration of the indenter with a certain force, the elastic recovery shows recovery of the surface after penetration. Earlier studies have shown that it is also possible to measure the elastic properties of the surface of wood (Wimmer et al. 1997; Tze et al. 2007; Rautkari et al. 2008; Yu et al. 2011) at the same time as measuring hardness, even though most of these studies concern nano-scale indentation of the cell walls of wood.

Papers I and IV shows that in untreated wood (Norway spruce, Douglas-fir and hybrid poplar) the elastic recovery is approximately 25-35%, depending upon the applied force used and the wood species. The results (Fig. 10) show that the elastic recovery can be up to 80% with laminated specimens. This means that the surface is highly elastic and will therefore most probably resist impacts relatively well. The surfaces of the laminated composites (Paper I) are more elastic until the indenter has reached the untreated wood (Fig. 7). The relationship between elastic recovery and indentation depth is shown in Fig. 10 for hybrid poplar with a 1.5 mm lamination (one layer). As may be seen, the elastic recovery and indentation depth correlate

well, especially in the laminated specimens. Fig. 10 shows that the forces used in this study were too high (same as in Fig. 8), because the indentation depth reached was close 5 mm (and even more), whereas the theoretical maximum depth is 5 mm (using 10 mm metal ball). Even if the maximum load used was less than the standard required (750 N) with untreated wood. This again raises doubts about the applicability of EN 1534 (2000) for evaluating the hardness of low-density wood.

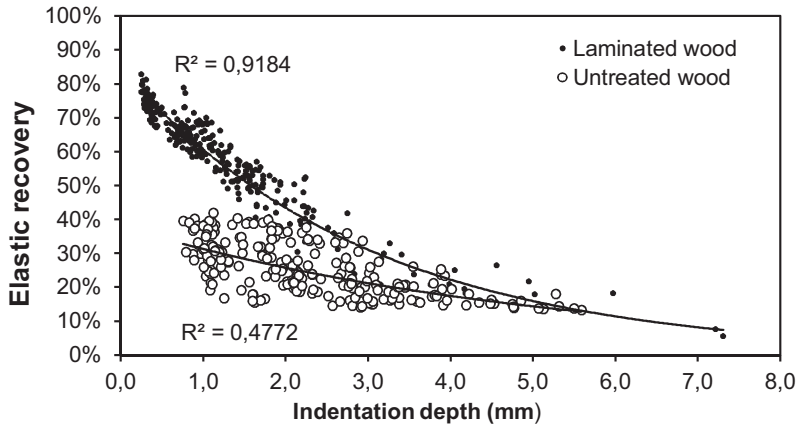

Fig. 10 The elastic recovery of laminated hybrid poplar and untreated wood (Paper I).

4.4 Vertical density profile

Vertical density profile (VDP) is the density through the thickness of the specimen and can be measured, for example, using a densitometer employing beta-, gamma- or X-rays. Using such an instrument, the average density of 'slices' through the thickness of a specimen can be measured at certain intervals e.g. 0.05 mm, in other words the densitometer measures the density through the whole thickness of the specimen at 0.05 mm intervals. It is well known that various process parameters influence the VDP created in wood-based panels such as MDF and oriented strand board (OSB) during their manufacture. In wood-based panel production, the VDP contributes greatly to the final product properties and as such has been widely studied (Wong et al. 1998; Wong et al. 1999; Wong et al. 2000). Density profiles are also important characteristics of compressed solid wood. Earlier studies have shown that compressing parameters have a significant role to play in generating the density profiles in bulk wood compression (Wang and Cooper 2005a,b; Kutnar et al. 2009) and surface densification (Rautkari et al. 2010c; Laine et al. 2011). Therefore density profile measurements are key to proving that densification has taken place

successfully and that the surface properties will be generated as required. Papers I - III show the vertical density profiles of surface densified solid wood, where the densification has been generated using lamination (Papers I and II) or by using the heated plate technique (Paper III). Fig. 11 shows a typical VDP in a composite formed from VTC densified hybrid poplar laminated to untreated hybrid poplar wood.

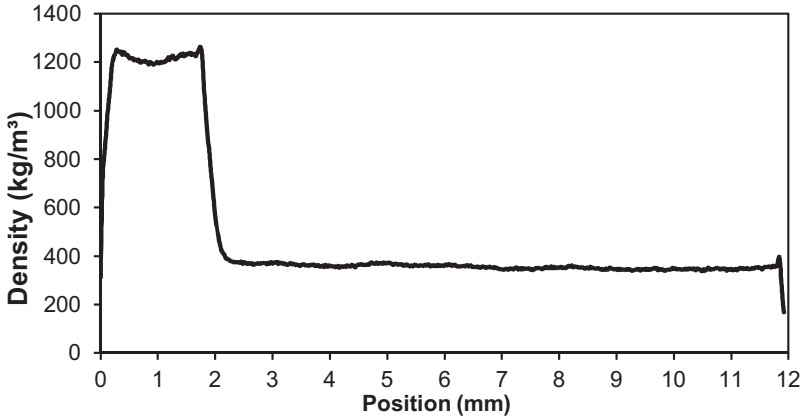

Fig. 11 A typical VDP of VTC densified hybrid poplar, which was laminated on untreated hybrid poplar wood (Paper I).

Paper II describes the potential error which can occur during VDP measurements. Thin (1.5 mm) densified (density 1.18 g/cm^3) lamellae were bonded to both sides of 18 mm untreated wood (density 0.36 g/cm^3) using adhesive. Using an X-ray densitometer it was observed that the absolute density values of the densified lamellae was in error when compared with gravimetric measurements made of each individual layer. This error is due to the recommended calibration process of the X-ray densitometer, which uses the overall density of the composite to determine the X-ray attenuation factor. Further details about the principles of the densitometer are reported by Chen et al. (2010). For the thin sections of densified wood, the density values were significantly lower (approximately 5%) when measured in the form of a composite. This finding raises the possibility that there might also be errors when density profiles are measured in wood composites using X-ray densitometry.

The effect of process parameters on the through thickness density profile of surface densified wood is described in Paper III. Different process parameters were obtained by changing the closing time, holding time and compressing temperature. Different sample moisture contents as well as different compression ratios were also used.

Overall, Paper III shows that process parameters play a significant role in the wood surface densification process, but it has to be remembered that all parameters are interacting with each other. In Fig. 12 two averaged (n=10) density profiles of surface densified Scots pine boards, which were compressed in the radial direction from 16 mm initial thickness to 15 mm with different process parameters, are presented. Both series had the same initial moisture content (approximately 12.4%) and the same press temperature, but the press closing time (0.5 min and 5 min) and holding time (1 min and 10 min) were different. These variations resulted in significant differences between the density profiles.

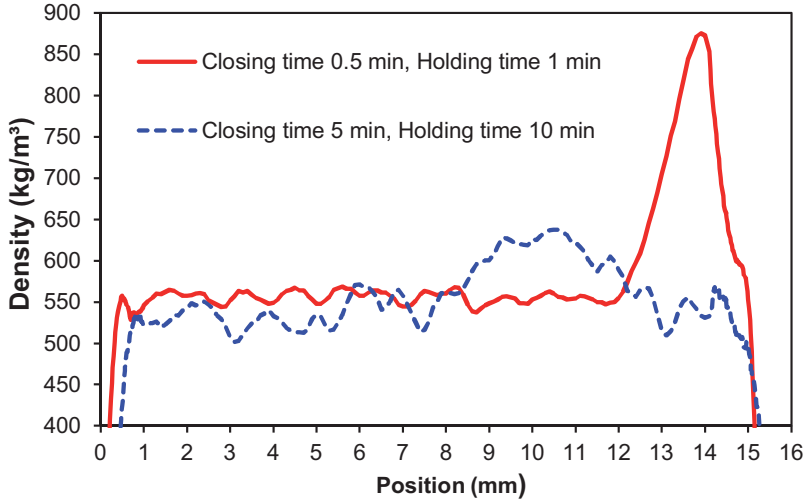

Fig. 12 The effect of press closing and holding time on the density profile generated in surface densified Scots pine (Data from Paper III).

All these findings reveal that the compressing parameters of solid wood have a significant role in generating the form of the VDP which, in turn, will have a significant effect on properties such as hardness and wettability (Pizzi et al. 2005).

4.5 Contact angle

Surface wettability can be measured through contact angle analyses. There are two main techniques to measure contact angle, the sessile drop method and the Wilhelmy plate method. In the sessile drop method, a droplet of liquid is placed on a solid surface, in this case wood, and three interfaces are formed between solid and gas, liquid and gas and between solid and liquid. The angle (θ), formed between the solid surface and the tangent of the liquid (droplet) surface at the point of contact with the

solid surface is known as the contact angle. If the liquid is water, surfaces with high contact angles (Fig. 13a) are deemed hydrophobic and those with low contact angles are hydrophilic (Fig. 13b).

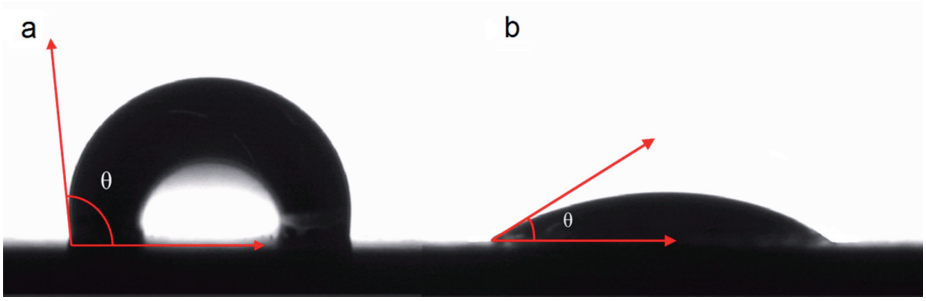

Fig. 13 A droplet of water is placed on hydrophobic (a) and hydrophilic (b) surfaces.

According EN 828 (1997), which determines contact angle measurement arrangements for solid surfaces using the sessile drop method, the contact angle should be recorded at a specified waiting time after the liquid has been applied to the surface. These specified waiting times are 1 or 2 minutes depending on the liquid used. However, contact angle measurements using the static sessile drop method on untreated solid wood is challenging because wood surfaces are rough, porous and hydrophilic. Therefore, if a water droplet is placed on the surface of wood, it immediately starts to absorb to cavities and cell walls as well as evaporating. Therefore it is highly significant that it is reported the time when the droplet is placed on the surface i.e. when the contact angle is measured. Another way to express the results is to use the dynamic contact angle (DCA) method, where contact angles are plotted as function of time.

The Paper V shows the wettability of Norway spruce and European beech surfaces densified by the friction technique outlined in Section 3.2.3. Wettability was assessed by dynamic contact angle analysis using the sessile drop method. The static contact angle on untreated wood was found to be 0°, 2 minutes after the droplets had made contact with the surface, which is indicative of the rapid absorption of the water on the surface. Fig. 14 shows contact angle as a function of time on the tangential face of surface densified Norway spruce, on a waxed wood surface and also on a steel plate. No significant difference in the absorption rate of the droplet was observed between the surfaces of spruce treated with wax or densified by 2.1 mm. The surface of specimens densified by only 0.8 mm had a significantly greater absorption rate

compared to the other treatments. It was hypothesised that water placed on steel does not penetrate, but evaporates. In contact angle measurements performed on glass and polycarbonate, Panwar et al. (2003) found that the mass of a water droplet decreases linearly as a function of time due to evaporation. It seems that main reason for the decreasing contact angle in these DCA measurements is evaporation of water. The water droplet evaporated on steel even faster than on the waxed or densified (by 2.1 mm) surface.

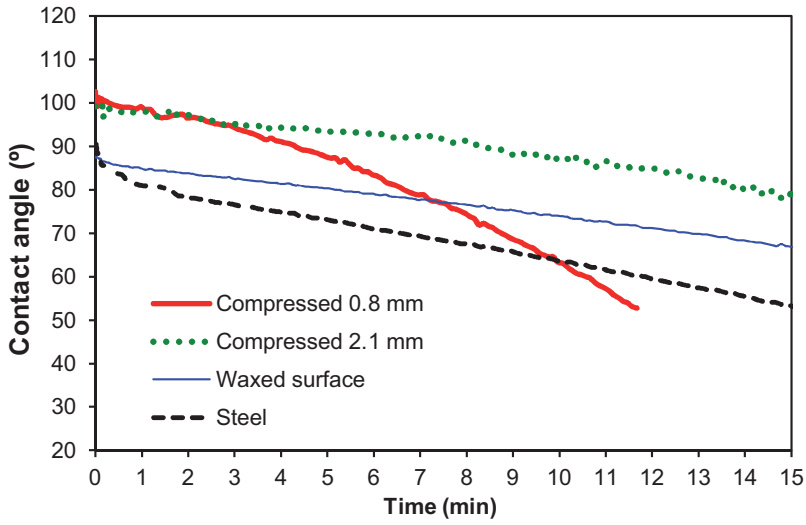

Fig. 14 Dynamic contact angle on different surfaces (Paper V + additional data).

There are several possible reasons for the decreased wettability of surface densified wood. It might be that closed lumens simply prevent water penetration. It is also reported that contact angle is higher on latewood than on earlywood, when contact angle is measured on Norway spruce and Scots pine, caused by smoother surface of latewood (Scheikl and Dunky 1998). On the other hand, decreased wettability might be caused by increased hydrophobicity. It has been reported that hydrothermal treatment has an effect on the contact angle, when wood is bulk densified in the VTC process (Kutnar et al. 2008a), however, Hakkou et al. (2005) have questioned whether thermal degradation is the origin of the hydrophobic character of heat-treated wood. The decreased wettability reported in Paper V is most probably not caused by the hydrothermal treatment, since the heating time was only 12 seconds.

On the other hand the contact angle can show same values even if the material has different wetting behaviour. In Fig. 15 are illustrated two droplets which are placed

on the surface and after certain waiting time the liquid has spread on the surface (a) and penetrated or/and evaporated (b). In both cases the contact angle is the same. Therefore the dimensions of the droplet could show the real wetting behaviour besides the contact angle.

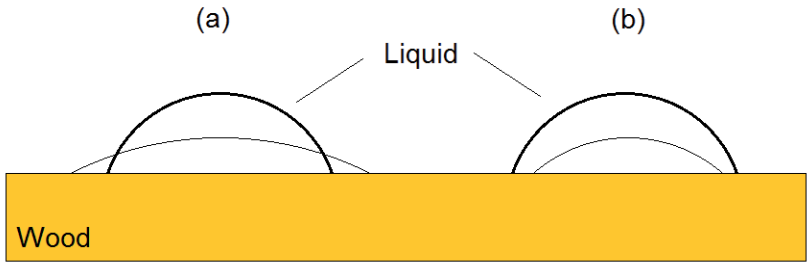

Fig. 15 Decrease of the contact angle after the droplets are placed on the surface. Liquid has spread on the surface (a) and the liquid has penetrated or/and evaporated (b).

In Norway spruce, surface densification using a single side heated press can allow canal resin to migrate to the surface and this has been verified visually. However, using motion the canal resin might be spread over the surface (Rautkari et al. 2010b). In an earlier study (Rautkari et al. 2008) it has been shown that glossiness values can be increased by up to 700% compared to untreated wood following surface densification using the friction technique. It has been suggested that this might be caused by canal resin migrating to the surface during the densification process. It is also been reported that extractives which migrate to the surface of wood create a hydrophobic surface (Nussbaum 1999; Nussbaum and Sterley 2002; Wålinder 2002). Moreover, it has been reported that polar and hydrophilic extractives might increase the wettability and nonpolar extractives decrease wettability (Maldas and Kamdem 1999). Therefore the possible changes in surface chemistry of surface densified wood might give some insight into whether migration of extractives to the surface takes place or not.

4.6 Surface chemistry

4.6.1 FTIR-ATR spectroscopy

Infrared spectroscopy coupled with ATR is a routine method used in wood research because it gives rapid information about the structure of the wood constituents and possible chemical changes due to treatments. Norway spruce, surface densified using the friction technique as well as untreated spruce specimens, were investigated using

FTIR-ATR spectroscopy in Paper V to analyse possible changes in the surface chemistry. Fig. 16 shows the spectra of the densified and the reference spruce specimens. Qualitatively there is no significant difference between the spectra, indicating that no chemical changes, detectable by FTIR-ATR spectroscopy, have occurred during the densification process. This is perhaps not unexpected given the short treatment time (12 s) and relatively low temperatures involved. The quantitative differences between densified and reference spectra is most probably caused by that the smooth densified surface has better contact with the ATR crystal and therefore a larger contact area and higher original conduction.

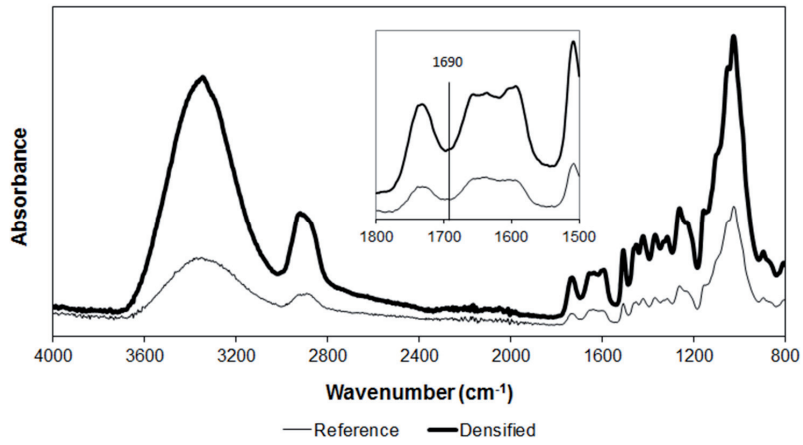

Fig. 16 FT-IR spectra of surface densified spruce and reference (Paper V).

It has been reported (Rautkari et al. 2010c) that in Norway spruce and Scots pine surface densified using the friction technique, the migration of canal resin to the surface has been detected visually, but no chemical evidence for such migration was put forwards. It is known that extractives reduce both the surface wettability (Nussbaum and Sterley 2002) and biological degradation (Taylor et al. 2002). A wood surface enriched with extractives has increased hydrophobicity (Nussbaum 1999; Nussbaum and Sterley 2002) and has antibacterial properties due to the biocidal nature of extractives (Milling et al. 2005; Vainio-Kaila et al. 2010). The enrichment of the surface by extractives was investigated with FTIR-ATR in Paper V. A canal resin droplet exhibited a strong absorption band in the carbonyl region at 1690 cm^{-1} (Fig. 17). In an earlier study (Nuopponen et al. 2003), tiny resinous spots were observed in the cross-sections of the heartwood of pine heat-treated at 100 °C. These resinous spots showed a strong band in the carbonyl absorption region at 1697

cm^{-1}. A study by Holmgren et al. (1999) found that pine oil resin (as a resin acid standard) has a strong absorption band at 1699 cm^{-1}. The canal resin absorption peak at 1690 cm^{1} was not found on the densified spruce, indicating that migration of canal resin to the densified surface was unlikely (Fig. 17).

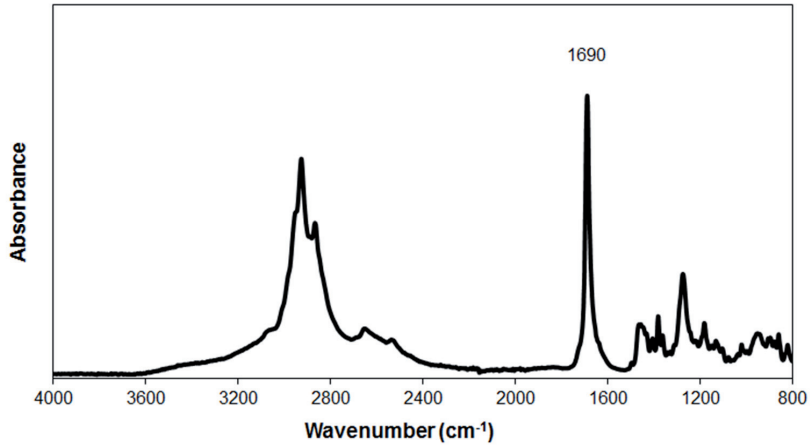

Fig. 17 FTIR spectra of spruce canal resin droplet (Paper V).

On other hand it might also be possible that the extractive layer on the surface is thinner than the analysis depth, which was 0.2–2 µm. The thickness of the earlywood cell wall of Norway spruce has been measured by Fengel (1969) to vary from 1.52 to 2.10 µm and by Sarén et al. (2001) to be from 2.8 to 3.5 µm, therefore the IR-beam is most likely measuring the cell wall properties. Any possible extractive layer on the surface is most probably extremely thin. Therefore, in this case the IR-beam might have simply gone through the extractive layer. A more sensitive method to measure the existence of a possible extractive layer is X-ray photoelectron microscopy.

4.6.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a highly sensitive technique used in the chemical analysis of surfaces to a depth of up to approximately 10 nm. It is reported the possibilities and limitations of XPS for the analysis of lignocellulosic surfaces, such as cellulosic fibres (Johansson et al. 1999; Koljonen et al. 2003; Stenstad et al. 2008), lignin (Zhou et al. 2011) and wood (Sinn et al. 2001; Bryne et al. 2010; Tuong and Li 2011). In Paper VI, chemical changes in the surfaces of densified Scots pine sapwood and heartwood were evaluated by XPS, with the focus on extractive migration to the surface, especially the differences between using friction movement and only heat and compression.

Using XPS, cellulose, lignin, and extractive contents may be determined by means of either O/C atomic ratios or the CC components from the high resolution carbon spectra, if these are recorded from both extracted and non-extracted specimens. However, XPS data can be presented in a correlation graph combining the two independent data sets (Johansson et al. 1999; Johansson 2002; Gustafsson et al. 2003; Johansson et al. 2005). The extractives, such as oleic acid, have high CC bonded percentage and low O/C atomic ratio, while it is the opposite for pure cellulose. This is due to high quantity of hydroxyl groups within cellulose.

The two correlation graphs for heartwood and sapwood samples, presented with references and model compounds, are presented in Figs. 18a and 18b. A comparison of the fresh wood reference with all the non-extracted treated wood samples shows a clear enrichment of non-cellulosic material onto the surface resulting from the treatment. It might be possible that thermal degradation may also have had some effect on the measurements, even if the modification process was relatively short (12 s.).

With both densification treatments the non-extracted heartwood samples have a high extractive content and small local scatter, indicating that a rather uniform extractive layer is formed on the surface (Fig. 18a). However, in the case of the sapwood, the non-extracted data in Fig. 18b is scattered, indicating a non-uniform surface composition and an incomplete film of extractives. In sapwood, only the friction densification appeared to result in uniform surface coverage, leading to surface compositions similar to all non-extracted heartwood samples.

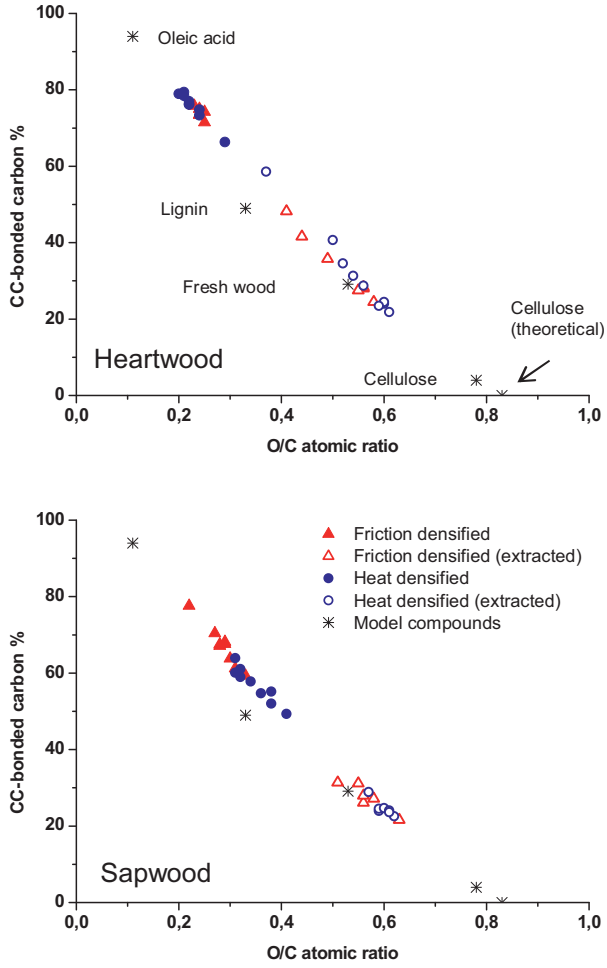

Fig. 18 O/C vs. C-C graphs of heartwood (a) and sapwood (b) of surface modified Scots pine and reference values. Values for cellulose, lignin and oleic acid (*) are calculated from theory, while the data points for pure cellulose reference and the non-treated, non-extracted wood surface are experimental (Paper VI).

Fig. 19 illustrates a sapwood surface modified by friction, whilst Fig. 20 show surfaces created through heating and compression without motion. In this case, darker spots are clearly seen (a), which are most probably due the migration of extractives to the surfaces (b). The same extractive spots are not visible in friction densified surfaces (Fig. 19). Similar findings were reported (Rautkari et al. 2010b) for Norway spruce (Fig. 21). These observations support the XPS data, namely that extractives have formed an even film on the surface of friction densified wood. No significant differences in the sub-surface anatomies of friction densified wood and wood modified without motion were observed.

Fig. 19 Surface of Scots pine sapwood, densified using friction (Paper VI).

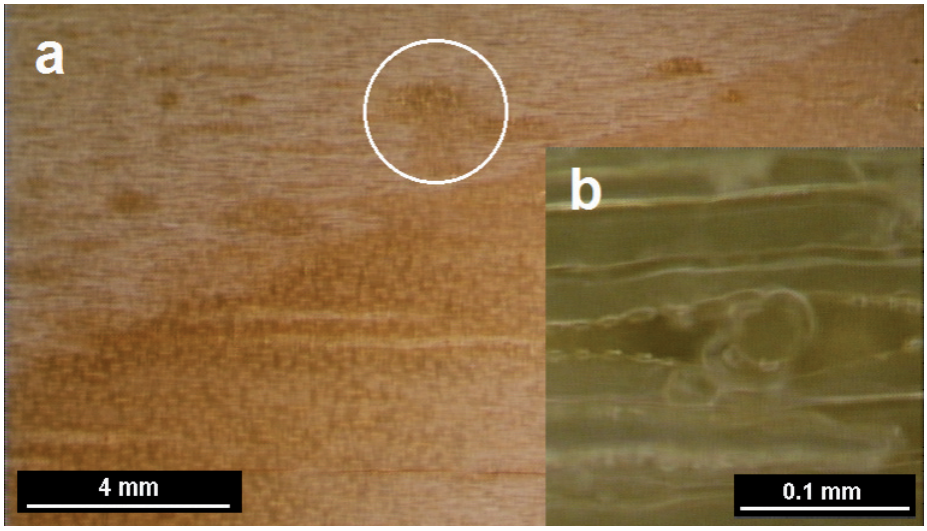

Fig. 20 Surface of Scots pine sapwood, densified using heated plate without motion (a). Extractive spots are seen clearly emanating from horizontal resin canals (b) (Paper VI).

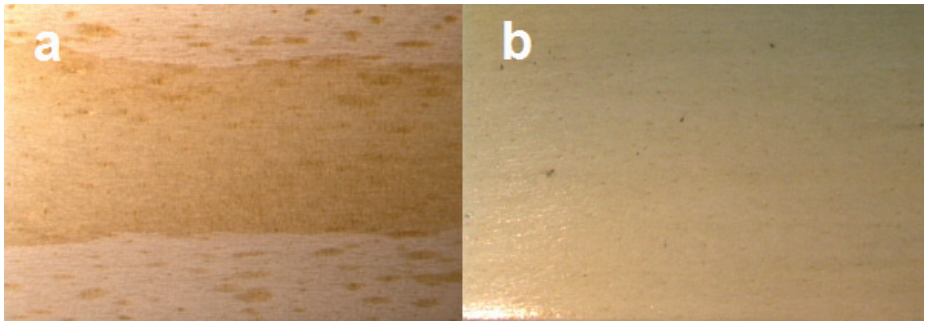

Fig. 21 The surface of Norway spruce densified without motion (a). Extractive spots are seen clearly. The surface of Norway spruce densified using frictional motion. Extractive spots are not seen (b) (Rautkari et al. 2010b).

Overall the results shows that using XPS a layer of extractives can be found on friction densified surfaces, that cannot be observed using FTIR-ATR spectroscopy. On the surfaces of friction densified sapwood, a thin, even layer of extractives was formed, whilst on the surface of wood densified without motion the extractive coverage was more irregular. Differences in extractive coverage were not as significant in heartwood as in sapwood, with both densification processes producing uniform, extractive rich surfaces. The extractive layer on the sapwood surface could possibly increase resistance to biological degradation, increase antibacterial properties and reduce the need for further coating.

4.7 Set-recovery

Under humid or wet conditions compressed wood has tendency to swell to its original dimension, or nearly original dimension, without further treatment. This is also known as irreversible swelling or set-recovery. The objective of this thesis was not to study the elimination of the set-recovery, but still it is one of most important issues when dealing with wood that has been compressed. Navi and Heger (2004) explain the set-recovery in the following way: after wood has been compressed, significant internal stresses are locked into the helical, semi-crystalline, microfibrils. These stresses must be relaxed in order to avoid set-recovery. This relaxation can be done by post-treatment at high temperatures in a saturated steam environment. Treatment time reduces exponentially with increasing steam temperature (Navi and Heger 2004) and relative humidity (Navi et al. 2007). Various studies on compressed solid wood (Inoue et al. 1993; Morsing 1997; Dwianto et al. 1998; Ito et al. 1998b; Navi and Girardet 2000; Heger et al. 2003a,b; Heger 2004; Navi et al. 2007; Welzbacher et al. 2008) have reported that set-recovery can be almost totally eliminated if a high temperature (180–200°C) post-treatment is carried out, especially in a closed press system under humid conditions. These high humid/temperature conditions are only possible in a closed reactor system with high steam pressure (Simpson and Rosen 1981; Ishikawa et al. 2004). It has been reported (Viitaniemi et al. 2001) that it is also possible to eliminate set-recovery using steam heat-treatment. It has also been reported that the steam injection starting point temperature should be high enough (Rautkari and Hughes 2009) so that the compressed wood does not undergo set-recovery during the steam heat-treatment process (Gong et al. 2010). It is also possible to relax the inner stresses by heating

alone, but then the process time is much longer. Morsing (1997) found that it takes 20 hours at 190°C to eliminate inner stresses by heating in an oven, but with steaming in saturated steam, it is possible to eliminate the inner stresses within 15 min at 190°C. Moreover, the set-recovery can be eliminated partly by chemical impregnation. The chemicals could be resins such as be phenol formaldehyde (Gabrielli and Kamke 2010) or melamine formaldehyde (Inoue et al. 1993b).

Elimination of set-recovery by heat and steam alone has been studied, but a uniform explanation has yet not been discovered. However, several theories are linked to the inner stresses, which are formed during wood compression. Navi and Heger (2004) suggest that hydrolysis of hemicelluloses during post-treatment is the main mechanism allowing internal stresses to be relaxed and thus eliminating the set-recovery. Heger et al. (2003a,b) suggests that the elimination of this recovery would be due to the formation of strong new bonds between the densified wood components during post-treatment. Moreover, Dwianto et al. (1998) have reported that the fixation of deformation might result from the release of stresses stored in the cell wall polymers by their degradation as well as by a reduction in hygroscopicity of the cell wall polymers. Ito et al. (1998b) discussed that hemicelluloses and lignin might not have affected the fixation of compressive deformation but the fixation is caused by a structural change in cellulose. It can be concluded that the inner stresses stored in the microfibrils and the matrix must be eliminated, or the formation of cross linkages between molecules of the matrix must occur or that the wood polymers, especially hemicellulose, have to be isolated from moisture and heat to prevent re-softening (Norimoto et al. 1993).

The set-recovery of compressed wood was measured in Paper I and the set-recovery of surface densified wood in Paper V. There is no clear description for the arrangements for measuring set-recovery. All methods for measuring set-recovery attempt to show, percentage-wise, how much compressed wood recovers its thickness when it is exposed to humid or wet conditions. The set-recovery measured in Paper I is referred to as irreversible swelling, where oven dried thin lamellae were water soaked for 48 hours, oven dried again and the percentage swelling calculated. The initial thickness of the Douglas-fir was 4 mm and that of hybrid poplar 5.5 mm. Both were compressed to a target thickness of 1.5 mm. After the soaking-drying

phases, the irreversible swelling was calculated using Eq. 4 and found to be 22.5 and 8.1% for hybrid poplar and Douglas-fir, respectively. As mentioned, the compression ratios were different with the wood species; therefore the results are not totally comparable. However, the set-recovery was rather high and not totally eliminated by the slight heat-treatment given in the VTC process. Another method to present the set-recovery is to use Eq. 3, where it takes in to account the degree of compression. It is more useful when specimens have been compressed in different degree of compressions. One of the issues with Eq. 3, in Paper V, is the problem of the hysteresis behaviour of wood and secondly a reduction in wood hygroscopicity after repeated humidity cycles (Garćia Esteban et al. 2004). These repeated humidity cycles were performed in Paper V. Moreover, in Paper V wood was compressed by only few millimetres or even less than 1 mm. Therefore the accuracy of measurements and sample stabilization to equilibrium moisture content most probably had an influence on the results.

The set-recovery of surface densified wood (Paper V) was also visualised by reflectance light microscopy. The anatomical structure of densified spruce wood with radially oriented annual rings is presented in Fig. 22a. The same sample after 7 days soaking in water and then drying in an oven is shown in Fig. 22b. It may be seen that the annual ring collapse following densification is almost fully recovered after the soaking–drying cycle. Densified Norway spruce wood with tangentially oriented annual rings is presented in Fig. 23a. The same sample after 7 days soaking in water and drying in an oven is presented in Fig. 23b. The earlywood can be seen to have almost totally recovered. Similar results showing that compressed wood has totally or almost totally recovered its original thickness were found by Blomberg et al. (2006).

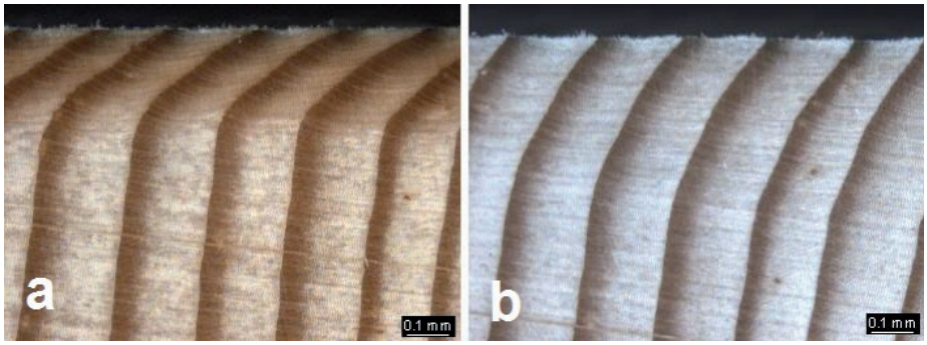

Fig. 22 Surface densified spruce with radially oriented annual rings, before (a) and after (b) water soaking (Paper V).

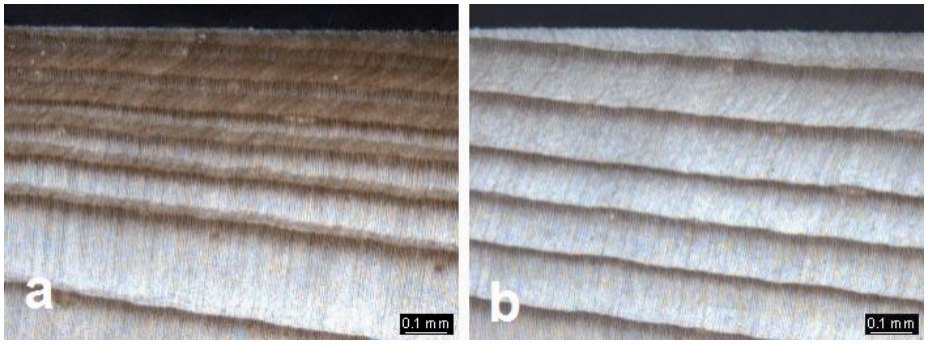

Fig. 23 Surface densified spruce with tangentially oriented annual rings, before (a) and after (b) water soaking (Paper V).

5 CONCLUSIONS

Solid wood density correlates with its mechanical properties and therefore by increasing density, mechanical properties such as hardness can be improved. Compression can be restricted to only the surface of solid wood and therefore only the surface properties are altered. Three solid wood surface densification methods were studied and their effects on certain properties were evaluated.

Low density solid wood was laminated with high density VTC wood using an adhesive and the influence of lamination thickness and applied load on hardness was investigated. It is clear that hardness increased significantly through lamination, but more importantly the results showed that the hardness values were highly dependent upon the applied force used in the measurements. This is important because the applied force is often different in different studies. Moreover, elastic recovery, which is the ability of the surface to recover more readily after impacts, can be increased. Furthermore, the results indicate that the standards covering the measurement of hardness in wood and wooden products need revision.

Solid wood surfaces can be densified only if the surface of the wood is softened and compressed. This phenomenon was investigated using a single side heated press and the influence of the process parameters on VDP was investigated. The variables were closing time, holding time and compressing temperature. Moreover, different sample moisture contents were used as well as different compression ratios. The result showed that process parameters play a significant role in the wood surface densification process, but that all parameters interact with each other. Furthermore, a possible error was found in VDP measurements using X-ray densitometry in composites that had large density differences. The heated plate technique allows extractives, especially of coniferous species, to migrate to the surface making spots.

Heat is needed to soften the surface in the surface densification process; this can, however, be obtained through frictional movement on the surface. When a solid wood surface is densified using a friction technique the process temperature is rather difficult to control. Linear vibrational friction with a heating element was used for solid wood surface densification. The results show that hardness is correlated with the degree of densification. Moreover, wettability decreased significantly, probably caused by closed lumens, a smooth surface and an extractive layer on the surface. The extractives on the surface were analysed by FTIR-ATR spectroscopy and XPS. Using FTIR-ATR spectroscopy there was no trace of extractives, but with XPS an extractive layer was found. The extractive layer could provide a natural coating lessening the need for further coating.

6 REFERENCES

Adachi K, Inoue M, Kanayama K, Rowell RM, Kawai S (2004) Water removal of wet veneer by roller pressing. J Wood Sci 50: 479-483

American Society of Testing Materials (ASTM) (1997) Standard test methods for small clear specimens of timber. ASTM D 143. Annual book of ASTM standards, vol 4.10. Philadelphia, PA, USA

Back EL, Salmén NL (1982) Glass transitions of wood components hold implications for molding and pulping processes. Tappi 65: 107-110

Bekhta P, Hiziroglu S, Shepelyuk O (2009) Properties of plywood manufactured from compressed veneer as building material. Mater Design 30: 947-953

Bekhta P, Niemz P (2003) Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. Holzforschung 57: 539-546

Bektas I, Alma MH, As N (2001) Determination of the relationships between Brinell and Janka hardness of Eastern beech (*Fagus orientalis* Lipsky). For Prod J 51: 84–88

Blomberg J, Persson B, Bexell U (2006) Effects of semi-isostatic densification on anatomy and cell-shape recovery on soaking. Holzforschung 60: 322-331

Bryne LE, Lausmaa J, Ernstsson M, Englund F, Wålinder MEP (2010) Ageing of modified wood. Part 2: Determination of surface composition of acetylated, furfurylated, and thermally modified wood by XPS and ToF-SIMS. Holzforschung 64: 305-313

Cai Z, Muehl JH, Winandy JE (2006) Effects of panel density and mat moisture content on processing medium density fiberboard. For Prod J 56: 20-25

Camm A, Quilter K (2001) Discussion on the effect of moisture and heat transfer during continuous MDF pressing. In: Proceedings of the fifth panel products symposium. Llandudno, Wales, UK

Candan Z, Hiziroglu S, McDonald AG (2010) Surface quality of thermally compressed Douglas fir veneer. Mater Design 31: 3574-3577

Chen S, Liu X, Fang L, Wellwood R (2010) Digital X-ray analysis of density distribution characteristics of wood-based panels. Wood Sci Technol 44: 85-93

Dinwoodie JM (2000) Timber: its nature and behaviour. Second edition, Taylor & Francis, Abingdon, UK

Diouf PN, Stevanovic T, Cloutier A, Fang C-H, Blanchet P, Koubaa A, Mariotti N (2011) Effects of thermo-hygro-mechanical densification on the surface characteristics of trembling aspen and hybrid poplar wood veneers. Appl Surf Sci 257: 3558-3564

Doyle J, Walker JCF (1985) Indentation hardness of wood. Wood Fiber Sci 17: 369-376

Dumail J-F, Castéra P, Morlier P (1998) Hardness and basic density variation in the juvenile wood of maritime pine. Ann Sci For 55: 911-923

Dwianto W, Norimoto M, Morooka T, Tanaka F, Inoue M, Liu Y (1998) Radial compression of sugi wood (*Cryptomeria japonica* D. Don). Holz Roh Werkst 56: 403-411

EN 828 (1997) Adhesives – wettability – determination by measurement of contact angle and critical surface tension of solid surface. CEN – European Committee for Standardization, Brussels

EN 1534 (2000) Wood and parquet flooring – determination of resistance to indentation (Brinell) – test method. CEN – European Committee for Standardization, Brussels

EN ISO 6506-1 (2005) Metallic materials – Brinell hardness test – part 1: test method (ISO 6506-1:2005) CEN – European Committee for Standardization, Brussels

Fang C-H, Mariotti N, Cloutier A, Koubaa A, Blanchet P (2011) Densification of wood veneers by compression combined with heat and steam. Eur J Wood Prod DOI 10.1007/s00107-011-0524-4

Fengel D (1969) The ultrastructure of cellulose from wood. Part 1: Wood as the basic material for the isolation of cellulose. Wood Sci Technol 3: 203-217

Fuchs I, Raatz C, Peter M, Pflüger T (2007a) Some special problems of thermosmoothing and coating. In: Proceedings of 18th international wood machining seminar, Vancouver, Canada

Fuchs I, Raatz C, Peter M, Pflüger T (2007b) Thermo-mechanical processing of wood materials and the effect on the surface roughness. In: Proceedings of 3rd international symposium on wood machining, COST E35, Lausanne, Switzerland

Fukuta S, Takasu Y, Sasaki Y, Hirashima Y (2007) Compressive deformation process of Japanese cedar (*Crytomeria japonica*). Wood Fiber Sci 39: 548-555

Gabrielli CP, Kamke FA (2010) Phenol-formaldehyde impregnation of densified wood for improved dimensional stability. Wood Sci Technol 44: 95-104

García Esteban L, Gril J, de Palacios de Palacios P, Guindeo Casasús A (2005) Reduction of wood hygroscopicity and associated dimensional response by repeated humidity cycles. Ann For Sci 62: 275-284

Geimer RL (1982) Steam injection pressing. In: Proceedings of the 16th Washington State University international symposium on particleboard. Pullman, WA, USA

Gfeller B, Properzi M, Zanetti M, Pizzi A, Pichelin F, Lehmann M, Delmotte L (2004) Wood bonding by mechanically-induced *in situ* welding of polymeric structural wood constituents. J Appl Polym Sci 92: 243-251

Gfeller B, Zanetti M, Properzi M, Pizzi A, Pichelin F, Lehmann M, Delmotte L (2003) Wood bonding by vibrational welding. J Adhesion Sci Technol 17: 1573-1589

Gindl W, Hansmann C, Gierlinger N, Schwanninger M, Hinterstoisser B, Jeronimidis G (2004) Using a water-soluble melamine-formaldehyde resin to improve the hardness of Norway spruce wood. J Appl Polym Sci 93: 1900-1907

Gong M, Lamason C, Li L (2010) Interactive effect of surface densification and post-heat-treatment on aspen wood. J Mater Process Tech 210: 293-296

Goring DAI (1963) Thermal softening of lignin, hemicellulose and cellulose. Pulp Pap Mag Can 64: T517-T527

Grossman PUA (1976) Requirements for a model that exhibits mechano-sorptive behaviour. Wood Sci Technol 10: 163-168

Gustafsson J, Ciovica L, Peltonen J (2003) The ultrastructure of spruce kraft pulps studied by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Polymer 44: 661-670

Hakkou M, Pétrissans M, El Bakali I, Gérardin P, Zoulalian A (2005) Wettability changes and mass loss during heat treatment of wood. Holzforschung 59: 35-37

Heger F, Girardet F, Navi P (2003a) Post-treatment of thermo-hydro-mechanical densified wood with a new multiparameter reactor. In: Proceedings of the 1st European conference on wood modification, Ghent, Belgium

Heger F, Girardet F, Navi P (2003b) Shape stabilisation of densified wood through THM post-treatments with a new multiparameter reactor. In: Proceedings of 2nd international conference of the European society for wood mechanics, Stockholm, Sweden

Heger F, Groux M, Girardet F, Welzbacher C, Rapp AO, Navi P (2004) Mechanical and durability performance of THM-densified wood. Final workshop COST action E22, Lisbon, Portugal

Heräjärvi H (2004) Variation of basic density and Brinell hardness within mature Finnish *Betula pendula* and *B. pubescens* stems. Wood Fiber Sci 36: 216-227

Heräjärvi H (2009) Effect of drying technology on aspen wood properties. Silva Fennica 43: 433-445

Hill CAS (2006) Wood modification – chemical, thermal and other processes. John Wiley and Sons Ltd., Chichester, UK

Hillis WE, Rozsa AN (1978). The softening temperatures of wood. Holzforschung 32: 68-73

Hirata S, Ohta M, Honma Y (2001) Hardness distribution on wood surface. J Wood Sci 47: 1-7

Hoffmeyer P, Davidson RW (1989) Mechano-sorptive creep mechanism of wood in compression and bending. Wood Sci Technol 23: 215-227

Holmberg H (2000) Influence of grain angle on Brinell hardness of Scots pine. (*Pinus sylvestris* L.). Holz Roh Werkst 58: 91-95

Holmgren A, Bergström B, Gref R, Ericsson A (1999) Detection of pinosylvins in solid wood of Scots pine using Fourier transform Raman and infrared spectroscopy. J Wood Chem Technol 19: 139-150

Inoue M, Norimoto M, Otsuka Y, Yamada T (1990) Surface compression of coniferous wood lumber I. A new technique to compress the surface layer. Mokuzai Gakkaishi 36: 969-975

Inoue M, Norimoto M, Tanahashi M, Rowell RM (1993a) Steam or heat fixation of compressed wood. Wood Fiber Sci 25: 224-235

Inoue M, Ogata S, Kawai S, Rowell RM, Norimoto M (1993b) Fixation of compressed wood using melamine-formaldehyde resin. Wood Fiber Sci 25: 404-410

Irvine GM (1984) The glass transitions of lignin and hemicellulose and their measurement by differential thermal analysis. Tappi 67: 118-121

Ishikawa A, Kuroda N, Kato A (2004) In situ measurement of wood moisture content in high-temperature steam. J Wood Sci 50: 7-14

ISO 3350 (1975) Wood—determination of static hardness. International Organisation for Standardization

Ito Y, Tanahashi M, Shigematsu M, Shinoda Y, Ohta C (1998a) Compressive-molding of wood by high-pressure steam-treatment: Part 1. Development of compressively molded squares from thinnings. Holzforschung 52: 211-216

Ito Y, Tanahashi M, Shigematsu M, Shinoda Y (1998b) Compressive-molding of wood by high-pressure steam-treatment: Part 2. Mechanism of permanent fixation. Holzforschung 52: 217-221

JIS Z 2101 (1994) Methods of test for woods. Japanese Industrial Standard

Johansson L-S (2002) Monitoring fibre surfaces with XPS in papermaking processes. Microchim Acta 138: 217-223.

Johansson L-S, Campbell JM, Koljonen K, Stenius P (1999) Evaluation of surface lignin on cellulose fibers with XPS. Appl Surf Sci 144-145: 92-95

Johansson L-S, Campbell JM, Fardim P, Hultén AH, Boisvert J-P, Ernstsson M (2005) An XPS round robin investigation on analysis of wood pulp fibres and filter paper. Surf Sci 584: 126-132.

Kamke FA (2006) Densified radiata pine for structural composites. Maderas Cienc Tecnol 8: 83-92

Kamke FA, Rathi VM (2010) Apparatus for viscoelastic thermal compression of wood. Eur J Wood Prod 69: 483-487

Kamke FA, Rautkari L (2009) Modified wood veneer for structural applications. In: Proceedings of the 4th international symposium on Veneer processing and products, Espoo, Finland

Kamke FA, Sizemore H (2008) Viscoelastic thermal compression of wood. US Patent No. US 7,404,422 (B2)

Kelley SS, Rials TG, Glasser WG (1987) Relaxation behaviour of the amorphous components of wood. J Mater Sci 22: 617-624

Kellog RM, Wangaard FF (1969) Variation in the cell-wall density of wood. Wood Fiber Sci 1: 180-204

Koljonen K, Österberg M, Johansson L-S, Stenius P (2003) Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM. Colloids and surfaces A: Physicochem Eng Aspects 228: 143-158

Kontinen P, Nyman C (1977) Hardness of wood-based panel products and their coatings and overlays. Paper Timber 9: 531-545 (in Finnish with English summary)

Kutnar A, Kamke FA, Petrič M, Sernek M (2008a) The influence of viscoelastic thermal compression on the chemistry and surface energetics of wood. Colloids and Surfaces A: Physicochem Eng Aspects 329: 82-86

Kutnar A, Kamke FA, Sernek M (2008b) The mechanical properties of densified VTC wood relevant for structural composites. Holz Roh Werkst 66: 439-446

Kutnar A, Kamke FA, Sernek M (2009) Density profile and morphology of viscoelastic thermal compressed wood. Wood Sci Technol 43: 57-68

Laine K, Rautkari L, Hughes M, Laflin N (2011) Wood surface densification by compression: Analysing the effect of process parameters. COST action FP0904 workshop "Mechano-chemical transformation of wood during THM processing", Biel, Switzerland

Lamason C, Gong M (2007) Optimization of pressing parameters for mechanically surface-densified aspen. For Prod J 57: 64-68

Maldas DC, Kamdem DP (1999) Wettability of extracted southern pine. For Prod. J 49: 91-93

Milling A, Kehr R, Wulf A, Smalla K (2005) Survival of bacteria on wood and plastic particles: Dependence on wood species and environmental conditions. Holzforschung 59: 72-81

Morsing N (1997) Densification of wood. The influence of hygrothermal treatment on compression of beech perpendicular to the grain. Ph.D. thesis, Department of Structural Engineering and Materials, Technical University of Denmark

Navi P, Girardet F (2000) Effects of thermo-hydro mechanical treatment on the structure and properties of wood. Holzforschung 54: 287-293

Navi P, Girardet F, Vulliemin P, Spycher M, Heger F (2007) Effects of post-treatment parameters on densified wood set-recovery. In: Proceedings of the 3rd international symposium on wood machining, Lausanne, Switzerland

Navi P, Heger F (2004) Combined densification and thermo-hydro-mechanical processing of wood. MRS Bull 29: 332–336

Navi P, Pittet V, Plummer CJG (2002) Transient moisture effects on wood creep. Wood Sci Technol 36: 447-462

Niemz P, Stübi T (2000) Investigations of hardness measurements on wood based materials using a new universal measurement system. In: Proceedings of the symposium on wood machining, properties of wood and wood composites related to wood machining, Vienna, Austria

Norimoto M, Ota C, Akitsu H, Yamada T (1993) Permanent fixation of bending deformation in wood by heat treatment. Wood research 79: 23-33.

Nuopponen M, Vuorinen T, Jämsä S, Viitaniemi P (2003) The effects of a heat treatment on the behaviour of extractives in softwood studied by FTIR spectroscopic methods. Wood Sci Technol 37: 109-115

Nussbaum RM (1999) Natural surface inactivation of Scots pine and Norway spruce evaluated by contact angle measurements. Holz Roh Werkst 57: 419-424

Nussbaum RM, Sterley M (2002) The effect of wood extractive content on glue adhesion and surface wettability of wood. Wood Fiber Sci 34: 57-71

Nzokou P, Kamdem DP (2004) Influence of wood extractives on moisture sorption and wettability of red oak (*Quercus rubra*), black cherry (*Prunus serotina*), and red pine (*Pinus resinosa*). Wood Fiber Sci 36: 483-492

Panwar AK, Barthwal SK, Ray S (2003) Effect of evaporation on the contact angle of a sessile drop on solid substrates. J Adhes Sci Technol 17: 1321-1329

Pizzi A, Leban J-M, Zanetti M, Pichelin F, Wieland S, Properzi M (2005) Surface finishes by mechanically induced wood surface fusion. Holz Roh Werkst 63: 251-255

Rautkari L, Hughes M (2009) Eliminating set-recovery in densified wood using a steam heat-treatment process. In: Proceedings of the 4th European conference on wood modification, Stockholm, Sweden

Rautkari L, Hughes M (2011) Wood surface densification using different techniques. COST action FP0904 workshop "Mechano-chemical transformation of wood during THM processing", Biel, Switzerland

Rautkari L, Hughes M, Kamke FA (2010a) A preliminary study into the properties of laminated viscoelastic-thermal-compressed wood. In: Proceedings of the 5th European conference on wood modification, Riga, Latvia

Rautkari L, Hughes M, Properzi M, Pichelin F (2010b) Properties and chemical changes of surface densified wood. In: Proceedings of the 11th world conference on timber engineering, Riva del Garda, Italy

Rautkari L, Kutnar A, Hughes M, Kamke FA (2010c) Wood surface densification using different methods. In: Proceedings of the 11th world conference on timber engineering, Riva del Garda, Italy

Rautkari L, Properzi M, Pichelin F, Hughes M (2008) An innovative thermo densification method for wooden surfaces. In: Proceedings of 10th world conference on timber engineering, Miyazaki, Japan

Rehm K, Raatz C (2005) Developing of dust-free finishing process for the industry. In: Proceedings of the 17th International wood machining seminar, Rosenheim, Germany

Salmén L (1984) Viscoelastic properties of *in situ* lignin under water-saturated conditions. J Mat Sci 19: 3090-3096

Salmén L, Kolseth P, Rigdahl M (1986) Modelling of small-strain properties and environmental effects on paper cellulosic fibres. In: Composite systems from natural and synthetic polymers, Salmén L, de Ruvo A, Seferis JC, Stark EB (eds.) Materials science monographs. Elsevier, Amsterdam, Netherlands 86: 211-223

Salmén L. (1990). On the interaction between moisture and wood fibre materials. In: Materials Interactions Relevant to the Pulp, Paper, and Wood Industries, Passaretti JD, Caulfield D, Roy R, Setterholm V (eds.) Mater Res Soc Symp Proc, Pittsburgh, USA 197: 193-201

Sarén M-P, Serimaa R, Andersson S, Paakkari T, Saranpää P, Pesonen E (2001) Structural variation of tracheids in Norway spruce (*Picea abies* [L.] Karst.). J Struct Biol 136: 101-109

Scheikl M, Dunky M (1998) Measurement of dynamic and static contact angles on wood for the determination of its surface tension and penetration of liquids into the wood surface. Holzforschung 52: 89-94

Schwab E (1990) Die Härte von Laubhölzern für die Parkettherstellung. Holz Roh Werkst 48: 47-51 (in German with English summary)

Schwarze FWMR, Spycher M (2005) Resistance of thermo-hygro-mechanically densified wood to colonisation and degradation by brown-rot fungi. Holzforschung 59: 358-363

Simpson WT, Rosen HN (1981) Equilibrium moisture content of wood at high temperatures. Wood Fiber 13: 150-158

Sinn G, Reiterer A, Stanzl-Tschegg SE (2001) Surface analysis of different wood species using X-ray photoelectron spectroscopy (XPS). J Mater Sci 36: 4673-4680

Skyba O, Niemz P, Schwarze FWMR (2008) Degradation of thermo-hygro-mechanically (THM)-densified wood by soft-rot fungi. Holzforschung 62: 277-283

Stamm AJ, Hansen LA (1937) Minimizing wood shrinkage and swelling: Effect of heating in various gases. Ind Eng Chem 29: 831-833

Stenstad P, Andresen M, Tanem BS, Stenius P (2008) Chemical surface modifications of microfibrillated cellulose. Cellulose 15: 35-45

Subyakto, Kajimoto T, Hata T, Ishihara S, Kawai S, Getto H (1998) Improving fire retardancy of fast growing wood by coating with fire retardant and surface densification. Fire Mater J 22: 207-212

Tarkow H, Seborg R (1968) Surface densification of wood. For Prod J 18: 104-107

Taylor AM, Gartner BL, Morell JJ (2002) Heartwood formation and natural durability – a review. Wood Fiber Sci 34: 587-611

Teranishi M, Koizumi A, Hirai T (2008) Evaluation of quality indexes of bending performance and hardness for hardwoods. J Wood Sci 54: 423-428

Tze WTY, Wang S, Rials TG, Pharr GM, Kelley SS (2007) Nanoindentation of wood cell walls: Continuous stiffness and hardness measurements. Compos A: Appl Sci Manuf 38: 945-953

Tuong VM, Li J (2011) Changes caused by heat treatment in chemical composition and some physical properties of acacia hybrid sapwood. Holzforschung 65: 67-72

Vainio-Kaila T, Kyyhkynen A, Viitaniemi P, Siitonen A (2011) Pine heartwood and glass surfaces: easy method to test the fate of bacterial contamination. Eur J Wood Prod 69: 391-395

Viitaniemi P, Kontinen P (1994) Method for compressive shape-drying of wood. Patent application publication WO 94/26485 (A1)

Viitaniemi P, Jämsä S, Kontinen P, Ek P (2001) Process for producing compressed wood pieces. Patent application publication WO 01/00377 (A1)

Wang J, Cooper PA (2005a) Vertical density profiles in thermally compressed balsam fir wood. For Prod J 55: 65-68

Wang JY, Cooper PA (2005b) Effect of grain orientation and surface wetting on vertical density profiles of thermally compressed fir and spruce. Holz Roh Werkst 63: 397-402

Wang S-Y, Wang H-L (1999) Effects of moisture content and specific gravity on static bending properties and hardness of six wood species. J Wood Sci 45: 127-133

Wang S, Winistorfer PM, Young TM, Helton C (2001) Step-closing pressing of medium density fiberboard; Part 1. Influences on vertical density profile Holz Roh Werkst 59: 19-26

Welzbacher CR, Wehsener J, Rapp AO, Haller P (2008) Thermo-mechanical densification combined with thermal modification of Norway spruce (*Picea abies* Karst) in industrial scale - Dimensional stability and durability aspects. Holz Roh Werkst 66: 39-49

Wilfong JG (1966) Specific gravity of wood substance. For Prod J 16: 55-61

Wimmer R, Lucas BN, Tsui TY, Oliver WC (1997) Longitudinal hardness and Young's modulus of spruce tracheid secondary walls using nanoindentation technique. Wood Sci Technol 31: 131-141

Wong ED, Zhang M, Wang Q, Kawai S (1998) Effects of mat moisture content and press closing speed on the formation of density profile and properties of particleboard. J Wood Sci 44: 287-295

Wong ED, Zhang M, Wang Q, Kawai S (1999) Formation of the density profile and its effects on the properties of particleboard. Wood Sci Technol 33: 327-340

Wong ED, Zhang M, Wang Q, Han G, Kawai S (2000) Formation of the density profile and its effects on the properties of fiberboard. J Wood Sci 46: 202-209

Wålinder MEP (2002) Study of Lewis acid-base properties of wood by contact angle analysis. Holzforschung 56: 363-371

Yu Y, Fei B, Wang H, Tian G (2011) Longitudinal mechanical properties of cell wall of Masson pine (*Pinus massoniana* Lamb) as related to moisture content: A nanoindentation study. Holzforschung 65: 121-126

Zhang Y, Zhang SY, Chui YH, Wan H, Bousmina M (2006) Wood plastic composites by melt impregnation: Polymer retention and hardness. J Appl Polym Sci 102: 1672-1680

Zhou X, Tang L, Zheng F, Xue G, Du G, Zhang W, Lv C, Yong Q, Zhang R, Tang B, Liu X (2011) Oxygen plasma-treated enzymatic hydrolysis lignin as a natural binder for manufacturing biocomposites. Holzforschung 65: 829-833

Aalto-DD 4/2012

ISBN 978-952-60-4464-4
ISBN 978-952-60-4465-1 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934
ISSN 1799-4942 (pdf)

Aalto University
School of Chemical Technology
Department of Forest Products Technology
www.aalto.fi

BUSINESS +
ECONOMY

ART +
DESIGN +
ARCHITECTURE

SCIENCE +
TECHNOLOGY

CROSSOVER

DOCTORAL
DISSERTATIONS