Improving the properties of wood by surface densification

Kristiina Laine

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Abstract

  Mechanical properties generally correlate positively with wood density and, therefore, it might be beneficial to increase the density of otherwise low-density wood species to improve certain characteristics. The aim of the dissertation was to examine the possibility to improve wood properties, such as hardness, by increasing the density of wood, a modification method referred to as 'densification'. The purpose was to target the densification at the very surface of wood, where the property improvements are most needed. Surface densified wood would be suitable in applications where the surface is generally exposed to use, such as flooring or worktops. An increase in density was obtained by reducing the porosity of wood by compressing the structure in a laboratory scale hot press. Densification was targeted at the surface by heating only one plate in the press and utilising wood of relatively low moisture content to inhibit the softening of the sample throughout the thickness.

It was discovered that during surface densification the deformation occurs mainly in the earlywood cells close to the heated plate. The density profile development can be controlled by the parameters used in the densification process. Furthermore, the process parameters and density profile formation correlate directly with property changes, such as hardness, which was almost doubled by surface densification. Microscopic analysis with SEM suggested that no significant damage occurs in the cell wall during densification.

The densified state tends to recover when exposed to high humidity. However, a minor part of the densification was considered permanent and irrecoverable after water soaking - most likely due to rearrangement of the molecular bonds and viscoelastic flow of the matrix during densification. Recovery of the densified state was significantly reduced by thermally modifying the samples after densification. Both, densification and thermal modification reduce the hygroscopicity of wood. In addition, hysteresis was reduced after repeated humidity cycles, possibly resulting from relaxation of the inner stresses which were developed during densification as well as during thermal modification.

The knowledge obtained through this dissertation enhances optimization of the wood densification process for desired property improvements. The results provided knowledge of solid wood behaviour under compression and at high temperature, as well as, behaviour of modified wood in changing humidity conditions.

Tekijä
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Tiivistelmä

Puun mekaaniset ominaisuudet korreloivat positiivisesti puun tiheyden kanssa. Alhaisen tiheyden puulajien laatua voitaisiinkin parantaa tiheyttä lisäämällä. Väitöskirjatyön tavoitteena oli tutkia massiivipuun tiheyden lisäämistä puun pinnalla, jossa ominaisuudet, kuten pinnan kovuus, ovat erityisen tärkeät. Pinnalta tiheä puu voisi sopia kohteisiin, jossa etenkin pinta on kulutuksen kohteena, kuten lattiat ja työtasot. Väitöskirjatyössä puun tiheyttä lisättiin puristamalla puun huokoista rakennetta kasaan kuumapuristimella. Puristuminen kohdennettiin yhdelle pinnalle lämmittämällä vain toinen puoli puristimessa ja käyttämällä kohtuullisen kuivaa puuta, jolloin lämmön vaikutuksesta puu muovautui vain toiselta pinnalta.

Tulokset osoittivat, että tiheys kasvoi läheltä lämmitettyä pintaa ja tiheysprofiilin muodostumista pystytään kontrolloimaan muuttamalla puristusprosessin parametreja, kuten lämpötilaa tai puristimen sulkeutumisaikaa. Tiheysprofiilin muoto sekä prosessiparametrit korreloivat hyvin puun ominaisuuksien kanssa, kuten pinnan kovuuden, joka lähes kaksinkertaistui puristetulla pinnalla. Mikroskooppitutkimus osoitti, että pintapuristus ei aiheuta merkittäviä halkeamia soluseiniin.

Puristettu tila ei ole sellaisenaan pysyvä, vaan palautuu vedelle altistettaessa. Pieni osa puristuksesta ei kuitenkaan palautunut vedessä uitettaessa, vaan oli pysyvää - todennäköisesti molekyylisidosten uudelleen järjestäytymisen sekä ligniinin muovautumisen takia. Puristuksen palautuminen saatiin vähennettyä merkittävästi lämpökäsittelemällä puuta puristuksen jälkeen. Sekä puristaminen että lämpökäsittely vähensivät kosteuden sitoutumista puuhun. Lisäksi hystereesi pieneni kosteussyklejä toistettaessa, mikä johtui todennäköisesti purkautuvista sisäisistä jännityksistä, jotka olivat syntyneet sekä puristuksen että lämpökäsittelyn aikana.

Väitöskirjatyössä saadut tutkimustulokset edistävät merkittävästi puun puristusprosessin suunnittelun optimointia haluttujen ominaisuuksien saavuttamiseksi. Tutkimustulokset lisäsivät ymmärrystä puun käyttäytymisestä puristuksessa ja korkeassa lämpötilassa sekä modifioidun puun käyttäytymisestä vaihtelevassa ilmankosteudessa.

PREFACE

The work reported in this thesis was mainly carried out in the Department of Forest Products Technology at Aalto University (Espoo, Finland) during 2010-2014. Significant contribution was also accomplished in Sweden at KTH Royal Institute of Technology and SP Technical Research Institute of Sweden, as well as in the UK at Bangor University and Edinburgh Napier University and in Slovenia at the University of Primorska.

LIST OF PUBLICATIONS

This doctoral dissertation consists of a summary of the following publications which are referred to in the text by their Roman numerals.

I   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. *Journal of Materials Science*, 46:4780–4786.

II   **Laine K**, Rautkari L, Hughes M (2013) The effect of process parameters on the hardness of surface densified Scots pine solid wood. *European Journal of Wood and Wood Products*, 71:13–16.

III   **Laine K**, Antikainen T, Rautkari L, Hughes M (2013) Analysing the density profile characteristics of surface densified solid wood using a computational approach. *International Wood Products Journal*, 4:144–149.

IV   Belt T, Rautkari L, **Laine K**, Hill CAS (2013) Cupping behaviour of surface densified Scots pine wood: the effect of process parameters and correlation with density profile characteristics. *Journal of Material Science*, 48:6426–6430.

V   **Laine K**, Segerholm K, Wålinder M, Rautkari L, Ormondroyd G, Hughes M, Jones D (2014) Micromorphological studies of surface densified wood. *Journal of Materials Science*, 49:2027–2034.

VI   **Laine K**, Rautkari L, Hughes M, Kutnar A (2013) Reducing the set-recovery of surface densified solid Scots pine wood by hydrothermal post-treatment. *European Journal of Wood and Wood Products*, 71:17–23.

VII   **Laine K**, Belt T, Rautkari L, Ramsay J, Hill C.A.S, Hughes M (2013) Measuring the thickness swelling and set-recovery of densified and thermally modified Scots pine solid wood. *Journal of Materials Science*, 48:8530–8538.

VIII   Hill C.A.S, Ramsay J, Keating B, **Laine K**, Rautkari L, Hughes M, Constant B (2012) Water vapour sorption properties of thermally modified and densified wood. *Journal of Materials Science*, 47:3191–3197.

AUTHOR'S CONTRIBUTION

Publication I
Participated in defining the research plan and in the writing process and was responsible for the experimental work and analysis.

Publications II, III, VI, VII
Defined the research plan with input from co-authors, supervised the experimental work and analysis and wrote the first draft of the manuscript.

Publication IV
Participated in defining the research plan, undertook the experimental work and the writing process, excluding the correlation analysis.

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

Publication VIII
Participated in defining the research plan, undertook the experimental work and the writing process, excluding the modelling and modulus analysis. Only sorption isotherms and hysteresis analysis were included in the dissertation.

LIST OF ABBREVIATIONS

CR   Compression ratio

D   Densified

DTM   Densified + thermally modified

DVS   Dynamic vapour sorption

EMC   Equilibrium moisture content

FSP   Fibre saturation point

MC   Moisture content

MD   Mean density

PA   Peak area

Pb   Peak base

PD   Peak density

Pdi   Peak distance

RH   Relative humidity

SEM   Scanning electron microscope / microscopy

t_d Thickness after densification

t_i Thickness

t_u Thickness before densification (undensified)

t_s Thickness after soaking/increased RH

T_g Glass-transition temperature

TM   Thermal modification / Thermally modified

U   Untreated

UV   Ultraviolet

VDP   Vertical density profile

CONTENTS

1   INTRODUCTION

Wood is widely used in the built environment, including applications which require good mechanical properties. For example, the quality of a flooring material is often evaluated by its scratch resistance and hardness and these properties generally correlate positively with wood density. Therefore, wood species with high density are often more desirable than those with low density in such applications. Since density plays an important role in the desirability of wood, the value of low-density wood species might be improved by increasing density, using a modification method referred to as densification.

Wood tissue consists of tightly aligned cells that generally have a hollow cavity inside, the so-called lumen, making the wood material porous. The density of the cell-wall is approximately 1.5 g/cm^3 regardless of the wood species or cell-type (Stamm 1929, Kellogg & Wangaard 1969), therefore, the bulk density of wood is dependent upon the porosity, that is, the thickness of the cell-wall and the size of the lumen. In the work carried out for this dissertation, densification was performed by compressing wood between heated metal plates to reduce the void space in its porous cell structure and therefore increase its density. If the modification can be targeted to the wood surface, where the property improvements are most needed, rather than the entire bulk of the material, less process energy may be required whilst obtaining the desired property improvements, such as improved surface hardness. Therefore, it is pertinent to examine whether it is possible to control the location of the densification in the wood and to examine how the wood properties are affected. An example of surface densified wood in comparison to untreated wood is shown in Fig 1.

Another significant issue in wood densification is the recovery of the deformed state when the compressed wood is exposed to conditions of high relative humidity. In order to produce a long-lasting and usable material, the

recovery of the densified state (i.e. set-recovery) should be eliminated and the phenomena related to set-recovery understood.
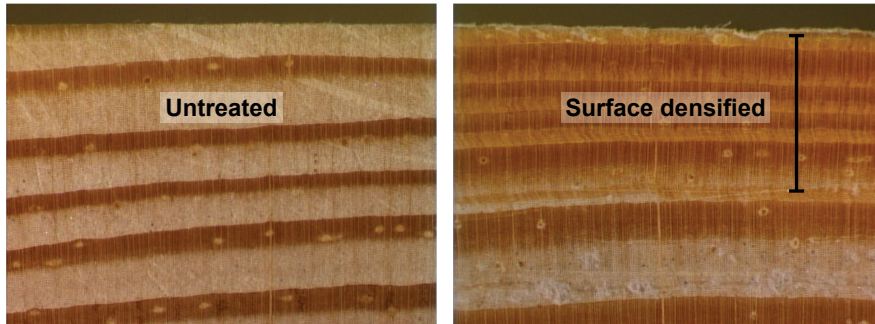
Figure 1. *Cross-sections of an untreated and a surface densified Scots pine sample.*

Improving the properties of wood by modification and thereby widening the possibilities of using wood in the built environment might be beneficial in many cases. An important reason for improving the properties of wood is to extend the service life of wood-based products. A growing tree binds CO_2 in its polymer structure, removing this climate change gas from the atmosphere. The carbon is stored in wood products until the end of their life-cycle, and therefore, it is reasonable to produce long-lasting solid wood products from sustainably grown forests.

Besides the environmental benefits, increasing the use of wood in the built environment might have a positive effect on the human psyche (Nyrud & Bringslimark 2010). For example, when touching different materials, wood induces less stress (measured as heart rate or pulse rate) compared to other non-natural materials, such as plastic or metal (Morikawa et al. 1998, Sakuragava et al. 2008) and wood is generally perceived by the public to be, for example, "warm", "natural" and "relaxing" (Rice et al. 2006).

1.1 Objectives of the dissertation

The overall aim of the work carried out for this dissertation was to *improve the properties of solid wood by surface densification*. The focus was to discover the specific conditions to be used in the densification process, as well as link these conditions to changes in properties. With this aim, the dissertation focussed on the following four research questions:

1) How do different **process parameters** (*wood moisture content, temperature, press closing time, press holding time and compression ratio*) affect the **properties** (*density profile, hardness and cupping*) of surface densified wood?

2) Can surface densification be performed **without causing fracture** in the cell-wall?

3) Can the **set-recovery** of surface densified wood be reduced by **thermal modification** and how is this measured?

4) Does densification or thermal modification alter the thickness swelling and **water vapour sorption properties** of wood?

Research questions 1 and 2 dealt with the effect of the process parameters used in the densification procedure upon the properties of surface densified wood. These questions are addressed in Papers I–V. Questions 3 and 4 focussed on the links between the phenomena causing set-recovery and the data provided by the different measurement methods and are covered in Papers V–VIII.

1.2   Structure of the thesis

The dissertation begins by introducing the theoretical background to wood densification, with focus on selected phenomena related to the process, such as wood softening. Thereafter, the materials and methods used are briefly described and the core results summarised, analysed and discussed. Lastly, conclusions are drawn from the results with suggestions for future research. The publications which form the basis for this dissertation are appended in the end.

2   BACKGROUND

In the work carried out for this dissertation, densification was effected by softening wood under suitable conditions of temperature and moisture and compressing the cell structure to reduce its porosity. In order to understand the factors influencing the densification process, the theoretical background to wood softening and deformation is first presented. This is followed by the theory of the densification process itself and after that, a presentation of the background to 'fixing' the deformed state.

2.1   Wood softening and deformation

The knowledge related to wood softening and deformation has been utilised in wood processing for thousands of years. For example, over 5000 years ago the Saami people are thought to have softened the tips of their skis in fires to enable them to be bent upwards more easily for better performance (Insulander 1998, Åström 1993). Nowadays, knowledge about the softening behaviour of wood is widely exploited in wood-based products manufacturing, such as in veneer peeling and in pulp and paper manufacturing, however, the deformation of solid wood under compression has received less research attention. It is generally known that wood softening and deformation is affected not only by the wood structure, moisture interactions and temperature, but also the duration of loading is of importance. Therefore, these factors are discussed next in the context of solid wood compression.

Cell-wall structrure and moisture content

Wood can be described as a composite structure at different levels. At the macroscopic level, wood tissue is formed from the reinforcing wood cells (in softwoods, mainly tracheids) which are joined together by the middle-

lamella, illustrated in Fig 2b. The average length of a Scots pine tracheid is approximately 3.5 mm and the diameter around 0.035 mm with a hollow cavity, known as the lumen, inside (Siau 1984). Two main tissue types - earlywood and latewood - form the growth rings (Dinwoodie 2000, Fengel & Wegener 1984). The earlywood cells, with thin cell-walls and large cavities, are formed early in the growing season and the latewood cells, with thick cell-walls and small cavities, are formed later in the season and function as mechanical support (Navi & Sandberg 2012). Havimo et al. (2009) found the thickness of Scots pine cell walls to be 2.0 µm (standard deviation 0.31) for earlywood and 3.7 µm (standard deviation 0.89) for latewood. The variation of earlywood and latewood is not visible in all species but, particularly in conifers, the latewood is clearly darker. The transition between growth rings is generally sharp whilst the transition from earlywood to latewood is gradual. The outer part of the wood trunk is the so-called sapwood (see Fig 2a), whilst the inner part is called heartwood and includes more extractives, which improve the resistance to fungal and insect attack (Dinwoodie 2000, Ek et al. 2009).
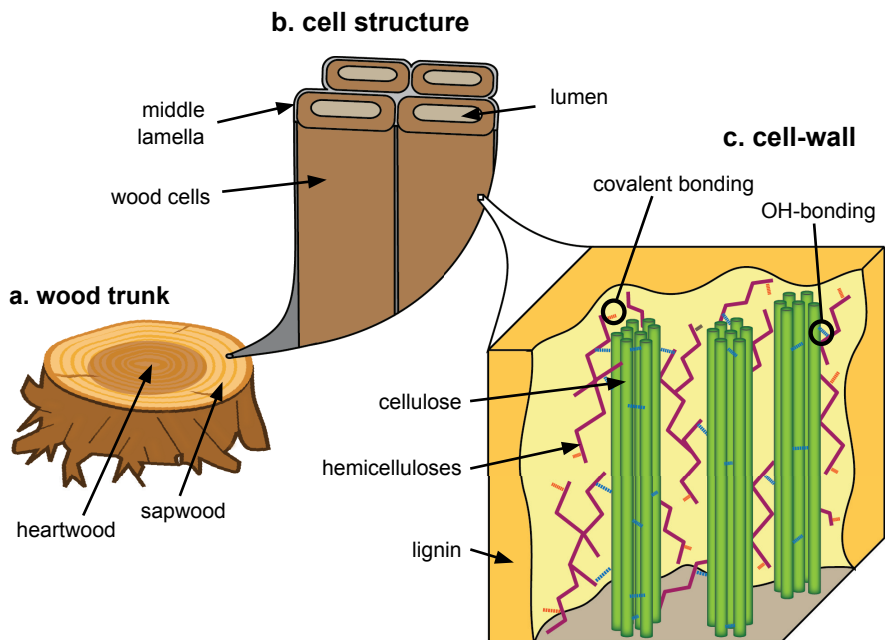
Figure 2. *Schematic illustration of the wood and cell-wall structure.*

At the molecular level, the cell-wall is composed of cellulose microfibrils which reinforce the matrix of hemicellulose and lignin (Salmén 2004), illustrated in Fig 2c. Indeed, the main components of the wood cell-wall are cellulose,

hemicelluloses and lignin, in addition, there are other components termed extractives that account for approximately 3.7-4.8 % (by weight) in Scots pine (Rautkari et al. 2012a).

Cellulose chains align in layers by intermolecular hydrogen bonds and the layers further bundle together with Van der Waals forces, forming the microfibril (O'Sullivan 1997), illustrated in Fig 2c. The so-called, disordered/amorphous regions of cellulose are susceptible to moisture, which is thought to be due to the availability of OH-groups in the polymer, whereas, the ordered/crystalline regions of cellulose are more tightly aligned, with less access to the OH-groups and therefore less affinity with moisture (Fengel & Wegener 1989). Thus, the level of crystallinity in cellulose partly affects the MC and softening properties of wood (Back & Salmén 1982).

The cellulose microfibrils are further attached to the surrounding matrix of the cell-wall through the hemicelluloses, again with hydrogen bonds (Fengel & Wegener 1984). Water molecules entering the wood structure are expected to form hydrogen bonds with the available OH-groups in the cell-wall and therefore the amount of accessible OH-groups in the structure is strongly linked to the wood moisture-content (MC) (Fengel & Wegener 1984, Hill 2006, Spell & Mason 1961, Rautkari et al. 2013b). As water molecules enter the structure, besides occupying the available OH-groups, they may break existing hydrogen bonds among and between the amorphous cellulose and hemicelluloses forming new hydrogen bonds with the released OH-groups (Fengel & Wegener 1989, Gibson 1965, Ek et al. 2009, Navi et al. 2002). This is expected to cause separation of the microfibrils and swelling of the wood (Skaar 1988). A hydrogen bond between two cellulose chains that involves water is thought to be weaker than a hydrogen bond not involving water (Gibson 1965), which might account for a loosening of the structure and thus a softening of wood with increasing MC.

Hemicelluloses are a group of generally amorphous polysaccharides (such as, xylan or glucomannan) with accessible OH-groups (Hill 2006) and have a more branched and random structure compared to cellulose (Fengel & Wegener 1989). Therefore, they are thought to associate with water molecules and contribute significantly to the softening of wood (Jääskeläinen & Sundqvist 2007). Hemicelluloses are thought to act as interfacial coupling agents between cellulose microfibrils and lignin (Hill 2006); furthermore,

hemicellulose and lignin are joined together by covalent bonds, which are stronger than hydrogen bonds and therefore not as susceptible to moisture (Fengel & Wegener 1989).

Lignin is found in the secondary cell-wall in varying amounts, acting as a matrix between the microfibrils (Dinwoodie 2000), whereas in the compound middle lamella the concentration of lignin is very high (Bailey 1936, Fergus et al. 1969), binding the cells together (Siau 1984), maintaining wood in its form, providing rigidity to the wood material (Fengel & Wegener 1989, Ek et al. 2009) and, therefore, thought to be particularly critical in wood softening (Salmén 1984). Indeed, the compressive deformation of wood in the tranverse direction has been suggested to be a matrix-dominated process (Bergander & Salmén 2002, Gindl 2004). Lignin in the middle lamella is described as a random three-dimensional network polymer, whereas, in the secondary wall a non-random, ordered two-dimensional network polymer (Goring 1989, Åkerholm & Salmén 2003) and, unlike hemicellulose and cellulose, even suggested to be hydrophobic (Baumberger et al. 1998, Iiyama et al. 1994). Therefore the significance of lignin in wood softening might be more strongly related to temperature which is discussed later. The important role of MC in wood softening is further examined next, under the topic of wood water sorption properties.

Water vapour sorption properties

As presented earlier, water molecules in wood are expected to bind with the available OH-groups of the wood constituents (Hill 2006). In general, the accessibility of wood OH-groups below the fibre saturation point (FSP) can be analysed by measuring the number of adsorbed water molecules which correspond to the number of available OH-groups in wood (Rautkari et al. 2013b).

An interesting feature of wood (as well as other lignified plants) is that at a given relative humidity (RH), the equilibrium moisture content (EMC) is generally lower during adsorption than during desorption. This difference between the adsoption and the desoption cycles is referred to as hysteresis and can be seen from measured sorption isotherms (Fig 3). Several theories have been proposed to explain this phenomenon; for example, in a natural organic material, such as wood, the cell-wall micropores deform during

increases and decreses in MC and therefore, adsorption and desorption occur in different physical environments (Lu & Pignatello 2002). Lignin has been found to greatly influence the sorption properties of plants and indeed plants with higher lignin content have been found to exhibit higher EMC levels and higher levels of hysteresis (Hill et al. 2009). The significance of lignin content may be related to the ability of the lignin network to deform and enable an opening up of the structure for increased accessibility of the OH-groups (Hill et al. 2009). Therefore it can be suggested, that the presence of lignin enhances relaxation of the wood structure, and indeed, changes the physical environment of wood with varying RH.
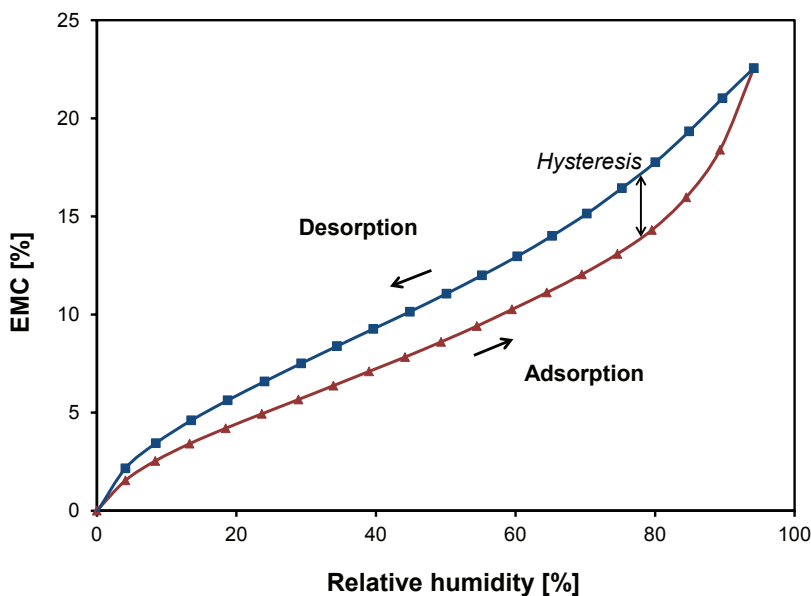
Figure 3. *Example water vapour isotherm of a Scots pine sapwood sample.*

It has been shown that wood cells dried from the green state never reach the original water-swollen state after re-wetting, which is thought to result from a phenomenon known as hornification (Jayme 1944, Scallan 1974). Hornification is described as the irreversible aggregation of microfibrils during drying (Fernandez Diniz 2004, Kontturi & Vuorinen 2009, Suchy et al. 2010).

In more detail, the aggregation may results from the formation of irreversible or partially reversible hydrogen bonding (Luo et al. 2011) or covalent cross-linking (Fernandez Diniz 2004) between wood constituents, or even co-

crystallisation of adjacent microfibrils (Newman 2004). The phenomenon has been demonstrated by an observed reduction in the number of accessible OH-groups during repeated drying-humidty cycles (Pönni et al. 2012, 2014). Indeed, the hygroscopicity of wood has been known to reduce after repeated humid-dry cycles (Hill et al. 2010, Rautkari 2013b) which, it has been suggested, result from the hornification phenomenon illustrated in Fig 4.
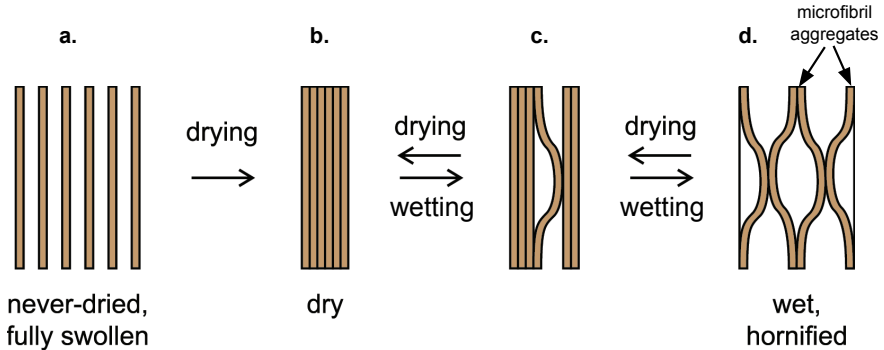
Figure 4. *Aggregation of the microfibrils in the cell-wall during drying (based on Scallan 1974)*

The interaction of wood and moisture is a complex topic and relevant to wood softening, since water molecules associate with the molecular bonds and affect the connections between wood constituents. In addition, temperature has a strong influence on wood softening, with moisture and temperature interplaying with each other. This aspect is further described in the next section.

Temperature

Under certain conditions, wood can be described as a hard and brittle material; however, with an increase in temperature and/or MC, the state changes and the wood becomes soft and rubbery. Between these different states there is a transition zone and the glass transition temperature (T_g) defines the approximate point of softening. T_g is highly dependent upon the MC and this dependency has been studied for the main constituents of wood: cellulose, hemicelluloses and lignin, and is presented in Fig 5.
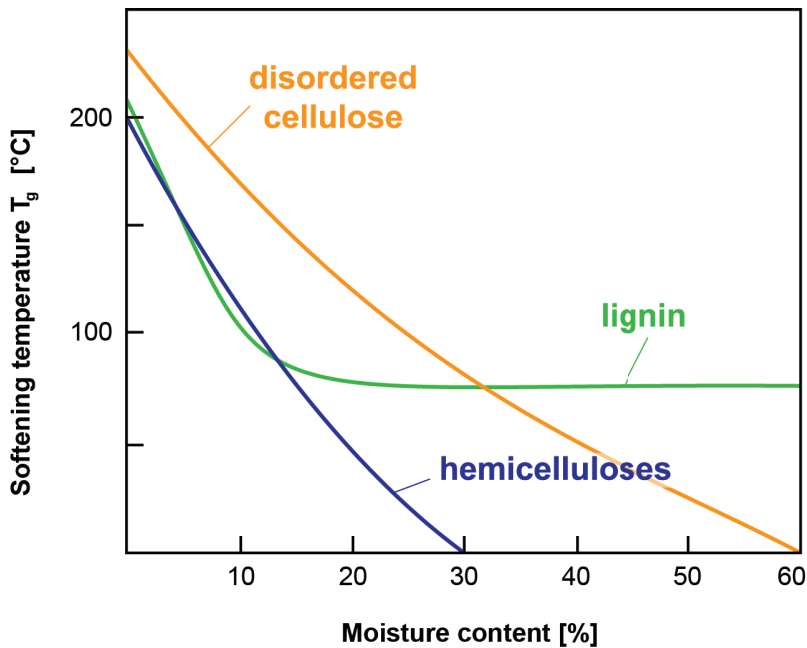
Figure 5. *Schematic illustration of the dependency of the softening temperature of lignin, hemicelluloses and amorphous cellulose as a function of moisture content (Salmén 1990).*

The T_g of wood has been examined and found to increase with increasing lignin content (Ahlgren et al. 1972). Furthermore, it has been suggested that the T_g of wood at high MC is dependent upon the lignin structure; especially the amount of methoxyl side-groups in lignin that occupy the bonding site and therefore gives a low degree of cross-linking and low T_g (Olsson & Salmén 1997). According to Salmén (1982), the estimated T_g for lignin is 100 °C at ~10% MC. Defining the T_g for isolated wood components is, however, highly dependent upon the isolation procedure, measurement method and conditions (Irvine 1984).

Temperature influences the sorption behaviour of wood with the level of hysteresis decreasing with increasing temperature. Indeed above the T_g there is thought to be no hysteresis in wood (Hill et al. 2009, Keating et al. 2013). At higher temperatures, relaxation processes related to wood sorption take place more rapidly (Hill et al. 2009, Keating et al. 2013) which might be linked to the ability of the lignin network to reform more easily at elevated temperatures (Hill et al. 2009).

Viscoelasticity of wood

Wood material reflects a behaviour that combines elastic and viscous characteristics and it is therefore termed a viscoelastic material. An elastic material will recover its original form after being deformed by an external force, whereas, a viscous material under constant stress does not retain its deformed state, but continues to flow with time and deforms irreversibly. The viscoelastic properties of wood are strongly related to temperature, moisture condition and the duration of loading. Phenomena such as creep, stress relaxation and mechano-sorptive behaviour are all suggested to relate to the viscoelasticity of wood.

When wood is under constant strain, stress is released over time, a phenomenon referred to as stress relaxation, illustrated in Fig 6. Stress relaxation is highly dependent on the loading conditions; for example, higher temperature and increased MC enhance stress relaxation (Kelley et al. 1987), furthermore, cyclic changes in MC are known to increase stress relaxation, especially during desorption (Armstrong & Kingston 1960).
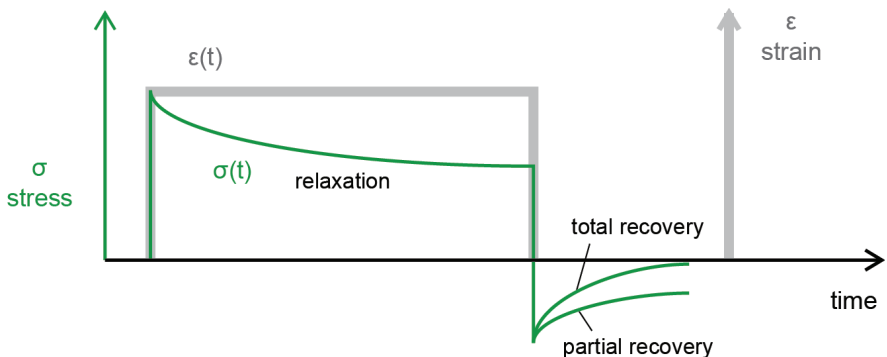
Figure 6. *Response of a viscoelastic material to strain, illustrating the stress relaxation phenomenon.*

Another manifestation of the time-dependent behaviour of wood is the increase of strain under a constant stress, which is referred to as creep, presented in Fig 7, and is mostly related to long-term loading. The combined effect of stress and changes in MC is referred to as mechano sorption and is generally observed in creep. Indeed, the level of creep is highly dependent on the loading conditions, with changes in MC in particular accentuating the deformation (Armstrong & Kingston 1960, Gibson 1965). As the load is removed, part or all of the deformation may recover immediately or over

time, and again, recovery may be enhanced with cyclic moisture changes (Gibson 1965, Entwistle 2005). The rate of creep and stress relaxation are accelerated by increased temperature (Iida et al. 2002a, 2002b, Kelley et al. 1987). Elevated temperatures during stress relaxation have been identified to influence especially the matrix constituents; lignin and hemicellulose (Kurenuma & Nakano 2012).
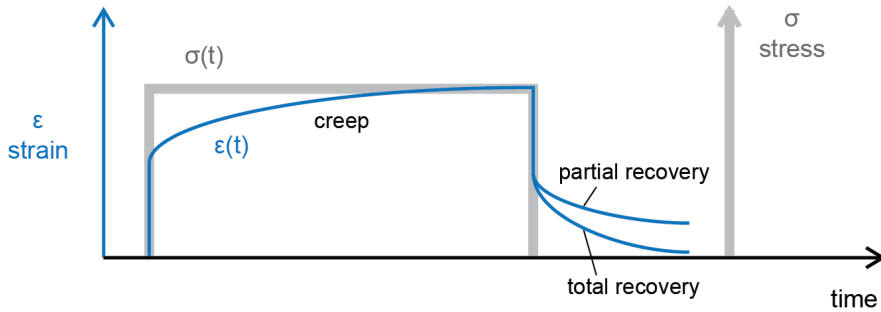
Figure 7. *Response of a viscoelastic material to stress, illustrating the creep phenomenon.*

Although viscoelasticity in wood has been a topic of research since the early 1960's (Armstrong & Kingston 1960, Armstrong & Christensen 1961), a comprehensive theory and complete understanding of the mechanisms are still lacking, though several potential theories have been put forward. Firstly, it has been suggested that lignin plays a significant role in the softening properties of wood and indeed lignin has been found to exhibit more strongly viscoelastic behaviour than cellulose and hemicellulose - even under dry conditions (Åkerholm 2003) and also the matrix has been found to move independently of cellulose during straining (Fratzl et al. 2004, Åkerholm 2003). Another explanation for viscoelastic behaviour is the occurrence of damage in the hemicellulose and lignin matrix (Sedighi-Gilani & Navi 2007), though this has not been emphasised by other researchers. Thirdly, and perhaps most interestingly, the breaking and forming of hydrogen bonds in the amorphous regions of the wood cell-wall has been suggested to be one of the main causes of viscoelastic behaviour (Armstrong 1972, Entwistle 2005, Gibson 1965, Hillis 1984, Navi et al. 2002). This theory, which is sometimes referred to as the 'stick-slip' mechanism (Adler & Buehler 2013, Keckes et al. 2003) and also as the 'Velcro-mechanism' (Frazl & Weinkamer 2007, Altaner & Jarvis 2008, Jarvis 2009, Keckes et al. 2003), might explain the development of permanent (as well as recoverable) deformation in wood under stress. According to this

theory, as wood is deformed, tensile stresses are created in the molecular bonds between and among the cell wall constituents. An increase in the stress results in de-bonding and a release of stress. For example, hydrogen bonds between a cellulose microfibril and hemicellulose are broken enabling the microfibril to slide and subsequently re-bond with adjacent fibril in a new position. The breaking and formation of new bonds occurs between the microfibrils in a manner similar to that of a Velcro-connection and, for this reason, it is referred to as the Velcro-mechanism (Altaner & Jarvis 2008, Frazl & Weinkamer 2007, Keckes et al. 2003). This phenomenon is illustrated in Fig 8.
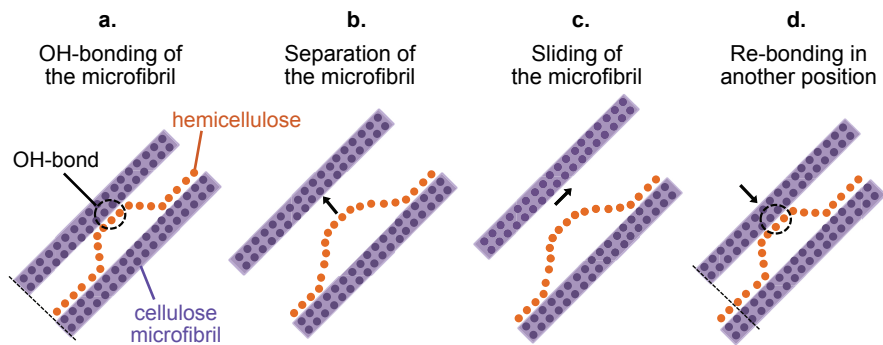
Figure 8. *Schematic illustration of the Velcro-mechanism occurring between cellulose and hemicellulose: a. bond between cellulose and hemicellulose, b. breaking of the hydrogen-bond, c. sliding of the microfibril, d. formation of the new bond (adapted from Altaner & Jarvis 2008).*

The stick-slip-mechanism is considered permanent, but not damaging to the microfibrils or the matrix (Adler & Buehler 2013, Keckes et al. 2003). Furthermore, the stick-slip-mechanism might also occur in the middle-lamella between cells, as the hemicelluloses are reordered during viscous flow of the matrix (Keckes et al. 2003, Entwistle & Zadoroshnyj 2008).

As discussed earlier, water-molecules may intervene with the hydrogen bonds between cellulose chains or between microfibrils and matrix, and, as wood dries, these hydrogen bonds are able to re-form (Ek et al. 2009, Siau 1984, Navi et al. 2002). Thus cyclic changes in wood MC possibly increase the movement of the molecules and facilitate the breaking of the hydrogen-bonds, sliding of the microfibrils and re-bonding in another position. Higher temperature is expected to further increase the movement of the molecules and therefore enhance the re-organisation of the molecular bonds. It can be concluded, that wood structure, moisture interactions, temperature and time of loading have

a strong interdependency in influencing wood softening and deformation behaviour, and this background is discussed next in light of the densification process and set-recovery.

2.2 Wood densification

In order to achieve an increase in solid wood density, the porosity has to be reduced and there are two main methods to achieve this: compressing the porous structure or by filling the voids in the cell structure. An improvement in properties, such as hardness, have been achieved by filling (Gindl et al. 2004, Zhang et al. 2006) or combined filling and compression (Gabrielli & Kamke 2010, Stamm & Seborg 1960) of solid wood, however, the voids are often filled with a synthetic resin, such as phenol-formaldehyde (Yano et al. 1997, Gabrielli & Kamke 2010).

Densification processes

Several solid wood compression processes have been reported over the last few decades (Anshari et al. 2011, Dwianto et al. 1998, Fang et al. 2011, Fukuta et al. 2007, Inoue et al. 1993, Ito et al. 1998a, Morsing 2000, Norimoto et al. 1993, Seborg & Stamm 1941, Seborg et at. 1956, Unsal & Candan 2008, Zhou et al. 2000), however, at the present time there are only a limited number of commercial products available. Thermo-hydro-mechanical (THM) modification refers to processes, which include the use of temperature, moisture and mechanical compression in order to improve the properties of solid wood. Several different THM processes have been developed by various research institutes, such as viscoelastic-thermal-compression (VTC) (Kamke 2006). The modification procedures generally include the same elements: 1) softening the wood structure, which is achieved at a certain temperature and MC, 2) compressing the wood structure, which is usually performed between metal-plates and 3) fixing the deformation which is, in most cases, obtained by thermal modification.

Surface densification

Most of the densification processes described in the previous section aim at compressing the wood throughout the whole thickness of the sample so as to produce a uniform structure and, therefore, the sample is softened through

the thickness. The aim of surface densification is to limit the densification to very near the surface of wood, and therefore, softening is targeted only at the surface. Surface densification has been studied by a number of workers, for example, Tarkow & Seborg (1968) developed a continous compression line with heated metal shoes on both sides of the sample followed by a second pair of water-cooled shoes before releasing the load. Inoue et al. (1990), on the other hand, cut narrow grooves on the wood surface across the grain, impregrated the surface with water and heated by microwave irradiation, afterwhich the surface was compressed and dried before relesing the load. Lamason & Gong (2007) pre-soaked one surface of wood in boiling water for 5 min, hot-pressed with heating only on the soaked side of the sample and cooled the system before releasing the load. Wang & Cooper (2005) soked both surfaces of the wood sample in water or urea solution for 30 min and compressed with different pre-heating and closing times. On the other hand, Rautkari et al. (2010) performed surface densification with a linear friction technique by vibrating pre-heated wood against smooth polished steel.

Improvements in properties have been obtained by surface densification, such as an increase in hardness (Gong et al. 2010, Inoue et al. 1990, Rautkari 2012b), an improvement in modulus of elasticity, nail withrawal (Lamason & Cong 2007) and abrasion resistance (Inoue et al. 1990, Tarkow & Seborg 1968), as well as, a reduction in wettability (Kutnar et al. 2012). In addition, migration of extractives has been noted to occur at the densifed surface (Rautkari et al. 2012a) leading to a smooth surface layer and possibly reducing the need for surface treatment (Lamason & Gong 2007). In order to measure the location and level of deformation, analysis of the density profile through the sample thickness was performed, which is described in the next section.

Density profile formation

Density profile analysis is a general method used, in particular, during the manufacturing of wood-based panels, such as particleboard or medium density fibreboard (MDF) as it describes density variations through the thickness of the panel. The density profile is formed during hot-pressing of the panel with different process parameters affecting the shape of the profile and, furthermore, the properties of the end-product, such as hardness or bending strength (Wong et al. 1998, 1999, 2000).

During solid wood compression the wood surface next to the hot-plate becomes heated, which produces a softening effect that moves at a finite pace into the bulk of the material (Fortino et al. 2013). The density profile formation is strongly dependent on the softening during compression, which is affected, for example, by the initial MC and grain orientation of wood (Wang & Cooper 2005). Furthermore, higher temperature accelerates the softening; however, with very slow closing speeds the very surface might also begin to dryout, moving the softening region away from the surface, deeper into the sample (Wang et al. 2000, 2001, Wang & Cooper 2005). Also, pre-heating the sample has been found to move the softening region deeper in the sample due to drying of the surface and the softening region migrating towards the core (Wang & Cooper 2005).

The density profile formation is expected to be related to the thermal conductivity of wood, which is known to be influenced by several factors, such as wood species, grain angle (Yapici et al. 2011) and microstructure (Suleiman et al. 1999). In more detail, the porous structure of wood reduces thermal conductivity due to diminished conduction through voids (Suleiman et al. 1999). Importantly, higher MC is known to increase thermal conductivity (Sonderegger et al. 2011) and, therefore, surface densification should be performed on wood with a rather low overall MC to inhibit softening in the core. On one hand, higher MC at the surface might accentuate targeted densification at the surface (Inoue et al. 1990), on the other hand, higher moisture content is known to enhance thermal conductivity (Sonderegger et al. 2011) which might accelerate heat transfer inside the sample and softening the core during hot-pressing (Wang & Cooper 2005). During densification the void space in the densified region is reduced (Kutnar et al. 2009) and as thermal conductivity rises with increasing density (Wangaard 1940), the conductivity is probably increased.

2.3   Recovery of the deformation

Recovery of the densification is a significant issue since it defines the possible end-use conditions for the densified wood material. When densified wood is exposed to moisture, both reversible and irreversible swelling occurs. Reversible swelling is due to the hygroscopic nature of wood but irreversible swelling is a result of the densified wood partly or completely returning to its

original dimensions. This is commonly referred to as set-recovery, as it is in this dissertation, but it can also be referred to as shape memory or sometimes irreversible swelling. The term spring-back describes the immediate recovery of the deformation directly after press opening and is related to the elastic (and delayed elastic) recovery of the densification.

Temporary fixation

Temporary fixation of the deformed state can be achieved if the lignin is brought back to the glassy state (below its T_g) before press opening, making the matrix rigid again and maintaining the new cellular conformation (Tarkow & Seborg 1968, Navi & Heger 2004). Temporary fixation is also achieved as the wood dries during compression, removing the water-molecules and enabling hydrogen bonds to form between the cellulose and hemicellulose, which is partly fixing the microfibrils in the deformed state, however, when water-molecules enter wood they become associated with the hydrogen bonds, disrupting the compressed form (Dwianto et al. 1998, Navi & Girardet 2000, Navi & Heger 2004, Navi et al. 2007).

It is also believed that during the densification process, internal stresses are built-up and stored in the cellulose microfibrils (Navi & Heger 2004). As the structure of wood is forced into a new conformation, the covalent bonds (between hemicellulose and lignin) and hydrogen bonds (between hemicellulose and cellulose) are not broken and reformed and, therefore, the deformation is considered to be metastable and is recoverable when re-wetted or re-heated (Navi & Heger 2004). However, if the bonds between the microfibrils and the matrix are broken during compression, the internal stresses are relaxed and recovery is reduced leading to permanent fixation of the deformation (Dwianto et al. 1998, 1999, Grossman 1976. Heger et al. 2004, Kutnar & Šernek 2007, Morsing 2000, Navi & Girardet 2000, Navi et al. 2007).

The extent of set-recovery is dependent upon a number of factors, for example, higher densification ratio has been found to result in greater set-recovery due to the higher internal stresses induced during densification (Anshari et al. 2011, Blomberg et al. 2006, Grossman 1976, Kutnar et al. 2009).

Permanent fixation

Norimoto et al. (1993) have proposed three primary methods for preventing set-recovery:

- Formation of cross-linkages between the molecules of the matrix constituents
- Relaxation of the inner stresses stored in the microfibrils and the matrix
- Isolation of the wood polymers (especially hemicelluloses) from moisture and heat to prevent re-softening

A significant reduction in set-recovery usually requires additional post-treatment after densification; thermal modification (TM) being the most typical treatment. In the presence of heat and moisture during TM, lignin, non-crystalline cellulose and especially hemicelluloses degrade, reducing the hygroscopicity of wood and therefore lowering set-recovery (Dwianto et al. 1999, Hill 2006). Degradation of the wood polymers, especially hemicellulose which connects the cellulose microfibrils to the lignin, may further reduce set-recovey as the binding between the wood constituents is broken releasing internal stresses (Heger et al. 2004 Norimoto et al. 1993) and enabling the re-formation of the bonds in the compressed state (Morsing 2000, Navi & Heger 2004). Additionally, thermal degradation of hemicelluloses provides additional void space for the microfibrils to rearrange (Heger et al. 2004, Inoue et al. 1993).

The effectiveness of TM in reducing set-recovery has been found to be strongly related to mass-loss during modification (Inoue et al. 2008) and the effect can be enhanced by increasing the treatment temperature (Boonstra & Blomberg 2007, Gong et al. 2010, Heger et al. 2004, Kutnar & Kamke 2012b, Navi & Girardet 2000, Navi & Heger 2004, Welzbacher et al. 2008) and by increasing the treatment time (Inoue et al. 1993, Kutnar et al. 2009, Navi & Girardet 2000, Welzbacher et al. 2008). Furthermore, the presence of steam during densification and TM has been found to accelerate the reduction of set-recovery (Dwianto et al. 1999, Inoue et al. 1993, Kamke & Kutnar 2010, Kutnar & Kamke 2012a, Navi & Girardet 2000) mainly due to enhanced hydrolysis of cellulose and hemicelluloses (Ito et al. 1998a, 1998b, Heger et al. 2004).

2.4 Summary of the background

Wood softening is affected by wood structure, moisture interactions, temperature and time, with a strong interdependency of these factors. Wood deformation can be described as viscoelastic, and this is visible at the macro-level as, for example, creep and stress relaxation and both can be accentuated by factors including cyclic variation in RH, increased temperature and extended time. At the cell-wall level, the most important phenomena related to viscoelastic deformation seem to be the breaking and formation of hydrogen bonds, especially between and among cellulose and hemicellulose, but also, viscous flow of the lignin-rich matrix. The reorganisation of the OH-bonds and flow of the matrix are also expected to affect the water sorption properties of wood and manifest as, for example, hysteresis and hornification.

Even though wood softening and deformation is influenced by several factors in a complex manner, certain patterns can be recognised. Based on the different findings presented in this chapter and especially the results presented in Fig 5, it can be suggested that at lower temperatures (below ~75 °C), the dominating effect in wood softening is the level of wood MC which influences the hydrogen bonding of cellulose and hemicelluloses, while at higher temperatures (above ~75 °C), the significance of temperature is more ephasized through the softening and flow of lignin.

Density profile affects the mechanical properties of wood-based panels and is formed during the compression process. The formation of the density profile is controlled by processing parameters, such as temperature and closing time, which affect the softening and deformation of the panel. Similar links between process parameters and deformation are expected to exist in solid wood densification as well. As heat transfer in wood is rather slow and dependent MC and temperature, the T_g of wood is reached at different times in different locations. Therefore it is relevant to examine suitable process parameters in order to control the level and location of the deformation.

Different wood densification processes have been developed and one of the main issues to tackle is the recovery of the deformation. In order to obtain a stable deformation, cross-linking between wood constituents, relaxation of the inner stresses and/or reducing the sensitivity to moisture are needed. This is obtained with additional treatment, for example, thermal modification.

3   MATERIALS AND METHODS

The core of the thesis was densification modification, which was performed on the wood surface as well as through the sample thickness using different process parameters. In addition, thermal modification was performed to reduce recovery of the deformed state. This chapter briefly describes the densification and thermal modification processes as well as the testing methods which were used to analyse the effect of different modifications.

3.1   Wood material

The wood material used was Scots pine (*Pinus Sylvestris* L.) wood obtained from South-Eastern Finland with an average original density of approximately 0.5 g/cm^3 (RH 65 %, 20 °C). Scots pine was selected due to its relatively low original density, which holds potential for property improvements through an increase in density, as well as the extensive availability of the species in Finland. From a larger batch of wood boards, specimens were selected from the sapwood with even grain orientation, no knots or other visible irregularities and annual ring thickness as uniform as possible.

As different wood modifications, such as densification, TM or a combination of those two, were performed in the same study, the variously treated samples were obtained from the same board for coherent comparison. For example, one section of the same board was densified (D), one thermally modified (TM), one densified and thermally modified (DTM) and one left untreated (U).

3.2   Modification methods

The modification methods used in the work leading to this dissertation

include surface densification and through thickness densification, which were combined with TM.

Surface densification

Surface densification was performed in the radial direction using a specially designed heated press tool fitted to a universal material testing machine (Zwick 1475 combined with MTS Premium Elite controller). Surface densification was obtained on one side by heating only the sap side of the sample in the press, which is illustrated in Fig 9.
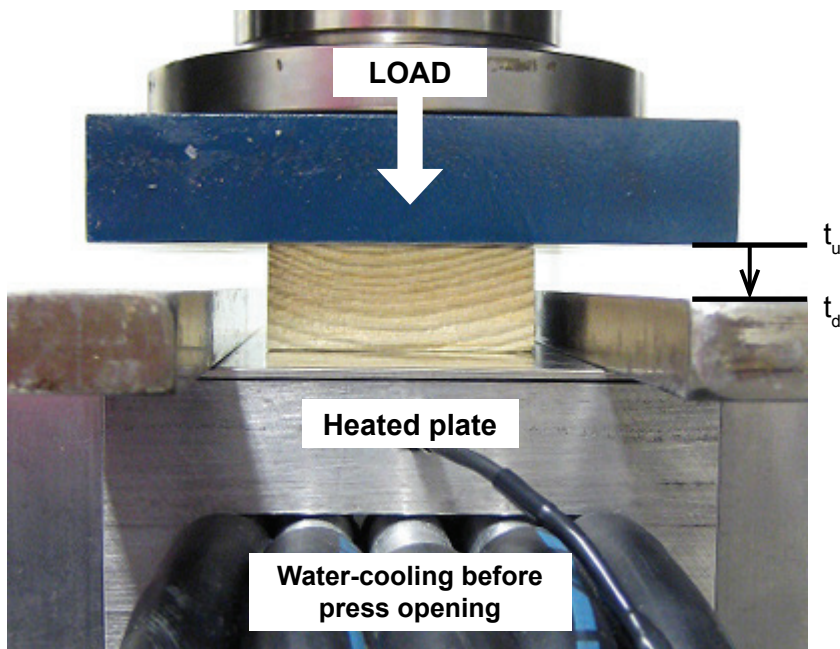
Figure 9. *Illustration of the densification equipment.*

Compared to some other surface densification processes presented in Chapter 2, this surface densification process does not include any pre-processing, such as cutting grooves or soaking of the sample. Also, a specially designed water-cooling system enabled the press to be cooled efficiently ($\sim$30 s) before releasing the load. The system was cooled to below 100 °C, which was expected to be sufficient to bring the wood back to below T_g to minimise the immediate spring-back of the deformation. The equipment enabled the use of different temperatures, closing times and holding times, which are illustrated in Fig 10. The compressive behaviour of wood is considered viscoelastic and therefore

the time of processing is essential. In order to study the time dependent deformation, closing times of 30 s and 300 s were utilised in Papers I-IV, whilst in Paper V closing times of 10 s, 30 s and 60 s were examined. The holding time in Papers I-IV was 1 min and 10 min, while in Papers V and VI it was 1 min. Since wood softening and deformation, as well as heat transfer through the wood structure are strongly related to wood MC, samples of different moisture contents (9.6, 12.4 and 15.6 %) were utilised in Papers I-IV. The influence of temperature was examined in Papers I-IV by using temperatures of 150 and 200 °C, and 100, 150 and 200 °C in Paper V. More details of the process and parameters are provided in Papers I-VI.
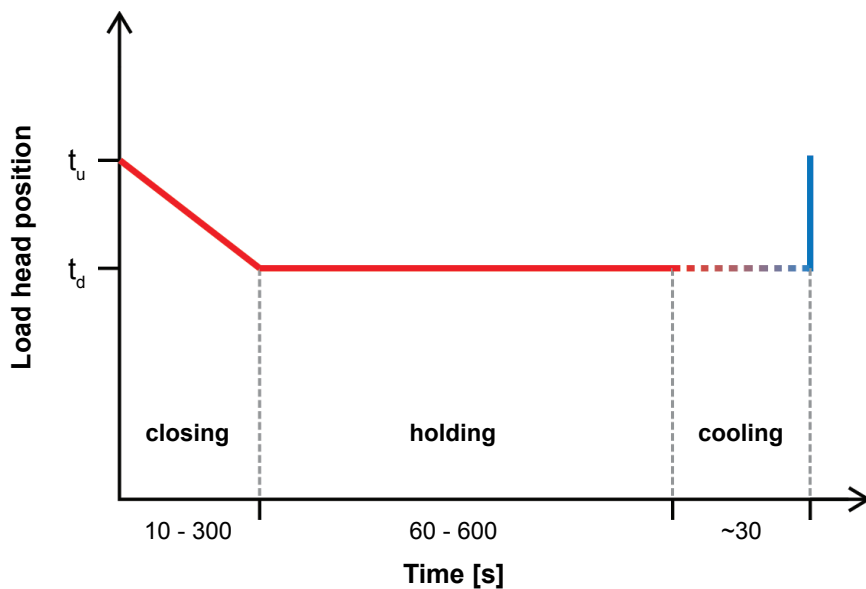
Figure 10. *Schematic diagram of the surface densification process*

The thickness of the sample is relevant in surface densification since the heat transfer inside the sample occurs at a relatively slow rate (depending on the conditions) and therefore it is essential to determine the level of deformation desired. The target densified thickness (t_d) was 15 mm in each study and it was controlled by metal stops between the plates and on either side of the wood sample (see Fig 9). The undensified radial thickness (t_u), which varied from 16 to 22 mm, therefore determined the targeted compression ratio (CR) which was calculated according to Equation 1.

$$\text{Compression ratio} = \frac{t_u - t_d}{t_u} * 100\% \qquad\qquad (Eq\ 1)$$

Through-thickness densification

Through-thickness densification was performed by compressing the wood sample in the radial direction (i.e. in the same direction as used for surface densification) in a hot-press between perforated metal plates. The size of the samples was 145 mm (longitudinal length) * 100 mm (tangential width) * 12 mm (radial thickness) and a target thickness of 5 mm was controlled with metal stops, giving a target compression ratio of 58 %. The samples were held under compression at 150 °C for 1 h and before opening the press the system was allowed to cool to below 100 °C (~3h) to minimise the immediate spring-back of the deformation. The process is described in more detail in Papers VII and VIII.

Thermal modification

Thermal modification was performed on oven-dried (at 103 °C) samples that were either densified or had not been densified. The thermal modification process is shown schematically in Fig 11 and can be divided into 4 different parts: a) temperature increase (from 103 °C to 120 °C) b) steam injection and temperature increase (to 200 °C) c) thermal modification with steam injection d) cooling and final oven-drying (at 103 °C). The steam-injection was started only at 120°C to avoid recovery of the deformation at high humidity (Rautkari & Hughes 2009). More details of the thermal modification process are provided in Papers VI, VII and VIII.
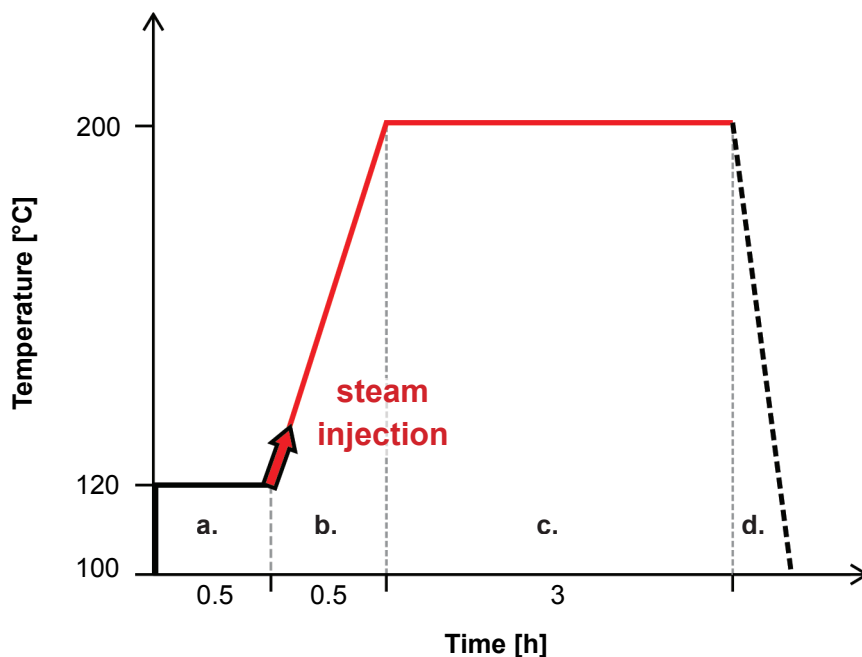
Figure 11. *Schematic diagram of the thermal modification process.*

3.3 Testing methods

The effect of the different densification and thermal modification process parameters was analysed using a range of analytical techniques including vertical density profile analysis, hardness measurement and microscopy, which are further described in this section.

Vertical density profile

After compression, the samples were conditioned (RH 65 %, 20 °C) and from each sample a specimen having dimensions of 50 mm (longitudinal) by 50 mm (tangential) (the radial thickness of the material remained constant) was cut for the density profile measurement. The ATR Density Profilometer, DPM201 (1995) which utilise a gamma ray source, scans through the wood sample (at 0.1 mm intervals), providing the average density of each layer. The average density of each layer was thereafter plotted against the corresponding location through the sample thickness, yielding a density profile for the sample. More details of the equipment used can be found in Papers I-V.

In Papers III and IV, the density profiles were numerically analysed by

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extracting the features of the profiles from the raw data using Matlab R2012a (Mathworks, MA, USA). The characteristics of the density profiles were defined according to Fig 15. Furthermore, Pearson correlation analysis was used to analyse the linear dependency of the density profile characteristics and process parameters with cupping, Brinell hardness and the elastic recovery of surface densified wood.

Hardness

The hardness of the densified samples was analysed in Papers II and III with a Brinell hardness test adapted from EN 1534 (2000) and JIS Z 2101 (1994). In the testing process a steel ball, with a diameter (D) of 10 mm, was indented on the wood surface in the radial direction with nominal 1 kN force (F). Instead of measuring the diameter of the indentation, as defined in EN 1534 (2000), the maximum depth of the indentation h_{max} was measured and hardness was calculated according to Equation 2:

$$Hardness \ = \ \frac{F}{\pi D h_{max}} \qquad\qquad (Eq\ 2)$$

Cupping

The cupping of surface densified wood was measured with a digital micrometer. The potential dependence of cupping on the vertical density profile characteristics was analysed by utilizing Pearson correlation analysis. More details of the cupping measurement and analysis are found in Paper IV.

Microscopy and sample preparation

In microscopic analysis, the wood sample should have a clear-cut surface and most preparation methods, such as slicing with a microtome, requires the wood samples to be softened, usually by water-soaking. However, the densification process leaves the samples sensitive to moisture and thus traditional sample preparation methods are not suitable. Furthermore, cutting the sample might damage or otherwise create artefacts on the surface which could affect the interpretation of micrographs. To avoid these difficulties, specimens for microscopic analysis were prepared from the densified samples utilising ultraviolet (UV)-excimer laser ablation technology. A schematic representation of the laser ablation process is shown in Fig 12.
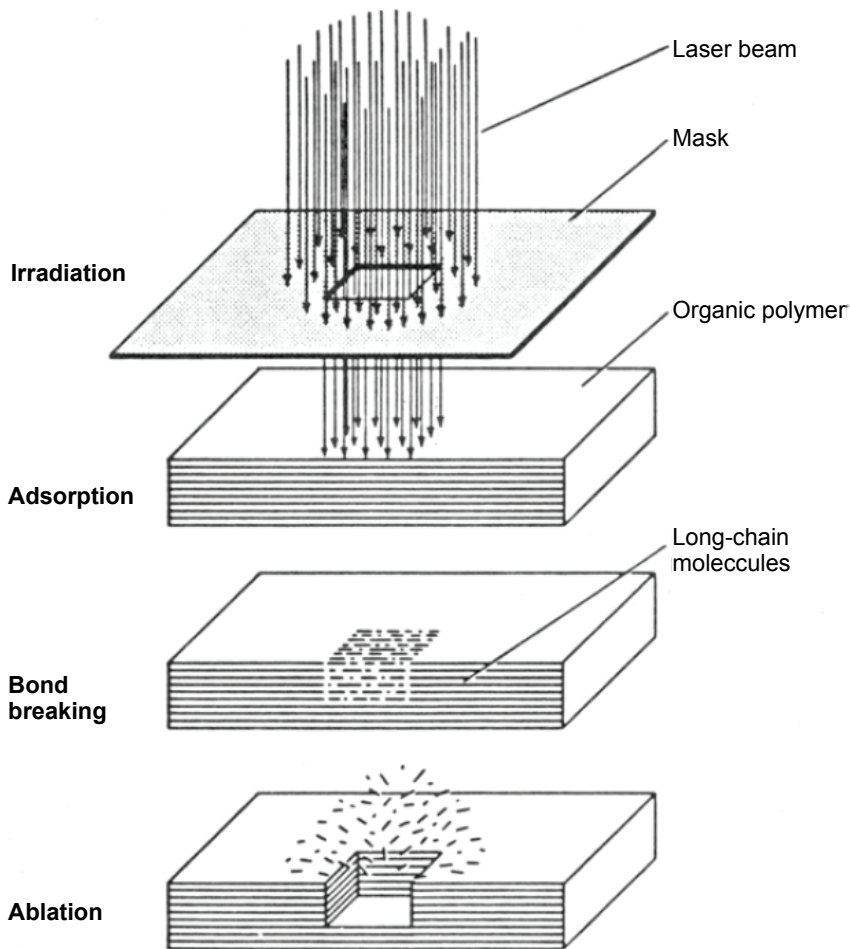
Figure 12. *Schematic representation of the UV-excimer laser ablation technique (Reprinted with permission from Srinivasan & Braren (1989) © American Chemical Society)*

The basic principle of the UV-excimer laser is that a high photon energy pulse adds just enough energy to break covalent molecular bonds in the surface region of the wood tissue, which effectively disintegrates into the air in a controlled way through ablation rather than burning (Seltman 1995; Panzner et al. 1998; Stehr et al. 1998). Previously, UV-laser ablation has been successfully used as a sample preparation technique for studying the micromorphology of some chemically and thermally modified wood (Wålinder et al. 2009) as well as high-density wood-plastic composites (Segerholm et al. 2012). The research published in Paper V was the first time that laser ablation was employed in the study of densified wood.

Before microscopic analysis, the cross-cut surfaces of the specimens were sputter-coated with a layer of gold. The micromorphology was thereafter analysed with a scanning electron microscope (SEM). More details of the microscopic analysis are presented in Paper V.

In Paper I, an overall view of the deformation of surface densified wood was obtained using two reflectance microscopes: Leica WILD MZ8 (equipped with Leica CLS150 light source) and Nikon OPTIP-HOT-2, both equipped with a JVC 3-CCD camera. The samples (approximately 10*10*10 mm^3) were prepared for microscopic analysis by abrading the cross-cut surfaces with fine sandpaper (grit size 1200). Further details of the equipment and processing are presented in Paper I.

Set-recovery

The swelling behaviour of densified and TM wood was analysed in Papers VI and VII. Through thickness densification was utilised in Paper VII instead of surface densification in order to focus the analysis only on the densified wood material. After the densification and TM treatments, the samples were equilibrated (RH 65 %, 20 °C), and sawn into the final test pieces having longitudinal and tangential dimensions of 10*10 mm (the thickness remained constant after densification). The same sample size was utilised for all the testing methods and the thickness swelling behaviour was measured in the radial direction.

Swelling was evaluated using three different methods with schematic illustrations presented in Fig 13: i) water-soaking at room temperature (15 days), ii) soaking in hot water (6 h), iii) soaking with continuous data-logging (15 days) and iv) exposure to high RH conditions (15 days). The RH conditions (RH 54, 65, 75, 84 and 94 %) were created by placing different saturated salt-solutions in sealed bell-jars. Between 1 and 3 soaking/high humidity cycles were carried out depending on the method, and the specimens were oven-dried (103 °C, 24 h) before and after each soaking/high humidity period. Thickness was measured with Mitutoyo slide calliper (resolution 0.01 mm, accuracy ±0.02) and the number of replicate specimens was 2-4 depending on the measurement method. The different testing methods are further described in Paper VII.
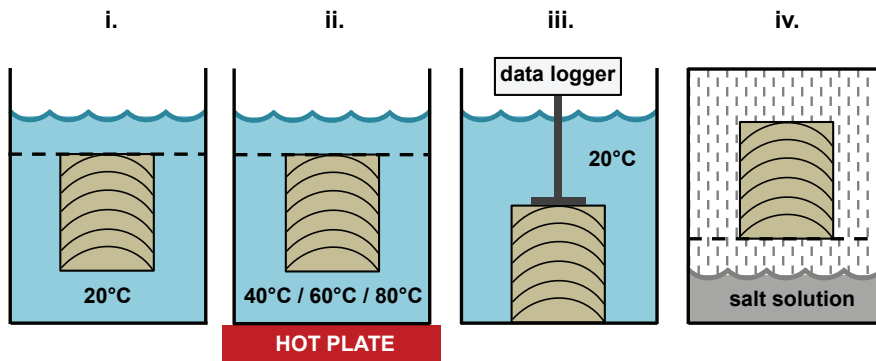
Figure 13. *Schematic illustrations of the different methods: i) soaking-drying cycles, ii) soaking-drying cycles in hot water, iii) soaking with continuous data logging and iv) humid-dry cycles at different RH.*

Set-recovery was calculated according to Equation 3.

$$Set\ recovery = \frac{t_s - t_d}{t_u - t_d} * 100\% \qquad (Eq\ 3)$$

where t_s is the oven-dry densified thickness after soaking, t_d is the oven-dry densified thickness before soaking and t_u is the initial uncompressed thickness. This formula has also been used in several other studies (Fang et al. 2012, Heger et al. 2004, Inoue et al. 1993, 2008, Kutnar & Kamke 2012a, Rautkari et al. 2010). Thickness swelling was used to analyse the swelling behaviour by comparing the thickness at any time during testing (t_i) in relation to the densified oven-dry thickness before the first soaking (t_d). Thickness swelling was calculated for all sample types (densified and non-densified) according to Equation 4 and a similar formula has been used by e.g. Fang et al (2011), Navi and Girardet (2000) and Welzbacher et al. (2008).

$$Thickness\ swelling = \frac{t_i - t_d}{t_d} * 100\% \qquad (Eq\ 4)$$

Water vapour sorption behaviour

The sorption behaviour of modified and untreated wood was reported in Paper VIII using a Surface Measurement Systems (London, UK) Intrinsic DVS (dynamic vapour sorption) apparatus. The system has a balance in a closed chamber with an adjustable atmosphere. The temperature remained constant (25 °C) and RH varied according to the scheme presented in Fig 14.
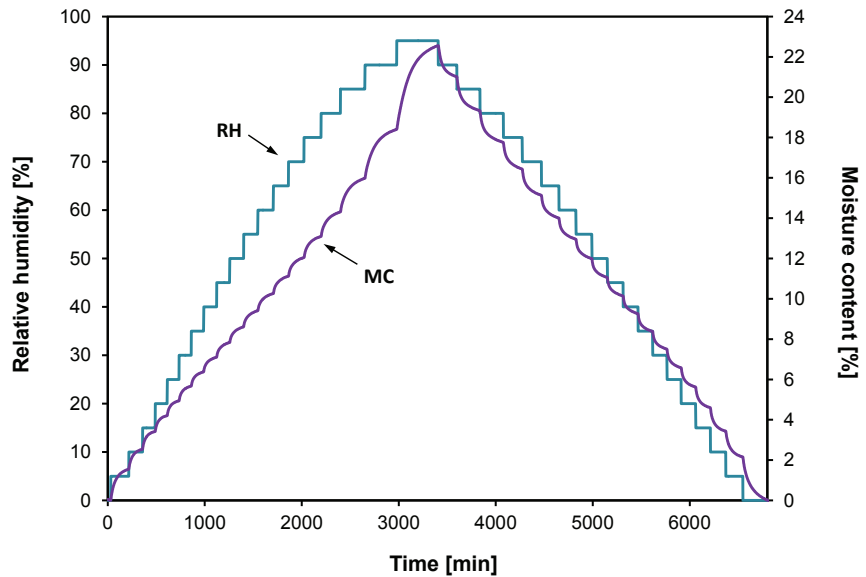
Figure 14. *Changes in MC of an untreated Scots pine sample stabilised at different levels of RH in a DVS apparatus during one adsorption and desorption cycle.*

Small wood samples of approximately 5 mg were removed from the through thickness densified and TM samples for the sorption analyses. After initial drying (in nitrogen gas), the sorption cycle started at 0 % RH and increased in 5 % steps to a maximum of 95 % RH. The highly accurate balance (±0.1μm) measures the changes in the sample weight and when the weight is stabilised the RH is increased/decreased to the next step. The weight is considered stabilised when the change in weight is <0.002 % per minute over a 10 minute period, a value found to produce sample MC within less than 0.1% of the equilibrium value at extended time (Hill et al. 2010). The equilibrium moisture content (EMC) is calculated from the stabilised weights and plotted against the corresponding RH, which creates a so-called sorption isotherm, an example of which was presented in Fig 3. Hysteresis was plotted by substracting the adsorption EMC values from the desorption values. Three sorption cycles were run and the experimental details are further described in Paper VIII.

4 RESULTS AND DISCUSSION

This chapter describes the main results with a discussion and reflection of the core findings in relation to the literature background.

4.1 Vertical density profile formation

The density through the thickness of a sample can be described with the vertical density profile (VDP). VDP has been commonly utilised in the manufacturing processes of wood-based panels, such as particle board, but in Papers I-V it has proven to be a viable method for analysing surface densified solid wood as well. In the study of surface densified wood, it was found that the formation of the VDP can be controlled through the process parameters, in a manner analogous to that of wood-based panels.

A typical density profile, superimposed on a micrograph of the corresponding surface densified wood specimen is shown in Fig 15. A series of variables (MD, PD, Pdi, Pb and PA – see below for explanation) were determined in order to support the numerical analysis of the density profile. These variables are partly based on a density profile analysis of particleboard carried out previously (Wong et al. 1998). The mean density (MD) is the average density value through the sample thickness and peak density (PD) was identified as the highest density value in the profile. Peak distance (Pdi) denotes the distance of the peak density from the densified surface while peak base (Pb) describes the width of the deformation and is measured as the crossing of the peak and the MD drawn through the profile. Peak area (PA) describes that part of localised deformation during compression, measured as the area outlined by the peak and the MD value drawn through the profile.
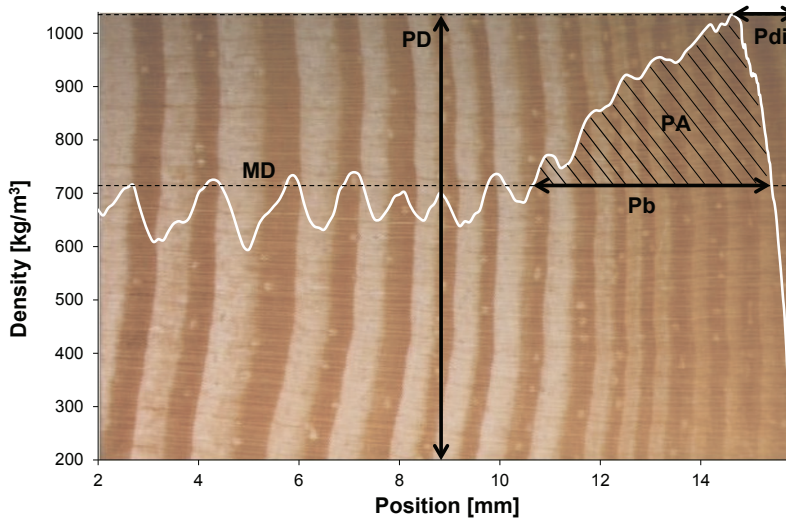
Figure 15. *The variables of the vertical density profiles used in numerical analysis.*

In order to further describe the links between the density profile characteristics and the processing parameters, Pearson correlations were calculated for these variables. These correlations have a maximum value of 1 and are presented in Table 1 with a darker shade denoting a stronger correlation. Values that were statistically significant (95 % significance level) are marked with asterisk.

Table 1. Correlation between density profile characteristics and process parameters. A darker shade denotes a stronger correlation and values marked with asterisk are statistically significant (Data from Paper III).

	Peak density	Mean density	Peak area	Peak base	Peak distance	
	PD	*MD*	*PA*	*Pb*	*Pdi*	
CR	* 0.65	* 0.76	0.00	*-0.37	*-0.41	0.7-
MC	* 0.20	0.04	0.01	0.03	*-0.19	0.6-
Closing time	*-0.52	*-0.14	0.02	* 0.32	* 0.16	0.5-
Temperature	*-0.12	-0.07	0.05	* 0.16	* 0.26	0.4-
Holding time	-0.06	0.06	* 0.11	* 0.12	* 0.03	0.0-

Table 1 shows that CR and closing time have the strongest correlations with the density profile characteristics, especially with PD, MD and Pdi. As might be expected, a higher CR resulted in higher PD and MD values, since a larger part of the sample thickness was deforming with higher CR. On the other hand, a slower closing time resulted in a lower PD and higher Pdi, meaning that the sample was deforming deeper and over a wider section of the sample

instead of a targeted density increase close to the sample surface. Wang et al. (2001, 2000) also found that a slower press closing speed resulted in a lower density peak in MDF (medium density fibreboard) and OSB (oriented strand board) manufacture. When a correlation was strong, it was also statistically significant, while values that were not statistically significant were generally rather low. This suggests it may not be even possible to control some of the poorly correlated density profile characteristics, such as PA, through process parameters.

Furthermore, a correlation amongst the density profile characteristics was discovered. For example, Pdi and PD had a strong negative correlation, suggesting that as the density peak moves further from the heated surface it becomes also lower. This is thought to result mainly from heat and moisture transferring deeper into the sample enabling a larger part of it to soften further from the heated plate. Also, with a slower closing speed the surface next to the heated plate begins to dry, moving the softening region deeper into the sample.

4.2   Changes in hardness

Hardness defines the resistance of a surface to point loads and is widely used in, for example, evaluating flooring products, such as parquets. Density is known to correlate positively with hardness and therefore, an improvement in hardness is to be expected from surface densification. In Papers II and III, hardness was measured with a modified Brinell hardness method (presented in Chapter 3) in which the indentation depth is measured instead of measuring the indentation diameter. Similar modifications to the measurement standard have been made previously (Niemz & Stübi 2000, Rautkari 2012b), since measurement of the indentation diameter is rather laborious and difficult to perform accurately on wood, while the indentation depth is measured automatically (with the universal testing machine).

It was clearly demonstrated in Papers II and III that hardness can be increased by surface densification and the increase is dependent on the process parameters used. Table 2 shows the hardness values obtained with different process parameter combinations in a cross-tabulation table. In Table 2 a darker shade denotes a higher hardness value and standard deviations are presented in parentheses.

		CR [%]		Closing time [min]	
		6.7	25	0.5	5
RH [%]	35	**14.9** (3.1)	**19.2** (3.6)	**19.1** (4.0)	**15.0** (2.7)
	65	**14.0** (2.1)	**17.7** (4.4)	**18.3** (3.7)	**13.3** (2.0)
Temperature [°C]	150	**15.1** (3.1)	**18.9** (3.6)	**19.3** (3.6)	**14.7** (2.5)
	200	**13.8** (2.0)	**18.0** (4.4)	**18.1** (4.1)	**13.7** (2.4)
Holding time [min]	1	**14.5** (2.6)	**18.0** (3.5)	**18.3** (3.4)	**14.2** (2.3)
	10	**14.4** (2.7)	**18.9** (4.5)	**19.1** (4.3)	**14.1** (2.7)

19-
18-
17-
15-
13-

Reference value for untreated Scots pine is **13.0 N/mm^2**

Higher CR (25 %) and faster closing time (0.5 min) produced the highest hardness values, whereas RH, temperature and holding time had only a minor effect. The significance of CR in improving the hardness of surface densified wood was also found by Lamason & Gong (2007). The reason for this is to be found from the density profile formation which is strongly linked to the process parameters, especially CR and closing time. This issue is further exemplified in Fig 16, which presents the density profiles of samples densified with different CR and closing times and includes the corresponding hardness values.
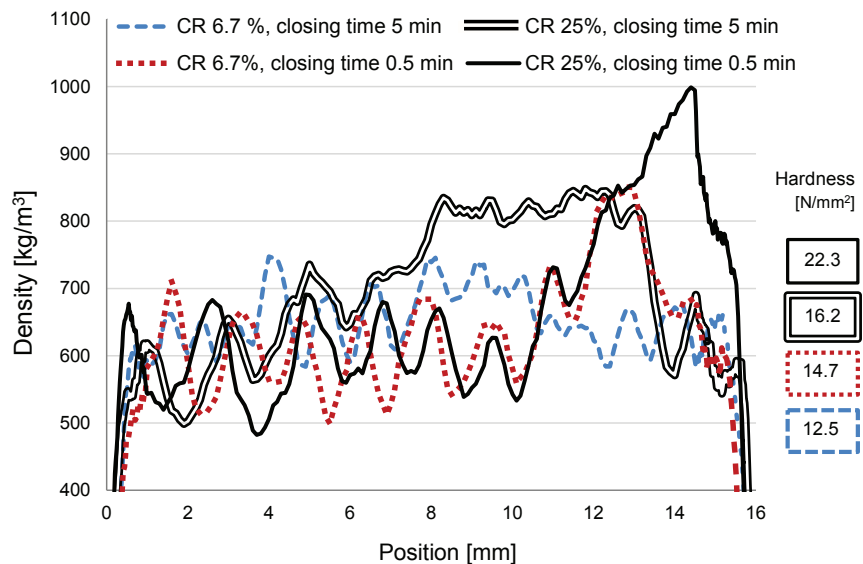

Figure 16. *Example density profiles of surface densified samples and their hardness values (each profile and hardness value represents one sample).*

In Fig 16, the dashed blue line represents the density profile of a sample compressed with low CR and slow closing time. There is no clear change in the density profile compared to an untreated profile (not shown), and the hardness value is therefore the lowest; 12.5 N/mm^2 (even lower than the average untreated hardness of 13.0 N/mm^3). By shortening the closing time (from 5 min to 0.5 min), a more distinct peak is formed close to the heated surface and is denoted by the dotted red line, and also, the hardness value is increased to 14.7 N/mm^2. If the closing time remains slow (5 min), but the CR increased (from 6.5 % to 25 %), hardness is increased to 16.2 N/mm^2 and the profile (double black line) shows a density peak which is rather wide and a few millimetres from the densified surface. The location of the density peak is relevant in the hardness test as the steel ball is penetrating the surface of the wood to a depth of approximately 1-3 mm and, in the case of the double black line, not necessarily reaching the densified part of the sample. If the CR is increased and the closing time is faster, as in the solid black line, the peak is higher and closer to the surface and the hardness almost doubles to 22.3 N/mm^2. This example therefore shows the significance of the process parameters, especially CR and closing time, in controlling hardness through the formation of the density profile.

4.3   Changes in cupping behaviour

The aim of surface densification is to produce a raw-material for products with mainly one surface exposed to use, such as flooring, worktops or furniture. Therefore, only one surface is densified, while the opposite side is left undensified for possibly easier cutting and mounting. This however, produces an uneven through thickness density, which might cause the material to cup or otherwise deform in an unwanted manner when exposed to changes in RH. This phenomenon has been recognised in wood-based panels (Ganev et al. 2005, Wu & Suchsland 1996). Therefore, the cupping of surface densified wood was examined in Paper IV and cupping was observed to occur either on the densified side (negative values for cupping) or on the undensified side (positive values for cupping) (see Fig 17a). The possible dependency of cupping on the process parameters used is presented for different original MC values in Fig 17. Closing time did influence cupping, but its effect was highly inconsistent, resulting in a non-existent correlation and it was therefore omitted from this analysis.

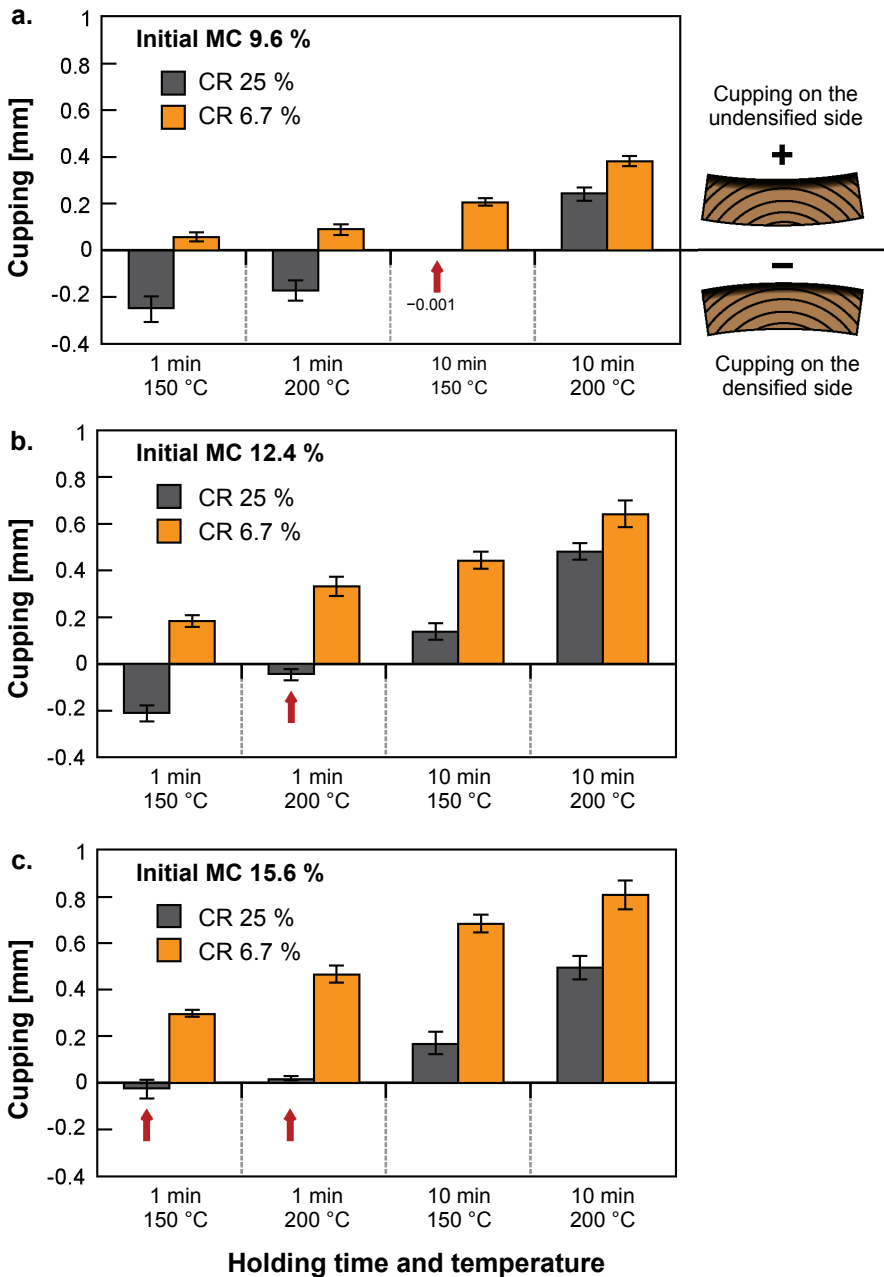**Figure 17.** *Average cupping of samples with CR of 6.7 and 25 % after different combinations of holding time and temperature and initial MC (a) 9.6 %, (b) 12.4 % or (c) 15.6 % (data from Paper IV).*

The level and orientation of cupping was relatively difficult to link with the process parameters used. This is probably because the cupping is dependent on several factors related to the densification process such as uneven drying of

the sample and the creation of moisture gradients, which has been recognised as the reason behind cupping of regular (undensified) sawn wood (Dengyun et al. 2007, Jakieła et al. 2008, Kang et al. 2011, Svensson & Toratti 2002, Ormarsson et al. 1999). However, there seems to be specific combinations of process parameters that produce very minimal cupping; these are marked with arrows in Fig 17. It can be speculated that with suitable process parameters, the cupping of solid wood might even be reduced by surface densification this, however, would require further investigation. A lower CR resulted the cupping always developing on the undensified side, whilst a higher CR generally resulted in a lower level of cupping. It also seems that the increase in initial MC generally increased the level of cupping on the undensified side and reduced the level of cupping on the densified side (samples with high CR). This is possibly because with higher initial MC the moisture gradient is expected to be stronger and therefore result in a higher level of cupping in the same direction as an undensified sample would presumably cup, which is on the "undensified side" (see Fig 17a).

The correlation between cupping and density profile characteristics were also analysed and it was found that peak distance (Pdi) was the most influential characteristic, followed by peak density (PD), average density (AD), and peak base (PB). Peak area (PA) can be considered to have no effect on cupping. The reason for the stong influence of Pdi is possibly because it is describing the location of the density peak and thereby defining the distance of the peak from the "neutral axis" of the density structure. These results suggest some connection between the cupping behaviour and process parameters, however, the reasons behind these results are complex and more investigations are needed.

4.4   Changes in micromorphology

Micromorphological changes in surface densified wood were visually analysed by SEM to investigate the manner of deformation and identify possible fractures in the cell-wall. It was confirmed that during surface densification the deformation mainly occurred in the earlywood, while latewood did not seem to deform at all, as may be observed from Fig 18.
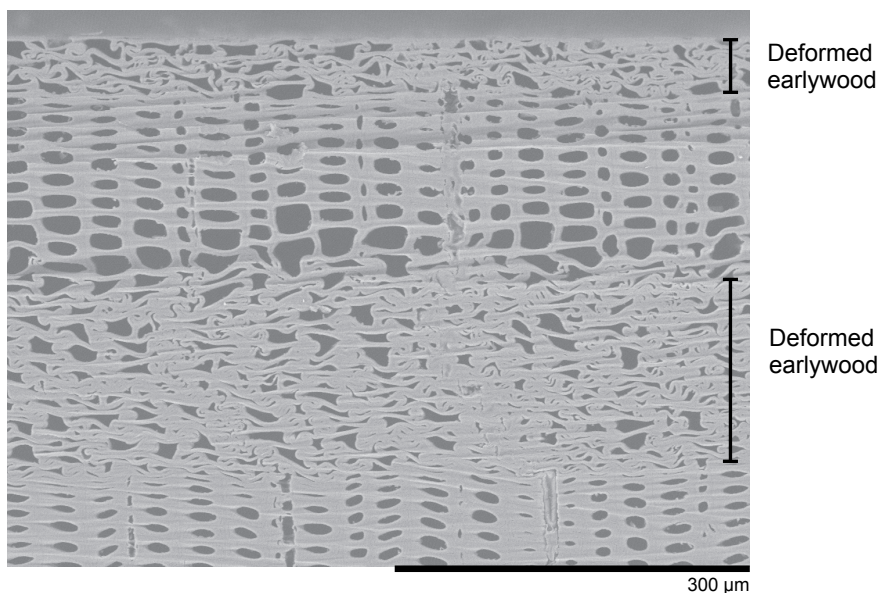
Figure 18. *Cross-section of surface densified (200 °C, 30 s closing time) Scots pine showing the deformed earlywood near the densified surface*

One key finding was that no major fractures were observed in the cell-walls – even with low press temperatures (100 °C) and a short closing time (10 s). Even if minor micro-cracks were found in the latewood of the densified samples, identical types of cracking in similar locations were also found in the latewood of untreated samples (Figs 19a and 19b). Therefore the micro-cracking was most probably due to drying of the wood (Siau 1984) and not caused by the densification process.
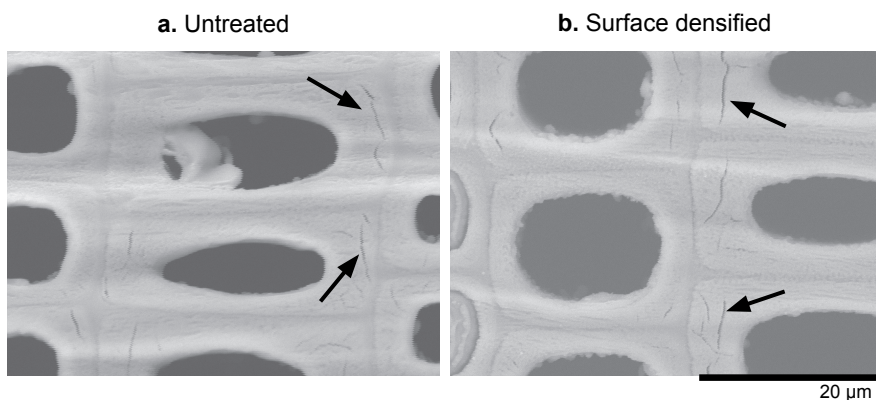
Figure 19. *Cross-sections of (a) an untreated and (b) a surface densified (200 °C, 30 s closing) latewood samples. Arrows point at micro-cracks in the cell-wall.*

In many cases the sample was deforming through the sample thickness and not only close to the heated plate, especially with low temperature and fast closure. In these conditions, the wood is not softening sufficiently at the sample surface for targeted deformation, but the densification occurs at the weakest points of the sample, that is, in this case, in the earlywood sections through the sample thickness. The sample is not expected to be in a softened state throughout the thickness; therefore part of the deformation occurs below the T_g of the cell-wall components. This, however, did not seem to have affected the possible fracture of the cell-wall. As may be seen from Fig 20, fractures were not observed even after soaking and drying of the samples. In this figure, bordered pits between cells may appear to have undergone delamination, however, actual delamination was not observed.

The overall thickness of the samples almost completely recovered during soaking; however, the deformed cells were left slightly distorted and did not return to their original form, as may be seen from Fig 20c. It is therefore suggested that during compression, the cell-walls (whether above or below T_g) partly undergo permanent deformation, not due to major fracture but rather as a result of the viscoelastic behaviour of wood. That is to say, the viscous flow of the matrix constituents (Fratzl et al. 2004, Keckes et al. 2003, Entwistle & Zadoroshnyj 2008) or the reorganisation of hydrogen bonds between the cell-wall components (Adler & Buehler 2013, Keckes et al. 2003, Navi et al. 2002), which may be enhanced by extended time, increased temperature and a change in the moisture content of wood. Most of the deformation induced by densification did recover during water-soaking; however, a significant reduction in this recovery can be obtained by thermally modifying the samples. This aspect will be discussed in the next section.
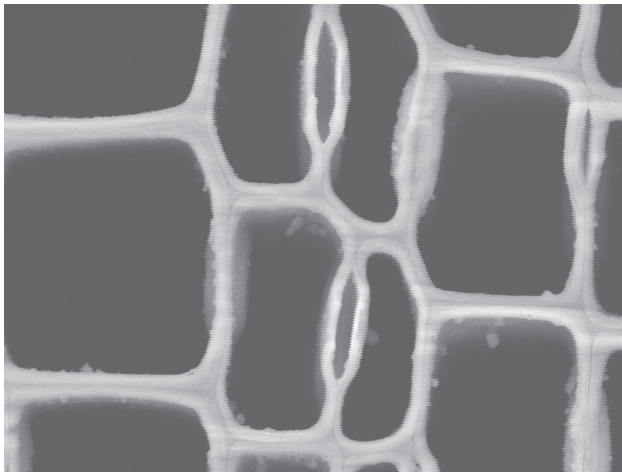
a. Untreated earlywood
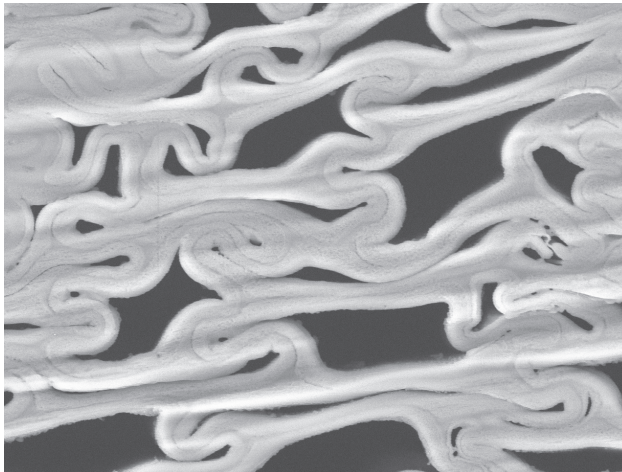
b. Surface densified earlywood (200 °C, 60 s closing time)
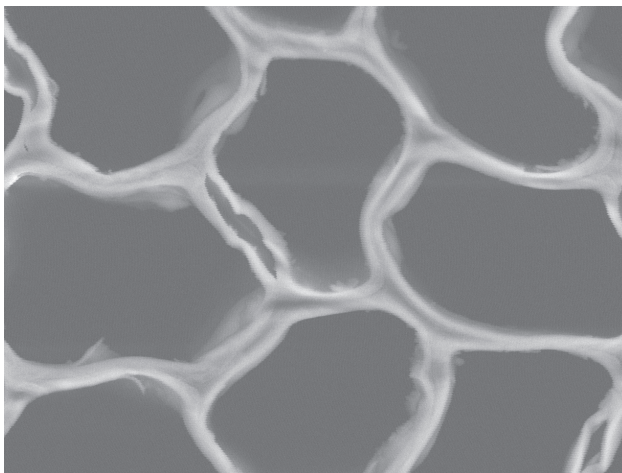
c. Surface densified earlywood recovered by soaking

20 µm

Figure 20. *Cross-sections of (a) an untreated sample, (b) surface densified sample before soaking and (c) surface densified sample after soaking.*

4.5 Reducing the set-recovery effect

The recovery of the compressed deformation in water-soaking or high humidity conditions is a significant issue when it comes to the usability of the material. Thermal modification (TM) has been widely used to improve the dimensional stability and decay resistance of sawn timber (Hill 2006) but also to fix the deformation of compressed wood (e.g. Kamke 2006, Navi and Girardet 2000, Seborg et al. 1956). The effect of TM on the 'set-recovery' of surface densified wood was examined in Paper VI for three different compression ratios. The results presented in Fig 21 show that set-recovery was significantly reduced following TM, from over 80 % to approximately 6 % with no major dependence of the compression ratio in this case.
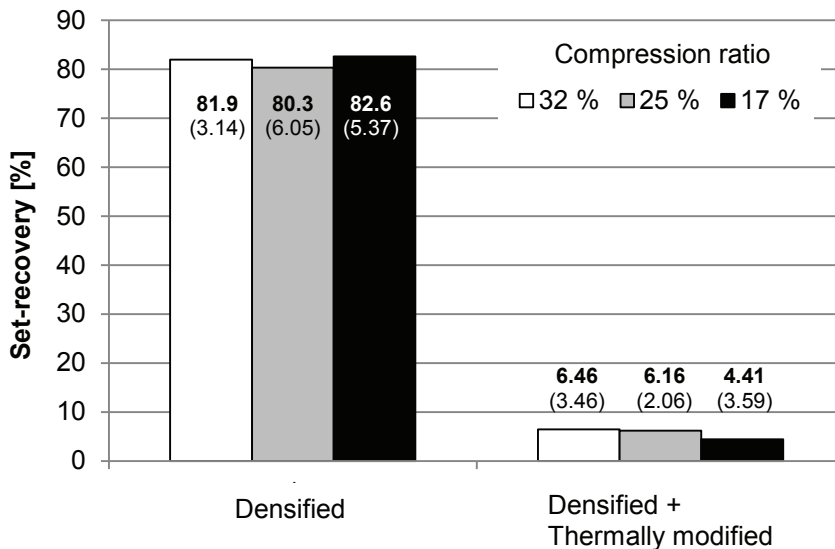
Figure 21. *Average set-recovery of surface densified specimens and surface densified + TM with different compression ratios after one soaking-drying-cycle (the standard deviation is shown in brackets) (Data from Paper VI).*

The reduction in set-recovery due to TM can be explained by degradation of the wood constituents, breaking or weakening of the molecular bonds and formation of new bonds in the deformed position during the TM (Inoue et al. 2008, Morsing 2000, Navi & Heger 2004). Also increased cross-linking within the lignin complex might increase the rigidity of the matrix and therefore restrict the movement and water-absorption of the microfibrils (Tjeerdsma

et al. 1998). Complete fixation of the compressive deformation is expected to be achieved with sufficient steaming, treatment time and temperature during processing (Heger et al. 2004, Inoue et al. 1993, Navi & Heger 2004).

Besides improving some of the properties of sawn timber, such as dimensional stability, TM is also known to cause a reduction in the mechanical properties of wood, such as reduced impact strength and hardness (Rautkari et al. 2014). Since densification aims to improve the mechanical properties of wood, a combination of these processes might produce a material with both improved mechanical properties and dimensional stability. Indeed, Rautkari et al. (2013b) examined the hardness of densified and TM wood and found no reduction in the hardness of surface densified wood after TM.

4.6   Set-recovery with different testing methods

Surface densification aims to modify only the sample surface, leaving the rest of the sample undensifed. When exposing the surface densified sample to high humidity conditions or water-soaking, the undensified part of the sample will also react (by swelling) and affect the overall thickness of the sample. Furthermore, if the sample is only slightly densified (e.g. 1 mm out of 20 mm), the changes in recovery behaviour are very small and present difficulties in accurate measurement (Rautkari et al. 2010). Therefore, in order to examine the material properties of the densified part of the sample, the set-recovery examination was performed on a more uniform material, in this case, wood densified through the whole thickness of the sample, to study the overall phenomena related to set-recovery.

The set-recovery of densified wood has been studied rather extensively (e.g. Fang et al. 2012, Heger et al. 2004, Inoue et al. 1993, 2008, Kutnar & Kamke 2012a, Rautkari et al. 2010) and, as a result, a range of testing methods have been utilised. However, general standards have not been developed which poses a problem in terms of comparability. Therefore, in Paper VII, different thickness swelling testing methods were used on densified and TM wood to examine the differences between methods and to provide more knowledge about the overall phenomen of set-recovery. The swelling behaviour was studied using four different methods (illustrated in Chapter 3, Fig 13): i) soaking-drying cycles (at room temperature), ii) soaking-drying cycles in hot water, iii) soaking with continuous data logging and iv) humid-dry cycles

at different RH. The set-recovery of densified and densified + TM samples after the different testing procedures adopted are presented in Fig 22 and 23 (note the different y-axis scale).
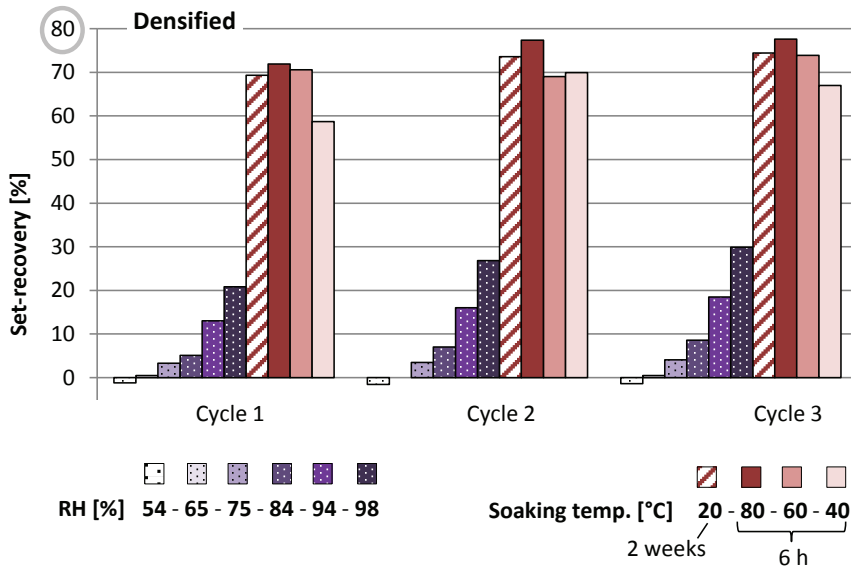

Figure 22. *Average set-recovery (%) of densified samples after cycles 1, 2 and 3 using RH method (dotted purple) and water-soaking methods (red) (Data from Paper VII.*
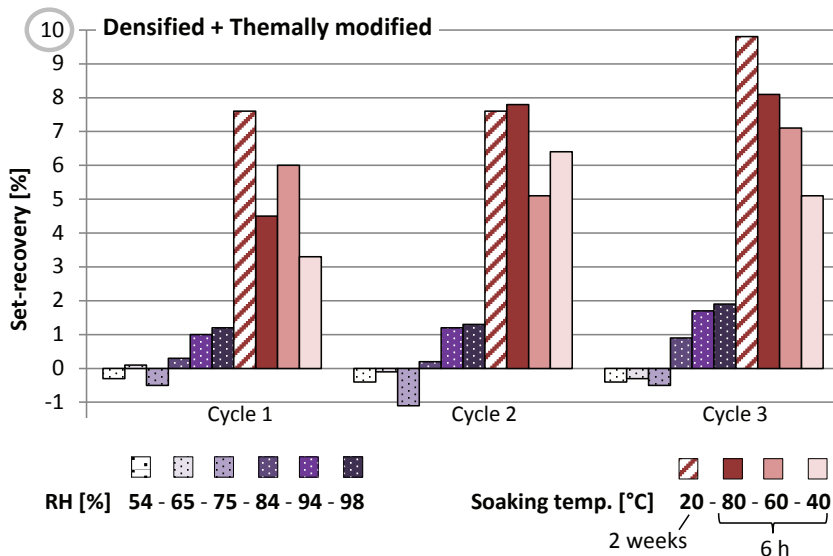

Figure 23. *Average set-recovery (%) of densified + thermally modified samples after cycles 1, 2 and 3 using RH method (dotted purple) and water-soaking methods (red) (Data from Paper VII).*

It was discovered that the level of set-recovery is dependent on the measurement method selected. It should be noted, that water-soaking at room temperature was performed over a 2-weeks period, whilst the hot-water-soaking was performed only over a period of 6 hours. However, the set-recovery in hot-water-soaking is, in some cases, even higher than soaking at room-temperature. Therefore, water temperature seems to play a more significant role in inducing set-recovery than the time of soaking. The enhanced swelling of undensifed wood in higher water temperature has been reported previously (Mantanis et al. 1994) and in this study too, higher water temperature generally produced higher levels of set-recovery. The reason for this is probably a result of the T_g of lignin being reached at the highest testing temperatures over the time of testing (6 h).

Furthermore, the swelling behaviour of densified wood has been known to change after repeated cycles of soaking or high humidity conditioning (Heger et al. 2004; Tarkow & Seborg 1968, Anshari et al. 2011) and indeed there seems to be some evidence of an increase in set-recovery after repeated cycles. Due to the viscoelastic nature of wood, the change in MC might lead to the enhanced breakage and formation of hydrogen bonds, leading to a weakening of the molecular structure and recovery of the deformation (Gibson 1965, Entwistle 2005). Furthermore, water-soluble extractives and degraded fragments of hemicelluloses may also dissolve during soaking which might, in part, account for the increase in set-recovery after repeated cycles. Therefore, the number of cycles in set-recovery measurement is essential and it is suggested that, in general, several cycles are run during set-recovery experiments in order to reach full relaxation of the inner stresses.

The set-recovery levels with RH testing were clearly lower compared to the soaking methods. With the lowest RH-levels, the set-recovery is close to zero or even negative, which suggests that actual set-recovery is not induced under these conditions. The RH threshold is stated here as the level of RH at which set-recovery starts to manifest itself and it was noted to be in the region of 65-75 % for the D samples and 84-94 % for the DTM samples. Both values are below the targeted level of indoor air humidity in Finland, that is, 20-60 % (Vinha et al. 2005). However, in reality, the relative humidity in indoors may exceed 60 %.
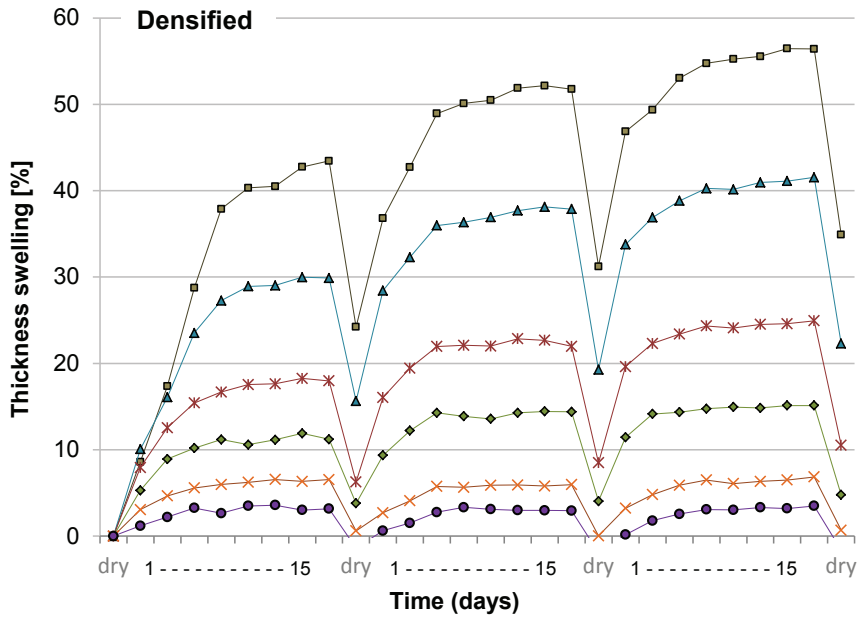
Figure 24. *Thickness swelling (%) of the densified samples in different relative humidity. See Fig 25 for legend. (Data from Paper VII)*
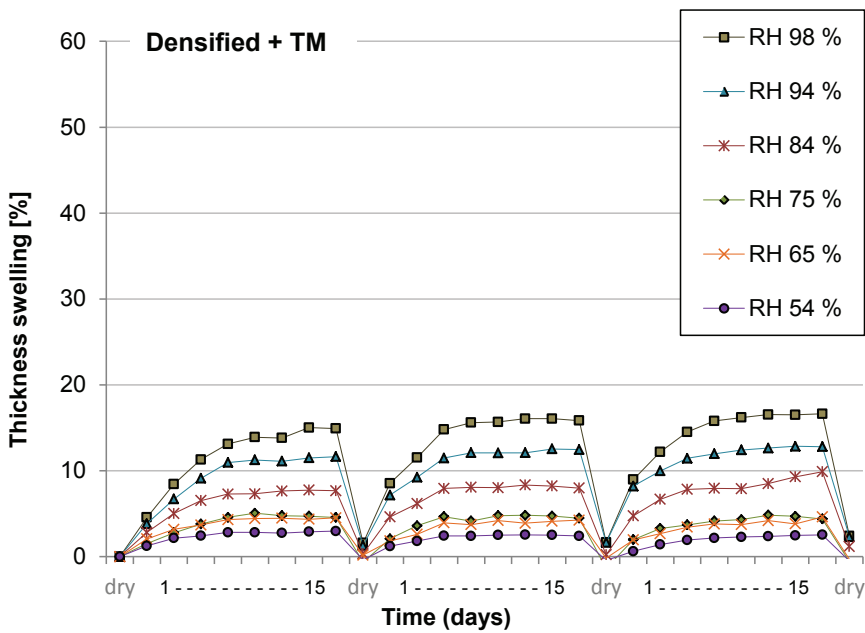

Figure 25. *Thickness swelling (%) of the densified + thermally modified samples in different relative humidity. (Data from Paper VII)*

In general, care should be taken when comparing the set-recovery results from different studies since the testing method appears to strongly affect the results acquired. Furthermore, if the modified wood is targeted for a certain application, the set-recovery measurement method should represent the possible end-use conditions. Usually, higher temperature water is utilised to shorten the time needed for testing. However, high temperatures and extended times of testing might bring the (moistened) lignin close to its T_g or even exceed it, enhancing the softening of the wood tissue and increasing the recovery. The time of exposure seems to be less significant in soaking than the time of exposure in high RH conditions. This is further examined in Figs 24 and 25, in which the thickness swelling at different RH is presented during three consecutive cycles.

In Figs 24 and 25, the first four measurements at the beginning of each cycle, which correspond to approximately 1 week of exposure, seem to increase more rapidly, after which the changes become smaller. This was also observed in the weight change, which suggested that 1 week is the time required to reach the EMC. The exception to this was at RH 98 %, as the weight stabilised only after 9–10 days exposure to this environment. In addition, the level of swelling increased after repeated humidity cycles, suggesting the occurrence of some viscoelastic relaxation process, possibly due to reorganisation of the molecular bonds (Gibson 1965, Entwistle 2005). In some cases, the thickness seems to increase slightly even after the weight has stabilised, which also suggests the occurrence of relaxation over extended humidity periods. This minor increase towards the end of the cycles, however, might also partly result from measurement inaccuracy, which could be improved by the use of a greater number replicates and by utilising more a stable measurement method (e.g. a micrometer instead of a slide calliper). In all cases, the time needed to reach EMC was reduced in cycle 2 by 2–3 days, however, further reduction was not observed in cycle 3, which might be an indication that a maximum relaxation state had been reached. The sorption behaviour after repeated humidity cycles is examined further in the following section.

4.7   Water vapour sorption behaviour

The sorption behaviour of densified and TM wood was examined in Paper VIII by utilising DVS equipment to measure the MC of wood at varying RH from

0% to 95% and plotting the values as sorption isotherms. Fig 26 shows the sorption isotherms over three consecutive cycles of adsorption and desorption for untreated (U), densified (D), thermally modified (TM) and densified + thermally modified (DTM) samples.
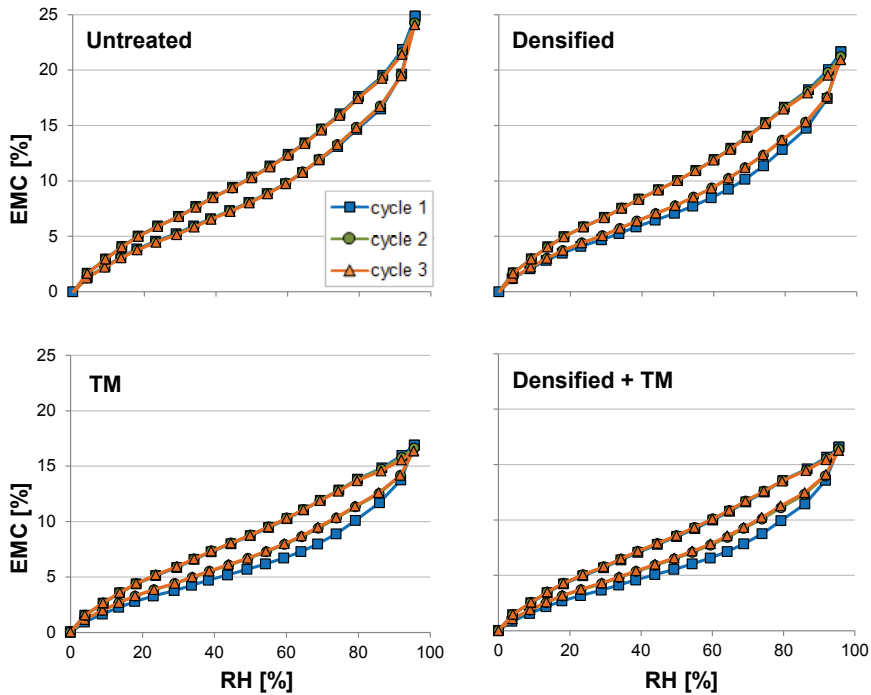
Figure 26. *Changes in sorption isotherms over three consecutive cycles for unmodified, densified, thermally modified and densified + thermally modified wood. (Data from Paper VIII)*

Fig 26 reveals that the maximum EMC at 95 % RH was ~25 % for untreated wood, ~22.5 % for densified wood and ~17 % for both TM and DTM samples. The reduced EMC for TM wood was anticipated from the results of several previous studies (e.g. Borrega & Kärenlampi 2010, Hakkou et al. 2005, Rautkari et al. 2013). Also, a slight reduction in the EMC of densified wood has been previously reported, however, only a limited number of studies have dealt with this issue (Heger et al. 2004, Navi & Girarder 2000). The reduction in EMC during densification at 150 °C is most likely due to minor thermal degradation, which has been reported to occur in hemicelluloses and cellulose already above 120 °C (Kollman & Fengel 1965). On the other hand, chemical changes in lignin have been suggested to cause irreversible reduction in wood MC after heating at 140 °C (Obataya & Tomita 2002) and loss in weight has

46

been reported already after heating at 105 °C (Hill & Jones 1996). It should be noted, that the wet-pressing of wood pulp has also been seen to reduce the accessibility of cellulose to cellulase (Luo et al. 2011), and therefore, compression of the cell structure might also have reduced the hygroscopicity of densified wood.

Sorption hysteresis describes the difference within the sorption isotherm loop and can be calculated by subtracting the adsorption EMC value from the corresponding desorption EMC value at a given RH. The corresponding hystereses of the isotherms in Fig 26 are presented in Fig 27.
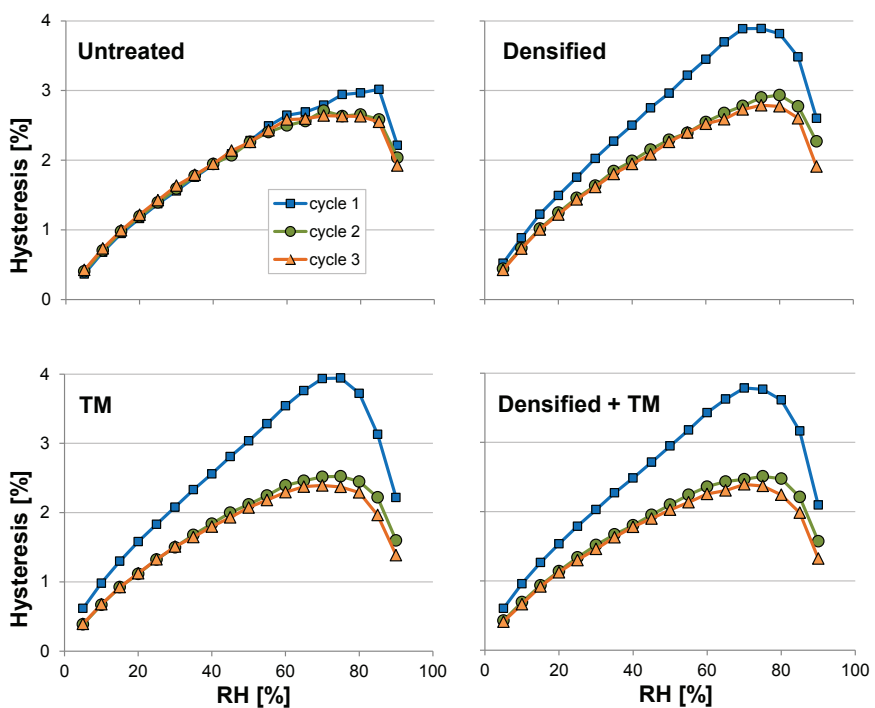
Figure 27. *Absolute hysteresis (obtained by subtracting the adsorption EMC from the desorption EMC values) plotted as a function of RH, for untreated (a), densified (b), thermally modified (c) and densified then thermally modified Scots pine. (Data from Paper VIII)*

Fig 27 shows that the sorption hysteresis was rather stable for untreated wood during humidity cycling. However, densification, TM and a combination of those treatments resulted in an increase in hysteresis during the first humidity cycle compared to untreated wood. Thereafter, a large change in the adsorption branch was recorded for all modified samples, leading to a

reduction in hysteresis in subsequent cycles. This result again suggests that a viscoelastic relaxation of the compressed form might occur for densified wood after repeated cycles, possibly due to reorganisation of the hydrogen bonds (Gibson 1965, Entwistle 2005) or the rearrangement of lignin (Hill et al. 2009), enabling an increase in the accessibility of water molecules into the wood polymers. However, it is surprising to find the same phenomenon occurring in TM wood as well (not densified). Indeed, previous studies on the sorption hysteresis of TM wood have been limited to sorption cycle only (Jalaludin et al. 2010a, 2010b), whereas, Paper VIII reported, for the first time, the changes in hysteresis between the first and subsequent cycles for TM wood. Drying has been studied rather extensively and increased temperature during drying is known to create stresses between microfibrils in solid wood (Jakieła et al. 2008, Svensson & Toratti 2002, Thuvander et al. 2002) and similar stresses might be created during TM as well. The results therefore suggest that inner stresses are created not only during densification but also during TM as well. These stresses may be released during the first exposure to high humidity which might account for the hysteresis change in further cycles.

The results from the water vapour sorption experiment suggest that densification and TM not only change the properties of wood, but also change the behaviour in the ultrastructural level - possibly due to rearrangement of the molecular bonds. However, the changes in sorption behaviour due to modification are not completely stable, but are affected by moisture cycling - presenting fundamental characteristics of modified wood under cyclic moisture change.

5   CONCLUSIONS

Density correlates strongly with wood mechanical properties and therefore increasing the density, might improve the properties and widen the usability of otherwise low-density wood species. The purpose of surface densification is to modify only the very surface of solid wood, where the property improvements are most needed, rather than the entire bulk of the material. Surface densified wood would be beneficial especially in applications where only one surface is mainly exposed to use, such as flooring or worktops. In this dissertation Scots pine sapwood was densified between heated metal plates and the properties analysed in comparison to untreated wood. In addition, the densified wood was thermally modified in order to diminish recovery of the deformation (set-recovery).

It was discovered that during surface densification the deformation occurs mainly in the earlywood cell-walls close to the heated plate. The results show that the process parameters, especially the compression ratio, temperature and closing time, have a significant effect on the density profile formation of surface densified wood. If the temperature is low (100°C) and press closing time short (10 s) the surface is not softened sufficiently and the deformation occurs more throughout the sample thickness. On the other hand, with a rather high temperature (200°C) and slow closing speed (5 min), heat and moisture migrate deeper into the sample, enabling softening and deformation in the core, leaving the very surface undeformed. Furthermore, the process parameters and density profile formation correlate well with the changes in properties, such as hardness. Indeed, the hardness may be almost doubled by surface densification which is strongly dependent on the process parameters – especially closing time and compression ratio. Surface densified wood exhibits cupping behaviour, most likely due to the uneven density structure, but also the creation of moisture gradients through the sample thickness during the

densification process. Cupping is also affected by the process parameters; however, in a complex manner which requires further investigation.

UV-laser ablation was utilised for the first time in the sample-preparation of densified wood for microscopic analysis and it proved to be very suitable for the purpose, creating no apparent artefacts or recovery of the deformation. In the microscopic analysis by SEM it was discovered that the surface densification process does not cause any major fractures in the cell-wall. After soaking the sample dimensions recovered almost completely, however, the cells did not completely recover their original form but were left distorted which was not thought to be due to fracture but due to rearrangement of the molecular bonds and viscoelastic flow of the matrix. The set-recovery can be reduced from 80 % to 6 % by thermal modification of the densified wood at 200°C for 3h with steam injection. Further studies in the combined process of densification and TM might result in an even greater reduction in set-recovery.

Care should be taken when comparing the set-recovery results from different studies, since the measurement method affects the results acquired. For example, a higher soaking temperature generally results in a higher level of set-recovery, possibly due to softening of lignin at the elevated temperature. Furthermore, repeated soaking-drying cycles increased the level of set-recovery, at least up to 3 cycles, which was thought to be due to the viscoelastic nature of wood and enhanced molecular rearrangement under varying moisture conditions. Densified wood starts to exhibit set-recovery at RH 65-75 %, while densified wood with TM exhibits set-recovery at RH 85-94 %. Densified and densified + TM wood may be therefore suitable for indoor conditions, since these values are above the target values for indoor air humidity in Finland; 20-60 % (Vinha et al. 2005). Both, densification and TM reduce the hygroscopicity of wood and increase hysteresis during the first humidity cycle. After the second humidity cycle, the level of hysteresis is reduced for densified, TM and densified + TM, most likely due to the release of the inner stresses. Changes in the sorption isotherm between the first and subsequent cycles for TM have not been previously reported and the results suggest that inner stresses are not only created during densification, but also during the themal modification of wood, and they are partly released during cyclic moisture change.

This dissertation provides new knowledge in terms of developing the densification process towards product applications or production at an industrial scale. The results also support research related to other wood processing that utilises the softening properties of wood, such as veneer peeling, and processing that includes compression, such as plywood production or any high-temperature treatment of wood.

5.1   Limitations and future work

The wood material in the study was limited to Scots pine sapwood free of visible abnormalities, such as knots and resin pockets. The scale of wood modification was also limited to laboratory equipment, and therefore, further study is required for the possible production of larger samples or at an industrial scale. The densification was carried out in an open press similar to those used in panel board production, such as plywood, which might be beneficial in the adaptation of the production in larger scale.

The dissertation provides insights into the mechanisms affecting wood softening and deformation, and an even deeper understanding might be achieved by investigating the moisture gradient development in situ during the densification process. Furthermore, the results of the water vapour sorption study gave new insights and valuable new knowledge about the relaxation behaviour of densified and TM wood during repeated humidity cycling, which could be further investigated by increasing the number of cycles and testing different levels of modification.

There are also other interesting aspects yet to be discovered for surface densified wood. Could the reduced porosity of surface densified wood improve the fire retardancy of the material (Subyakto et al. 1998)? Could surface densification provide a natural surface treatment (Rautkari et al. 2012a) whilst enabling the material to still "breath" and stabilise the indoor air humidity during high and low humidity peaks (Padfield 1998)?

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This doctoral dissertation describes a method for increasing the surface density of solid wood by compressing the porous cell structure in a hot press. The surface densification process was developed to improve the mechanical properties and value of otherwise low-density wood species. The method enables a targeted densification at the very surface of wood, where property improvements are most needed. The parameters used in the densification process correlated directly with improvement in properties, such as hardness, which was almost doubled.

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