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The effect of ionic liquid and superbse pre-treatment on the spring-back, set-recovery and Brinell hardness of surface-densified Scots pine

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Abstract: Compressing the surface of sawn timber results in a substantial increase in hardness, and this opens up new market opportunities of using low-density timber species as the raw material for high-value wood products. Unfortunately, widespread commercialisation is hindered by the lack of an industrially viable surface densification process, the major obstacle being the set-recovery (SR) of the densified wood cells upon exposure to moisture. Our hypothesis is that partial dissolution of the crystalline cellulose during densification will largely prevent the SR of densified wood. We therefore evaluated the effect of ionic liquid (IL) or organic superbse pre-treatment on the elastic spring-back (SB), SR and Brinell hardness (HB) of surface-densified wood. Specimens of Scots pine were treated with solutions of ILs or superbases, and then densified in a hot press at temperatures between 200°C and 270°C. The SR was reduced from 90% for the control group to only about 10% for the treated materials. The treated and densified specimens exhibited a higher HB than their untreated and densified counterparts. The method presented in this study is a precursor to the development of a continuous densification process adapted for an open system. Further studies are needed to understand the underlying mechanisms of the pre-treatment.

Keywords: chemical treatment, surface modification, wood compression, wood modification

Introduction

Although it is not a new research field in wood science, the surface densification of wooden boards has in recent years become a subject of increasing interest. Creating a layer of densified wood cells a few millimetres thick just beneath the surface can lead to a two-fold increase in hardness (Gong et al. 2010; Laine et al. 2013a), and open up new opportunities for the use of low-density wood species in high-value products such as wooden flooring or window frames.

In general, the densification process consists of three stages: plasticisation of the wood cells, followed by the actual compression, and finally solidification of the compressed wood in order to prevent elastic spring-back (SB) and moisture-induced set-recovery (SR) (Sandberg et al. 2013). During the past decades, many different methods for densification have been studied, as well as the effect of the densification process parameters on the wood properties. The first published study of the surface densification of wood was probably that conducted by Tarkow and Seborg (1968). Inoue et al. (1990) reported a rather complicated technique that involved cutting grooves in the wood surface to facilitate plasticisation with water. Pizzi et al. (2005) used friction welding equipment for surface densification, and a similar principle was employed by Rautkari et al. (2009), who found a positive correlation between the level of densification by a friction welding method and the hardness. More recently, most studies have used a hot press with a cooling system, where the combination of moisture and heat plasticises and densifies the wood surface. Laine et al. (2013a) used this method to obtain an almost two-fold increase in Brinell hardness (HB). An even greater increase in hardness was achieved by plasticising the wood in boiling water (Lamason and Gong 2007). Bekhta et al. (2017) studied a short-term theromechanical densification process on veneer of alder, beech, birch and pine wood. The authors reported that the increase in density is positively correlated to the pressing temperature and the applied pressure.

The surface densification process in a hot press takes only a few minutes (Laine 2014) and is therefore – in principle – suitable for transformation into an industrial process (Neyses et al. 2016). However, the major obstacle preventing the widespread commercialisation of surface-densified wood products is perhaps the elastic SB and in particular the SR of the compressed wood cells after exposure to moisture. The elastic SB – which occurs immediately when the compression force is released – is greatly reduced by introducing a...
cooling stage to reach a temperature of the densified wood below 80°C before the pressure is released (Neyses et al. 2016). The moisture-induced SR can be eliminated by chemical modification, by impregnation with resin or by a thermo-hydro-mechanical post-treatment (Kutnar et al. 2015). Already in the early 1990s, Inoue et al. (1993) showed that the SR can be virtually eliminated by post-steaming of the compressed wood at 200°C for 1 min or at 180°C for 8 min. Similar results were reported by Navi and Heger (2004). Kutnar and Kamke (2012) almost eliminated the SR by carrying out the densification process in a closed system under saturated steam conditions at 170°C. Similar effects were observed in other studies (Inoue et al. 2008; Gong et al. 2010; Fang et al. 2012). Laine et al. (2013b) showed that thermal post-treatment almost eliminates the SR, albeit with a process time of several hours. Other studies successfully employed impregnation treatment to reduce the SR (Stamm 1964; Gabrielli and Kamke 2010; Priem et al. 2012; Khalil et al. 2014). Unfortunately, these established methods are either very time-consuming or difficult to translate into a continuous process, and at the same time they often give rise to environmental concerns.

One of the major theories describing the underlying mechanisms of the elastic SB and SR was presented by Navi and Sandberg (2012) and further described by Navi and Pizzi (2014), who suggested that the SR is due to the elastic recovery of deformation of crystalline cellulose, which is ‘frozen’ inside the plastically deformed matrix of lignin and hemicellulose. A re-plasticisation of the matrix after it has been densified, for example, through moisture, leads to a recovery of the elastic deformation in the crystalline cellulose. Our hypothesis is that the SR will be greatly reduced if a plastic deformation of the crystalline cellulose can be achieved in the initial plasticisation stage before densification. This is, however, difficult to accomplish with the existing methods of plasticising wood, such as the combination of moisture and heat, or treatment with gaseous ammonia (Schuerch et al. 1966).

In the beginning of the 21st century, the possibility of dissolving and plasticising cellulose by treatment with so-called ionic liquids (ILs) was reported (Swatloski et al. 2002; Kilpeläinen et al. 2007). An IL is a salt that is liquid at temperatures normally below 100°C (Hanabusa et al. 2018), which means that they consist of ions instead of electrically neutral molecules. Apart from being considered to be ‘green solvents’ for cellulose, ILs are reported to have positive effects on antifungal and antimicrobial activity, and on the fire resistance and ultraviolet (UV)-stability of wood (Pernak et al. 2004; Patachia et al. 2012; Foksowicz-Placzyk and Walentowska 2013; Miyafuji and Fujiwara 2013). The first generation of ILs that were used to dissolve cellulose consist of imidazolium-based cations, often combined with a halogen anion, such as chloride or bromide. Zhang et al. (2017) reported a mechanism that relies on the synergetic effect of the cations and anions to cleave the hydrogen bonds between cellulose chains (Figure 1). The small anions of, for instance, 1-ethyl-3-methylimidazolium chloride, interact with the hydrogen atoms of the cellulose hydroxyl groups, whereas the larger imidazolium cations bond with the oxygen atoms that are less sterically hindered. Ou et al. (2014) reported that IL treatment transforms wood into a thermoplastic material, without or with only a very small elastic deformation under load. This suggests that the elastic SB and the SR can largely be reduced.

Imidazolium-based ILs are highly effective cellulose solvents, but they are also expensive (Hanabusa et al. 2018). For this reason, many researchers have started to focus on finding cheaper alternatives, and several studies have explored the potential of ILs made from amidine- or guanidine-based cations, combined with a carboxylic acid as the anion, for example, propionic acid or acetic acid (King et al. 2011). Due to their high basicity, these amidines

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**Figure 1:** Proposed mechanism of cleaving hydrogen bonds between cellulose chains with ionic liquids (Zhang et al. 2017), https://pubs.rsc.org/en/content/articlehtml/2017/qm/c6qm00348f. Permission to reproduce the figure was granted by the Royal Society of Chemistry.
and guanidines are also known as organic superbases (Ishikawa 2009). Parviainen et al. (2013) and Hanabusa et al. (2018) reported that this new generation of ILs is considerably cheaper and easier to recycle than imidazolium-based ILs, while maintaining the power to dissolve cellulose (Mäki-Arvela et al. 2010; Domínguez de María 2014). As wood is itself somewhat acidic, a pre-treatment with only the amidine or guanidine component as cation was tested in the present study, to see whether an IL in-situ with the wood’s acid groups as anions would be formed. The in-situ IL would then plasticise the cellulose.

A further hypothesis in this study is that the IL pre-treatment will increase the hardness of the densified wood surface in comparison with wood plasticised with heat and moisture and thereafter densified. The reasons are expected to be two-fold: firstly, an overall higher level of plasticisation in comparison with plasticising wood with heat and moisture, resulting in a more intense densification, and secondly, for untreated wood, the heated press platen will quickly dry the outermost wood surface upon contact, and reduce the level of plasticisation of this region. As a result, the density peak after densification will be somewhat below the surface. However, for IL-treated wood, moisture is not needed to reach the maximum level of plasticisation, and this will move the density peak towards the outermost region of the wood surface. This proposed effect originates from an analysis of the strain vs. time curve of HB testing reported in a previous study (Neyes et al. 2017).

The purpose of the present study was thus to evaluate the effect of IL and superbse pre-treatments on the elastic SB, SR and HB of surface-densified wood, various combinations of chemical compounds, solution concentrations and densification temperatures being tested.

### Materials and methods

**Specimen preparation:** The study was carried out on knot-free sapwood specimens of Scots pine (*Pinus sylvestris* L.) with dimensions of 124 mm (L) × 25 mm (T) × 18.5 mm (R). The annual ring orientation was within ±15° parallel to the tangential wood surface to be densified. The specimens were kept in a climate chamber at a temperature of 20°C and 65% relative humidity (RH) until they reached the equilibrium moisture content (EMC). In order to obtain specimen groups with roughly the same average density between the groups, the specimens were sorted into seven categories according to their density, and the specimens belonging to either the highest or the lowest density category were discarded. The remaining five density categories ranged from 400 kg m⁻³ to 525 kg m⁻³, and to make the final grouping, the specimens were then selected so that each specimen group (Table 1) had the same number of specimens from each density category.

<table>
<thead>
<tr>
<th>Specimen group</th>
<th>No. of specimens</th>
<th>Oven-dry density ± st. dev (kg m⁻³)</th>
<th>Chemical pre-treatment</th>
<th>CE (wt%)</th>
<th>T (°C)</th>
<th>MC (%)</th>
<th>P (MPa)</th>
<th>t₁ (s)</th>
<th>t₂ (s)</th>
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<tbody>
<tr>
<td>C150</td>
<td>6</td>
<td>438 ± 23</td>
<td>–</td>
<td>–</td>
<td>150</td>
<td>14.8</td>
<td>3.5</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>R270</td>
<td>5</td>
<td>438 ± 14</td>
<td>–</td>
<td>–</td>
<td>270</td>
<td>14.8</td>
<td>3.5</td>
<td>80</td>
<td>330</td>
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<tr>
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<td>250</td>
<td>14.8</td>
<td>3.5</td>
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<td>330</td>
</tr>
<tr>
<td>R230</td>
<td>5</td>
<td>437 ± 13</td>
<td>–</td>
<td>–</td>
<td>230</td>
<td>14.8</td>
<td>3.5</td>
<td>80</td>
<td>330</td>
</tr>
<tr>
<td>R200</td>
<td>5</td>
<td>435 ± 16</td>
<td>–</td>
<td>–</td>
<td>200</td>
<td>14.8</td>
<td>3.5</td>
<td>80</td>
<td>330</td>
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<tr>
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<td>10</td>
<td>434 ± 16</td>
<td>Bmim(Cl)</td>
<td>20</td>
<td>270</td>
<td>0</td>
<td>3.2</td>
<td>90</td>
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<td>435 ± 20</td>
<td>DBN(EtCO₂H)</td>
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<td>270</td>
<td>0</td>
<td>3.2</td>
<td>90</td>
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<td>DBN</td>
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<td>270TMG</td>
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<td>434 ± 15</td>
<td>TMG</td>
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<td>270</td>
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<td>3.2</td>
<td>90</td>
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<td>DBU</td>
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<td>270</td>
<td>0</td>
<td>3.2</td>
<td>90</td>
<td>240</td>
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<tr>
<td>250DBU</td>
<td>10</td>
<td>433 ± 20</td>
<td>DBU</td>
<td>20</td>
<td>250</td>
<td>0</td>
<td>3.2</td>
<td>120</td>
<td>240</td>
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<tr>
<td>230DBU</td>
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<td>434 ± 19</td>
<td>DBU</td>
<td>20</td>
<td>230</td>
<td>0</td>
<td>3.5</td>
<td>150</td>
<td>240</td>
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<tr>
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<td>432 ± 22</td>
<td>DBU</td>
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<td>200</td>
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<td>4.4</td>
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<td>240</td>
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<td>DBU</td>
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<td>250</td>
<td>0</td>
<td>3.2</td>
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<td>240</td>
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<tr>
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<td>439 ± 20</td>
<td>DBU</td>
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<td>250</td>
<td>0</td>
<td>3.2</td>
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<tr>
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<td>DBU</td>
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<td>250</td>
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<td>3.2</td>
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<tr>
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<td>434 ± 19</td>
<td>DBU</td>
<td>20</td>
<td>250</td>
<td>0</td>
<td>3.2</td>
<td>120</td>
<td>240</td>
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</tbody>
</table>

CE, Concentration in ethanol; T, press-platen temperature; P, densification pressure; t₁, time to reach target thickness; t₂, total time in press before cooling; specimen group naming; C, control; R, reference; numbers, densification temperature in °C; BMIM, pre-treated with Bmim(Cl); DBNIL, pre-treated with DBN(EtCO₂H); DBN, pre-treated with DBN; DBU, pre-treated with DBU; TMG, pre-treated with TMG; H, high concentration of chemical; L, low concentration of chemical; W, increased moisture content; N, no punctured holes to improve penetration of the chemical.
Preparation of chemicals: The specimens were treated with various ILs or organic superbases, diluted with ethanol to different concentrations (Table 1). The IL 1-butyl-3-methylimidazolium chloride [Bmim(Cl)], and the organic superbases 1,5-diazabicyclo(4.3.0)non-5-ene (DBN), 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) and 1,1,3,3-tetramethyl-guanidine (TMG) were purchased from Acros Organics, Geel, Belgium (purity: 98%). Another IL was made by mixing DBN with propionic acid in an equimolar ratio, resulting in DBN propionate [DBN(EtCO2H)].

Chemical pre-treatment: All specimen groups to be chemically treated were oven dried at 103°C to an MC of 0% prior to the pre-treatment. The chemical solutions were first applied with a pipette onto the tangential barkside-oriented wood surface to be densified. In order to keep the amount of solution consistent, the content of one pipette filling (3.5 g) was distributed over the surfaces of two specimens. Within 1 min, the solutions were completely soaked up by the wood. This procedure was repeated 3 more times for each specimen. In order to encourage the penetration of the chemicals into the wood, the surfaces were punctured with 3–4 mm deep holes with a diameter of about 0.8 mm and distance between the holes of 5 mm in the tangential direction and 10 mm in the longitudinal direction. This was done manually with a needle, which was marked with tape to ensure a constant depth of the holes. Only group 250DBU (Table 1) was left without holes. After the pre-treatment, the specimens were placed in an oven at a temperature of 60°C for 14 h to evaporate the ethanol. Omitting this step would lead to the destruction of the wood during the densification stage due to too high a steam pressure.

Densification process: The specimens were densified in the radial direction in a press with one of the platens heated and equipped with a water-cooling system. Two or three specimens were densified at the same time. For the first 10 s of the process, only a low pressure sufficient to maintain proper contact between the wood surfaces and the heated press platen was applied. The pressure was then increased to a level that would lead only to densification if the wood cells were sufficiently plasticised. The correct amount of pressure to achieve this behaviour was determined during a pre-study by calibrating the pressure levels for different densities of the raw material. Depending on the parameters and the treatment, the target thickness of 14.98 mm (set by metal stops in the press) was achieved after a time between 90 s and 240 s (Table 1). Regardless of the time taken to reach the target compression, the specimens were kept at the set temperature for a total of 240 s, after which the cooling system was started. The press was opened when the press platen temperature reached 60°C, and the SB was then measured (see section elastic SB), after which the specimens were kept in an oven at 60°C before the SR determinations were carried out (see section SR). No SR occurred during this stage.

Specimen grouping: Table 1 lists the specimen groups with their respective treatments and densification parameters. Group C150 is the reference group, densified with parameters similar to those commonly used in surface densification procedures. The purpose of groups R270-200 was to study the effect of thermal modification on the SB and SR and to separate it from the effect of the chemical pre-treatment. After being densified with the same parameters as group C150, these four groups were put back in the press for 240 s at temperatures between 270°C and 200°C, corresponding to the densification temperatures of the chemically treated specimens.

Elastic spring-back (SB): The SB was determined from measurements made with a digital calliper with a precision of ±0.03 mm (according to the manufacturer). SB is defined as:

\[
SB = \frac{B' - B}{B_0 - B} \tag{1}
\]

where \(B_0\) is the original dimension of the specimen in the densification direction before densification, \(B\) is the target dimension of the specimen after densification (in this case 14.98 mm) and \(B'\) is the actual dimension of the specimen after densification. The SB can thus vary between 0% and 100%, where 0% indicates no SB and 100% indicates total SB.

Set-recovery (SR): The SR measurements were carried out on specimens with dimensions of 20 mm \((L) \times 25 \text{ mm } (T) \times 15 \text{ mm } (R)\), cut from the densified specimens. Before the SR procedure the samples were kept in an oven at 60°C in order to prevent re-moistening. The specimens were measured with a digital calliper after one and two cycles of soaking in water for at least 14 h at room temperature, followed by oven-drying at 60°C for 24 h. The SR is defined as:

\[
SR = \frac{R'_c - R}{R_0 - R_c} \tag{2}
\]

where \(R_0\) is the oven-dry dimension of the specimen in the densification direction before densification, \(R\) is the dimension of the specimen after densification and \(R'_c\) is the dimension of the densified specimen after the wet-dry cycling. The SR can vary between 0% and 100%, where 0% indicates that there is no SR, i.e. that the compression-set is completely fixed, and 100% indicates that the recovery is total. After the first wet-dry cycle, the specimens exhibited cupping of the densified surface, and for this reason the average value of the maximum and minimum dimension over the surface of each specimen was used for \(R'_c\).

There was a problem in this way of calculating the SR because the initial, uncompressed oven-dry dimensions were not known for the specimens densified at an MC of 14.8% or 5.0%. In this case, the oven-dry dimensions of the specimens were assumed to be equal to the average dimensions of all the specimens densified at an MC of 0%. As the standard deviation in the dimensions of these specimens was only 0.07 mm, this assumption appears to be sufficiently accurate.

Brinell hardness (HB): The HB was measured in accordance with the standard EN 1534, but with several modifications (CEN 2010). A Zwick Roell ZwickiLine 2.5 TS universal testing machine equipped with a 2.5 kN load cell and a steel ball with a diameter \((D)\) of 10 mm was used. The force was increased at a rate of 4 kN per minute to a nominal force \((F)\) of 1 kN, which was held for 25 s before being released.

According to the standard, the HB is calculated from the diameter of the indentation in the specimen, but in this study the HB was calculated from the depth of the indentation. The reason for this modification of the test procedure was that it was difficult to measure the diameter of the indentation in wood. In contrast to steel or other metals, wood does not leave an indentation with a clear circular border because of its anisotropic properties. The depth of the indentation \((h)\) can, however, be measured with the hardness testing equipment with high accuracy and precision. The HB values in this study were used only for comparison between the test
groups. Niemz and Stübi (2000) and Laine et al. (2013a) previously implemented a similar approach. Thus, the HB is here defined as:

\[
HB(N \text{ mm}^{-2}) = \frac{F}{\pi D h}
\]

(3)

A total of 30 hardness measurements were made on each specimen group, 15 on the densified surface and 15 on the opposite, undensified surface as control measurements. The 30 measurements per group were distributed over five specimens with six measurements per specimen.

**Data analysis:** All the collected data were processed in Microsoft Excel, after which a principal component analysis (PCA) screening was done using the software package SIMCA provided by Umetrics (Umeå, Sweden). With the help of PCA, a multivariate data analysis method, it is possible to find correlations in large datasets that are difficult to detect with univariate data analysis methods.

**Results and discussion**

This study tested the effect of a pre-treatment with ILs or organic superbases on the elastic SB, SR and HB of surface-densified Scots pine.

**Elastic SB**

It has been reported that the SB of untreated surface-densified Scots pine is about 50% without a cooling stage after the densification stage (Neyes et al. 2017). With a cooling stage, the SB can be reduced to 10–15% (Laine et al. 2013b; Neyes et al. 2017), and this was confirmed in the present study by group C150, which had an average SB of 11%. For all other groups, the dimension of the specimen in the densification direction was, within the measurement accuracy, the same as the target compression, and the SB can thereby be considered negligible.

For untreated and surface-densified wood, Laine et al. (2013c) have reported a reduction in SB with increasing densification temperature, when the densification stage is followed by a cooling stage. In this case, however, the low degree of SB seems to be at least partly due to an effective plasticisation of the wood modified by the ILs or superbases, in combination with a very low deformation of the unmodified wood volume beneath the modified wood during the densification process.

**Set-recovery (SR)**

Figure 2 shows the average SR of the untreated specimen groups after two wet-dry cycles. For all the chemically treated groups, there was no significant difference in SR between the first and second wet-dry cycles, i.e. the SR did not increase after the first wet-dry cycle. For the untreated groups, there was a slight increase between the first and second wet-dry cycle.

The reduction in SR can be attributed both to the press-platen temperature and to the chemical treatment, but the SR of the R200-270 groups compared to that of the modified wood at the corresponding temperatures suggests that the effect of heat, i.e. thermal degradation, was much less than the effect of the chemical treatment. It was possible with all the tested chemicals to reduce the SR to 20% or even lower. For the DBU treatment, an increase in press-platen temperature (200DBU, 230DBU, 250DBU, 270DBU),

![Figure 2: Overview of the SR.](image-url)

Dark grey bars are untreated specimen groups and light grey bars are chemically treated specimen groups according to Table 1. The error bars show ±1 standard deviation.
or an increase in chemical concentration (250DBU, 250LDBU, 250HDBU) reduced the SR. An increase in MC of the specimen before densification (250WDBU) or the absence of punctured holes in the surface to increase the penetration of chemicals (250NDBU) increased the SR. It was not possible to see any influence on the SR due to the variation in annual ring orientation in the cross-sections of the specimens.

Figure 3 shows that the treatment with Bmim(Cl) or DBN(EtCO₂H), followed by densification at 270°C led to an almost black surface, whereas the superbase treatment resulted in a dark brown colour. This indicates that there are different mechanisms underlying the two types of chemical treatment. Our hypothesis of the formation of an in-situ IL after treatment with a superbase, may not be correct, and instead there may be a different mechanism.

Figure 4 shows the relationship between the average SR and the densification temperature. The light curve (squares) corresponds to specimens without chemical treatment (C150 and R200-270 groups), and the dark curve to the 270-200DBU groups. The reduction in SR increases with increasing temperature and, in the case of the specimens treated with DBU, the relationship appears to be almost linear.

Figure 5 (untreated specimens) and Figure 6 (specimens treated with DBU) show the colour changes in the specimens in relation to the pressing temperature. With increasing pressing temperature, the untreated specimens gradually became darker, but there were only small differences in colour between 200DBU and 230DBU, and between 250DBU and 270DBU, with a relatively large difference between 230DBU and 250DBU. However, there is no correlation between this observation and the reduction in SR. We suggest that even higher temperatures should be investigated and also lower temperatures in the case of the chemically treated specimens, in order to obtain a more complete picture of the relationship between the SR of the chemically modified specimens and the temperature.

A comparison of the 250DBU, 250HDBU and 250LDBU groups with, respectively, 20%, 30%, and 10% concentration of DBU in ethanol, indicates that an increase in concentration leads to a reduction in SR, but further studies are needed to determine the precise nature of this relationship.

The SR of group 250WDBU (initial MC = 5%) suggests that moisture is detrimental to the efficacy of the pre-treatment with DBU, as was expected on the basis of published studies on the dissolution of cellulose in ILs (Mäki-Arvela et al. 2010). Zavrel et al. (2009) reported that water molecules create hydrodynamic shells around the IL molecules and that this inhibits direct interactions between the IL and the cellulose. Nevertheless, the decrease in SR was substantial with a reduction from 81% to only 37%.

The surface of the specimens of almost all groups was punctured with small holes in order to facilitate penetration of the chemical solutions into the wood. Surprisingly, the SR of group 250NDBU without holes was only slightly higher than the SR of group 250DBU – which was otherwise treated and densified in the same way. Depending on possible applications of surface-densified wood and their requirements, the puncturing of the surface may thus not be necessary.

Most groups that were exposed to a temperature of at least 200°C show a high intra-group variation in SR (Figure 2), primarily due to outliers with a much higher SR than the other specimens. Based on colour changes in the wood surface caused by the high press-platen temperature, we suspect that an uneven temperature distribution within the press platen was responsible for this. Even though it was easier to notice in reality, it can be seen in Figures 3–6 that the densified surfaces are slightly darker at one end than at the other (the darker ends are facing the viewer). A PCA screening did not show a systematic relation between the uptake of the chemical solutions and the resulting SR.

Brinell hardness (HB)

Figure 7 shows the HB of undensified and densified specimen surfaces. There was no significant difference in the average HB of the undensified surfaces. The densification process resulted in an increase in the hardness of the densified surfaces. Densification without chemical treatment (groups C150 and R270-200) resulted in a two-fold increase in hardness from 13.4 N mm⁻² to 26.2 N mm⁻², and there
were no differences between the groups. This increase in hardness is in line with results from previous studies (Gong et al. 2010; Laine et al. 2013a; Neyses et al. 2017).

The chemically treated specimens showed a increase in HB after densification by a factor 2.7, i.e. from 12.9 N mm\(^{-2}\) to 34.4 N mm\(^{-2}\), which is a significant increase over that of the untreated specimens. There were no significant differences in HB between the different chemically treated groups.

It appears that the reason for the higher HB of the chemically treated specimens is a more thorough and targeted plasticisation than that of the untreated specimens. Figure 8a shows that, for the chemically treated specimens, the region with the highest level of densification is located at the very surface of the specimen, and in this respect the specimen shown is representative of all the chemically treated specimens. Directly beneath the surface there appears to be a layer approximately 1.2 mm in thickness with a three-fold increase in density. The density then gradually decreases towards the core of the specimen. In Figure 8b, which shows an untreated and densified specimen, it appears that the density peak of these specimens is not located at the very surface, but is somewhat below the surface. This could be due to the heated press platen drying the specimen surface, and thus inhibiting the plasticisation of this region. For the chemically treated specimens, this phenomenon is not relevant because their plasticisation does not rely on moisture. Another observation supporting our hypothesis is the bulging of the side surfaces in the densified area (Figure 8): the chemically treated specimens bulge out at the very surface, while the untreated ones bulge out slightly below the surface.

As the HB method is a volume-based measurement, it appears not to be representative of the perceived surface hardness of the specimens. In theory, the observed three-fold increase in density should result in a threefold increase in hardness, which was not confirmed.
by the calculated HB values. Perhaps another type of hardness or scratch resistance measurement method would provide more meaningful results – at least, with respect to the planned use of the densified wood. For this reason, we think it could be worthwhile to study the relationship between different hardness and scratch resistance measurement methods and surface-densified wood treated in different ways. This is especially important with regard to possible applications of surface-densified wood products.

The chemically treated specimens showed a higher intra- and inter-group variation (Figure 7) than the untreated specimens. We can only speculate on the reasons for this variation. A PCA screening revealed a positive correlation between weight gain due to the chemical treatment and HB. The weight gain varied significantly between the specimen groups and was particularly high for the 270DBNIL, 250HDBU and 250WDBU groups. Unfortunately, the data are not strong enough to explain intra-group variations in HB. The apparently uneven temperature of the heated press platen does not explain this variation either, as there was no correlation between press-platen temperature and HB.

**Conclusion**

The ILs Bmim(Cl), and DBN(EtCO₂H) and the organic superbases DBN, DBU and TMG have been shown to be strong plasticisers, which can reduce or even eliminate the elastic and SR components of deformation of surface-densified wood. The elastic SB was eliminated, and the SR after two wet/dry cycles in water was reduced to as low a value as 10% (100% means full recovery of the deformation). The superbases have an effect more or less equal to that of the ILs, but at this point it is not clear if treatment with superbases is due to the same mechanism as the treatment with ILs.

The chemical treatment resulted in a HB 1.3 times higher than that of the untreated and densified specimens, and in a 2.7 times increase relative to that of the

*Figure 7:* Average HB before (left-handed bar) and after (right-handed bar) densification. The error bars show ±1 standard deviation.

*Figure 8:* Densification close to the surface of (a) a chemically treated specimen and (b) an untreated specimen. The bars show the distance between annual rings.
undensified surface. This means that the HB of the chemically treated Scots pine approaches a level similar to that of oak, a wood species widely used for high-quality wooden flooring.

The process described here can be seen as a precursor to the development of a continuous open-system surface densification process. A closed system is not necessary and both the chemical treatment and the densification have the potential to be performed in a continuous manner. Further studies are however needed to optimise the treatment.

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