Enhancement of Phenol Formaldehyde Adhesive with Crystalline Nano Cellulose

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Abstract
The wood industries to this day use almost exclusively petroleum derived adhesives that are based mainly on the reaction of formaldehyde with urea, melamine or phenol. These adhesives have low cost and good adjustable properties which makes it hard for bio-based alternatives to compete. Phenol formaldehyde (PF), as an example of a synthetic adhesive, has been in use for over 100 years. In some parts of the world, legislation around formaldehyde is changing, and there is an increasingly voluntary awareness about the toxicity and unsustainability of formaldehyde. Industries realize that raw materials from oil is unsustainable. The latter is currently a driving factor behind research on alternatives to amino based adhesives. Also, consumer interest in healthy and sustainable products, such as emitting less formaldehyde indoors, increases the need for bio based adhesives.
Cellulose contained in plant cell walls is a renewable, abundant and nontoxic resource. During the last decades, many innovations have been achieved around cellulose and this trend does not seem to be slowing down. Cellulose shows excellent mechanical properties, high strength, high elastic modulus as well as having a low density.
Research about cellulose reinforced adhesives has been increased the last years. This thesis studied the enhancement of phenol formaldehyde adhesive with Crystalline Nano Cellulose (CNC) at 5wt% and 10wt% loading levels for producing plywood boards. Indecisive results when using CNC higher than 3wt%, especially with PF resin, have been reported by other authors.
In this thesis, European standards were applied. EN 314 was applied to test the panels shear strength. Three (3) treatment classes were selected, indoor room condition as well as pre-treatments 5.1.1 and 5.1.3. Other properties measured were modulus of elasticity, thickness swelling, formaldehyde emissions.
Results showed a shear strength increase for all pre-treatment classes. 10wt% CNC mixture with phenol formaldehyde in water bath, pre-treatment (5.1.1) for 24h showed the highest increase in shear strength (+73,9%). The 10 wt% CNC mixture panels also showed the highest wood fibre failure of all panel types produced. A decrease in MOE has been observed with 10 wt% CNC compared to the 5 wt% CNC panels. Formaldehyde emissions tests were inconclusive, but since less PF was used, there was a
general reduction in emissions. The 5 wt% CNC panels were
superior in terms of modulus of elasticity and swelling and also
showed improved shear strength.
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Introduction

1.1 Wood adhesives: present-day situation

The wood industries use almost exclusively petroleum derived adhesives to this day. These adhesives have low cost and good adjustable properties which makes it hard for bio-based alternatives to compete. A further increase in use of plants and wood would contribute to lower carbon dioxide emissions and to the establishment of a sustainable society based on renewable biomass resources (Hemmilä et al. 2017). The developments during the recent years show a trend towards successfully decreasing production cost and an increasing demand for high performance bio-based materials within nano composites, especially from plant cellulose. Phenol formaldehyde (PF) is one of these petroleum derived adhesives that performs well with respect to adhesive strength, water resistance, heat resistance, wear resistance, chemical stability. It also has a low cost. Although PF resin is moisture resistant and has acceptable strength properties, its mechanical properties can be further improved by reinforcement (Stoeckel, Konnerth, and Gindl-Altmutter 2013, Lei et al. 2010). Reducing adhesive consumption by combining it with other materials to a single adhesive system have been proved challenging, but if successful, will have the potential to increase bonding performance and reduce costs. Akira Isogai (2013) refer to micro fibrillated cellulose (MFC) as preferential and beneficial in terms of production process, energy consumption, environmental and safety issues, and related to pulp and paper industry. MFC also has the potential to decrease the use of formaldehyde.

1.2 Nano cellulose

Micro fibrillated cellulose (MFC) has received lately an increasingly higher degree of attention from both industries and research institutions since it is a promising bio-based material that can be converted to a wide spectrum of applications. Some areas are cellulose sheets, films, hydrogels, foams, aerogels with fibril network structures and reinforcement in composites. Matrix nanocomposites in most cases show an explicitly high mechanical strength and ductility despite being lightweight; they also show thermal stability and act as a gas barrier (Isogai 2013).
MFC has been known for a long time but have since discovery evolved in different directions with slightly different properties, typically MFC and cellulose nano whiskers (CNF) are produced mechanically using wood pulp. Crystalline nano cellulose (CNC) production on the other hand involves an additional acid hydrolysis step where non-crystalline cellulose is removed, resulting in highly crystalline cellulose whiskers. Due to the many and various names of MFC, from this point in the text, the meaning of it should be considered a fibrillated cellulose of either micro or nano sized particles unless otherwise specified. This is because the name of the cellulose differs depending on method of production and what type pretreatments that is used (Diop et al. 2017b). The term micro/nano cellulose comprises some variants of nanoscale cellulosic objects with typical diameters between 2 and 50 nanometer and length in the micrometer range. Usually MFC is being produced in an aqueous state with high water content with filtration being the most effective way to reduce or remove water (Isogai 2013). Absorption onto the large surface area that nano cellulose presents is related to high localized intermolecular forces, enabling very high water content. With high contact area, moisture will also be blocked by the cellulose matrix, both during absorption and desorption. This property can potentially also lock in formaldehyde. Once the nano cellulose is dried it will effectively form a barrier from moisture or delay adsorption considerably (Isogai 2013, Veigel et al. 2012). Production of MFC is usually done mechanically with a few types of processes currently being used: mechanical refining and high-pressure homogenization but also cryo-crushing and grinding. Common for all processes has been a high cost of production. A major obstacle with MFC was for a long time the high energy consumption connected to the mechanical disintegration of the fibers into nanofibers, often involving several passes through the disintegration device (Hellström et al. 2014). However by combining the mechanical treatment with pretreatments such as alkaline pretreatment, oxidative pretreatment, enzymatic pretreatment, and in some cases combined pretreatments, research spanning over decades has decreased energy consumption significantly and now there is some initial commercial production of MFC (Hemmilä et al. 2017).

Celluforce, Canada has had pilot production since 2012 with 1 ton/day of crystalline nano cellulose (CNC) for high tech fields, either as spray dried powder or in aqueous suspensions. CNCs
availability has been further increased by a production site in Norway, Borregaard. Therefore, a potential high-volume application such as wood adhesive modification is possible to be achieved in the near future. University of Maine has recently developed a method for production of ligno cellulose nano fibrils (LCNF) with a very low production cost, without changing temperature and pressure (Diop et al. 2017a, 2017b).

1.3 Previous research on uses of nano cellulose (MFC, CNC) in wood adhesives

There have been several studies aimed at improving the mechanical properties of wood adhesives by reinforcing the adhesives with nano particles (Atta-Obeng 2011, Veigel et al. 2011, Kaboorani et al. 2012, Salari et al. 2012, Veigel et al. 2012, Wei et al. 2017). Veigel et al. (2011) suggested that the optimum filler content is largely dependent on the adhesive and the type of cellulose filler used, but there are too few studies on this subject. Further, there are suggestions that the presence of MFC has a certain effect on cure kinetics of the adhesive. All studies on the topic reports of higher viscosity and higher curing time at a few wt% MFC. Previous studies have shown a general increase in strength when MFC is added to OSB’s and various particle boards, with both urea formaldehyde (UF) and phenol formaldehyde (PF) adhesives. They have also shown reduced shrinkage, lowered swelling and lowered emissions of formaldehyde. Kaboorani et al. (2012) proved that CNC improves properties by reinforcing the glue line strength, preventing PF resin from penetrating into wood pores and increasing resin coverage on the wood surface. This was later confirmed by Liu et al. (2014) and Mahrdt et al. (2015). Liu et al. (2014) also concluded that MFC migrate with resin into the cell lumen far from the glue line. The curing with PF and MFC mixes has shown a nonlinear heat reaction and there has been a suggested optimal of 3wt% added MFC (Atta-Obeng 2011). But Veigel et al (2012) suggests a rapid increase in strength between 3-6wt% and a minor increase between 6-10wt% MFC. Veigel et al (2012) also reports that particleboard strength decreased at 3wt% MFC. Heon Kwon et al (2015) showed a decrease in strength at 3wt% as well as at 5wt%. It should be mentioned that part of the problem with decreasing strength in studies could be attributed to known problems such as
insufficient blending. Successful studies have used high speed rotational blending devices such as Ultra thorax or have blended the mix for a longer period. Borregaard, Norway have a guide on how to successfully blend their product Exilva. Atta Obeng’s (2013) lap shear test revealed an increase in strength with the addition of CNF to PF adhesive. But the particleboards produced showed inferior mechanical properties in static bending tests. They also had higher thickness swelling than boards bonded with pure PF. Other studies show a general decrease in swelling using MFC. These changes have been attributed to less swelling and shrinking after hot-pressing. The CNC restricts spring back of the boards after released compression and cooling. Atta Obeng’s (2013) suggests that failure can occur with spring back effects resulting in debonding in either wood or adhesive. This in turn suggests high internal stress resulting in a decreased board performance.

Summing up the studies using urea formaldehyde (UF) while making oriented strand boards (OSB) or particle boards the result is generally an increase in strength, also at higher content MFC. But when using PF resin, the results at higher content are inconclusive. Most reports indicate that 3wt% or lower content MFC increase general strength of the adhesive. However, above 3%wt for especially PF resins, the mechanical properties have a higher degree of variance. This controversy indicates the need of further studies.

In common for all studies are a relatively fast pressing process with high temperature and low pressing time. This is because the studies have been performed towards using the same pressing time as standard for respective resin manufacturer, thereby modifying the process of pressing as little as possible. There is a limited amount of studies on manufacturing plywood boards using MFC.
Aim and Objectives
Due to the literature study above, the aim of this thesis is focused on what is needed to make the process work and to create viable panels. This thesis will look at producing plywood panels with over the top respect to the adhesive mix curing time, with low pressing heat and high pressing time to fully study possible results of CNC mixed with PF adhesive. The following points were determined as specific objectives:

- Establishing the adhesive mix curing time comparison at different loading levels of wt% added CNC.

- Determining viscosity for the adhesive CNC mixes.

- Establishing an acceptable heat and pressing time with consideration to curing time.

- Producing plywood boards with 0, 5, and 10 wt% added CNC to the adhesive.

- Determining shear strength differences and modulus of elasticity on the boards with consideration to current standards and pre-treatments.

- Determining thickness and swelling differences between CNC adhesive mixes.

- Measuring formaldehyde emissions for the different panels.
Materials and Methods

All experiments were performed at Georg August Universität, Göttingen, Germany.

3.1 Preparation and characterization of adhesive mixtures

For the preparation of 50×50 cm plywood boards, a PF resin commonly used in the board industry (Prefere 15J173, Prefere Resins, Germany GmbH) was used. The crystalline nano cellulose (CNC) came from Borregaard, Norway. Both adhesive and cellulose water content was controlled. The resin had a 45wt% solid content while the CNC from Borregaard was delivered as a 10wt% solid content solution in water. Beech veneers produced in Germany of medium quality were selected as the wood component.

Several factors were explored to determine optimal conditions for successful pressing.

Glue composition – The CNC with 10 wt% due to the high viscosity was in paste form and did not act as a liquid. Adding the CNC to the adhesive increased the water content of the mix. The minimum water determined by the water content with the highest CNC content, in this case, with 10wt% CNC in it. Lowering CNC’s water content could be unreliable due to the CNC starting to act as a solid instead of a paste. Machinery to break down CNC and mix a less aqueous version of CNC was not available. To get the same water content in all the adhesive mixtures and comparative results, samples with less than 10 wt% CNC content had to have water added to the formula.

Potassium carbonate, a known inexpensive hardener with easy accessibility was chosen and compared trough gelling time with “Prefere Resins” commercial hardener (also contained a filler.) for PF adhesives (Mahrdt et al. 2016).

Gel timer from Celnorm H.Saur was used to determine gel time of different combinations and amounts of CNC (0 wt%, 2.5 wt%, 5 wt%, 7.5 wt%, 10 wt%). 15 g of resin was prepared for each test, and the temperature of the device was set to 100°C. The results were then examined to determine pressing time requirements and temperature requirements. This was done by comparing the
different adhesive mixtures qualities with each other through
gelling time tests. 5g of resin mix from each combination was tested using a
“Viscosimeter HAAKE Visco tester 7L”. Different shear rates
ranging from 5 to 50 s\(^{-1}\) were tested using the standard L4 spindle.
To achieve homogenous adhesive distribution all adhesives
mixtures where mixed for 20 minutes at 2000 rpm using a IKA
EUROSTAR 60.

3.2 Plywood preparation

The veneers of medium quality were cut into 50x50 cm sections.
They were knot free but had a slight variance in thickness and
averaged between 3 - 4 mm thick. The adhesive with CNC and
hardener was mixed for 20 minutes at 2000 rpm using a IKA
EUROSTAR 60 and put on a scale. Thereafter 50 grams was
applied onto each veneer by using a roller, thereby following the
high end of Prefere Resins pressing norm (150-200g/m\(^2\)).
However, 200g of adhesive mixture per square meter results in
actual resin applied amounting lower end of the spectrum of
preference at 150 g/m\(^2\). The veneers were then stacked so that the
grains where perpendicular to the previous veneer. A total of 5
veneers per plywood panel were used. Between the mid layer of
veneers, a temperature gauge (Temperaturegauge GMH 3250,
Digitalthermometer, Eresinger Electronics) was put to measure
the core temperature of the stack during pressing. They were then
pressed at 150N/cm\(^2\) at 145°C using a Lap 40 press (Gottfried
Joos Maschinenfabrik, GmbH & Co, KG). When the core of the
panel had reached 130°C, the panels were left 10 more minutes in
the press. Total pressing time equaled to an average of 40
minutes. When the panels were taken out they were put in a cold
press for cooling down. In total 12 plywood panels where
produced, 3 with 0% CNC with added water, 3 with 5% CNC
with added water, 3 with 10% CNC and no added water. Three (3)
panels with 0% CNC and no added water were also prepared.
They were produced after the 3 other categories as control panels
in order as a way to understand how the adhesive properties might
change when a commercial filler is not present and added water is
introduced. The reason for preparing them was the high failure
rate of pretreatments for shear strength tests in panels without
CNC. More details on this issue can be found in chapter 4.2. The
panels where then stored for 2 weeks in room condition until test sample cutting.

3.3 Determination of plywood properties

The density and thickness swelling properties of the plywood panels was determined according to the European standards EN 323 and EN 317. A total of 4 samples per panel where cut out. They were then weighted, measured in their dimensions and submerged in a water bath and re-measured every 24 hours until 72 hours was reached.

Internal bond strength and 3-point bending test was performed with a Zwick/Roell Zmart PRO universal testing machine equipped with a 5KN load cell and a maximum displacement of 50 mm. The test speed was set to 10 mm/min⁻¹. 10 specimens per panel for shear strength testing was cut out and tested according to EN 314 standards. The 3 pretreatments used according to the standard were:

- 5.1: Stored in climate-controlled room (20°C)
- 5.1.1: Immersion in 20°C water for 24h
- 5.1.3: Immersion in boiling water for 4h, then drying in ventilated drying oven for 20h at 60°C, then immersion in boiling water for 4h, followed by cooling in water at 20°C for 1h.

In pretreatment 5.1.3: 4 samples were tested from each panel, the other 2 categories had 3 test samples cut out. For the 3-point bending test, 2 test specimens per panel were cut out, totaling 6 test specimens for each category. The size of each test specimen was 30x4 cm. They were then tested following the EN 310 standards with 20 cm spanning between supports.

Two (2) test specimens per panel were cut out for formaldehyde emissions’ testing by following the gas-analysis method described in EN 717 standards. The exception in testing was that the time the test pieces spent sealed in storage was long. Total length in storage was 3 weeks (21 days). A total of 6 tests in each plywood category and consequently in each adhesive mix was performed. Testing was performed with the gas analyzer chamber Formaldehyde test GreCon GA 5000). The extracted emissions were further processed in a spectrum analysis apparatus (Analytic jena specord 205).
3.4 *Table of adhesive composition*

A table of composition was created after investigating how much water that had to be added to each mix. Thereby the rest of the components of the adhesive mix could be calculated.
<table>
<thead>
<tr>
<th>CNC</th>
<th>Glue wt (g)</th>
<th>CNC wt (g)</th>
<th>Glue wc (g)</th>
<th>CNC wc (g)</th>
<th>Added water (g)</th>
<th>Wc% tot</th>
<th>Tot (g)</th>
<th>Potash min (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>5</td>
<td>0</td>
<td>6.11</td>
<td>0</td>
<td>3.89</td>
<td>66.66%</td>
<td>15g</td>
<td>0.125</td>
</tr>
<tr>
<td>2.50%</td>
<td>4.875</td>
<td>0.125</td>
<td>5.96</td>
<td>1.125</td>
<td>2.915</td>
<td>66.66%</td>
<td>15g</td>
<td>0.122</td>
</tr>
<tr>
<td>5%</td>
<td>4.75</td>
<td>0.25</td>
<td>5.81</td>
<td>2.25</td>
<td>1.94</td>
<td>66.66%</td>
<td>15g</td>
<td>0.119</td>
</tr>
<tr>
<td>7.50%</td>
<td>4.625</td>
<td>0.375</td>
<td>5.65</td>
<td>3.375</td>
<td>0.975</td>
<td>66.66%</td>
<td>15g</td>
<td>0.116</td>
</tr>
<tr>
<td>10%</td>
<td>4.5</td>
<td>0.5</td>
<td>5.5</td>
<td>4.5</td>
<td>0</td>
<td>66.66%</td>
<td>15g</td>
<td>0.113</td>
</tr>
</tbody>
</table>

Table 1: Composition of adhesive mixtures
Results & Discussion

4.1 Resin composition and pressing time

When the gelling test with just potassium carbonate as a hardener was compared to the test without hardener it showed a reduction in curing time of just under 1/3 h. The tests showed a slight reduction of efficiency with only potassium carbonate as a hardener as oppose to the commercial hardener. The gelling time of the different samples of CNC showed a substantial increase in curing time with added CNC. The 10% CNC showed a lower gelling time then 7,5% CNC, but this is attributed to the higher viscosity of this glue mix. The CNC content was so high that when water evaporated from the mix, the test stopped prematurely. Unfortunately, there is very little literature to compare gel time with due to different nano cellulose categories and adhesives. However, all literature conclude that there is a high increase gel time with just a few wt% nano cellulose added. Veigel (2012) used UF resin and had double gel time with just 3% added CNF. The probable value for the 10% CNC gelling test can be estimated by using the lower content sample tests.

Table 2: Gelling time average at 100°C

<table>
<thead>
<tr>
<th>Tests per category = 2</th>
<th>Resin No Hardener</th>
<th>Prefere Resin Commercial Hardener</th>
<th>Resin with potassium carbonate</th>
<th>Resin + 2,5wt% CNC With Potash</th>
<th>Resin + 5wt% CNC With Potash</th>
<th>Resin + 7,5wt% CNC With potash</th>
<th>Resin + 10wt% CNC With potash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelling Time Average</td>
<td>1h 33m 58s</td>
<td>58m 14s</td>
<td>1h 6m 8s</td>
<td>1h 21m 38s</td>
<td>1h 38m 7s</td>
<td>2h 4m 40s</td>
<td>1h 51m 34s</td>
</tr>
</tbody>
</table>

From table 2, it was concluded that the pressing time for the boards at low temperature (140°C) and 10 wt% CNC should slightly exceed twice the pressing time of the control adhesive. However, an increase in temperature makes water evaporate at a greater speed, thus, higher temperature could enable a lot faster curing time (Isogai 2013). The temperature and pressing time used for pressing is in this case purely a way of ensuring successful panel production. A commercial production of plywood will have to be optimized with respect to process factors and profitability. With higher temperatures during pressing, the increased pressing time that CNC addition is responsible for will
also be greatly reduced. The viscosity of the resin mix increased substantially with increasing CNC, unfortunately results from these resin mixes could not be measured with the current viscometer. The CNC showed ever changing readings and the viscometer could not keep up. For future viscosity tests, spindle-based machinery should be avoided. However, it should be mentioned that viscosity could be further reduced with low molecular weight PF resins.

4.2 Shear strength tests results

The average shear strength value for test samples stored indoors (EN 314, 5.1) was significantly increased (ANOVA, a = 0.05) for both the 5 wt% CNC (+21.7% increase) and the 10 wt% CNC (+62.3% increase) content (Figure 1). The results were also proven to be statisticly significant (Table 3). However, an increased shear strength spread can be observed with the highest content samples. This spread could be attributed to the method of applying the resin mix, which was done with a roller, but this is purely a speculation. After the 24 hour waterbath, pretreatment 5.11, (Figure 2) the strength gain average was greatly increased but with decreasing consistency for the 10 wt% CNC samples. The average shear strength gain was +32.6% for 5wt% CNC samples and +73.9% for the 10wt% CNC samples. In pretreatment 5.11 and 5.13 (Figure 3), the spread of values combined with fewer control samples resulted in no significant differences between the categories (Table 4 & 5, ANOVA, a = 0.05). It should also be noted that the control samples without CNC numbered only 3 for pretreatment 5.1.1. It was concluded that the adhesive without CNC did not perform well in water pretreatments without a filler present. This was concluded by creating 3 new boards without adding water. The 3 boards without water addition was subjected to the same pretreatment with the same amount of failed samples. The average shear strength gain between 5wt% CNC and 10wt% CNC was +31.1% (EN 314, 5.11), thus the boards with CNC performed very well after water treatments.

The pretreatment for outdoor use (Figure 3) is a very hard pretreatment that is meant to simulate long-term stress. Therefore, none of the control samples was intact while the CNC samples seemed to pass the test. Strength gain between the 5wt% CNC and
10wt% CNC was +19.9%, and that implies that the CNC boards can be used outdoors. It was thus concluded that CNC is a viable filler for this purpose.

The wood failure (Figure 5) for the filler-free samples was quite low with an average below 10%. With 5 wt% CNC it was drastically increased and yet it was even better with 10 wt%. The most demanding pretreatment for both the wood and the resin is pretreatment 5.1.3. Even so, the 10wt% CNC-based panels showed a greatly improved wood failure than in the other categories. In all the pretreatment categories there is a significant increase in wood failure with increasing CNC content. This suggests a stronger glueline bond, just as previous studies have suggested (Isogai 2013).
Figure 1: Shear strength for pretreatment 5.1, indoor conditions. PF-glued and CNC reinforced plywood with categories of 0, 5, 10% (wt) CNC. Statistical significant differences are marked with different letters between the plywood categories (A & B).

Table 3: Analysis of pretreatment 5.1. Statistical significant differences between plywood boards were discovered (ANOVA, a = 0.05).

<table>
<thead>
<tr>
<th>5.1</th>
<th>N Analysis</th>
<th>N Missing</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>SE of Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>9</td>
<td>0</td>
<td>2.96</td>
<td>0.53</td>
<td>0.18</td>
</tr>
<tr>
<td>5%</td>
<td>7</td>
<td>2</td>
<td>3.6</td>
<td>0.46</td>
<td>0.17</td>
</tr>
<tr>
<td>10%</td>
<td>9</td>
<td>0</td>
<td>4.85</td>
<td>1.17</td>
<td>0.39</td>
</tr>
</tbody>
</table>

DF | Sum of Squares | Mean Square | F Value | Prob>F |
Model | 2 | 16.62 | 8.31 | 12.61 | 2.24E-4 |
Error | 22 | 14.49 | 0.66 | 31.11 | |
Total | 24 | 31.11 |       |       |        |
Figure 2: Shear strength, pretreatment 5.1.1, immersion in 20c water for 24h. PF-glued and CNC reinforced plywood with categories of 0, 5, 10% (wt) CNC.

Table 4: Analysis of pretreatment 5.1.1. No significant difference between categories (ANOVA, $a = 0.05$).

<table>
<thead>
<tr>
<th>5.1.1</th>
<th>N Analysis</th>
<th>N Missing</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>SE of Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>3</td>
<td>7</td>
<td>1.28</td>
<td>0.22</td>
<td>0.13</td>
</tr>
<tr>
<td>5%</td>
<td>10</td>
<td>0</td>
<td>1.7</td>
<td>0.37</td>
<td>0.12</td>
</tr>
<tr>
<td>10%</td>
<td>9</td>
<td>1</td>
<td>2.23</td>
<td>0.91</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>2</td>
<td>2.48</td>
<td>1.24</td>
<td>2.92</td>
</tr>
<tr>
<td>Error</td>
<td>19</td>
<td>8.05</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>Total</td>
<td>21</td>
<td>10.53</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3: Shear strength, pretreatment 5.1, immersion in boiling water for 4h, then drying in ventilated drying oven for 20h at 60°C, then immersion in boiling water for 4h, followed by cooling in water at 20°C for 1h. PF-glued and CNC reinforced plywood with categories of 0, 5, 10% (wt) CNC.

Table 5: Analysis of pretreatment 5.1.3. No significant difference between categories (ANOVA, a = 0.05).

<table>
<thead>
<tr>
<th>5.1.3</th>
<th>N Analysis</th>
<th>N Missing</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>SE of Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>10</td>
<td>1</td>
<td>1.41</td>
<td>0.59</td>
<td>0.19</td>
</tr>
<tr>
<td>10%</td>
<td>11</td>
<td>0</td>
<td>1.7</td>
<td>0.46</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>DF</td>
<td>Sum of Squares</td>
<td>Mean Square</td>
<td>F Value</td>
<td>Prob&gt;F</td>
</tr>
<tr>
<td>Model</td>
<td>1</td>
<td>0.44</td>
<td>0.44</td>
<td>1.58</td>
<td>0.22</td>
</tr>
<tr>
<td>Error</td>
<td>19</td>
<td>5.24</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>20</td>
<td>5.67</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4: Modulus of elasticity from 3 point bending test.

Table 6: Analysis of 3 point bending. No significant difference between categories. (ANOVA, \( a = 0.05 \)).

<table>
<thead>
<tr>
<th>3 point bending</th>
<th>N Analysis</th>
<th>N Missing</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>SE of Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>11</td>
<td>2</td>
<td>9,79E3</td>
<td>861,27</td>
<td>259,68</td>
</tr>
<tr>
<td>5%</td>
<td>12</td>
<td>1</td>
<td>1,04E4</td>
<td>597,96</td>
<td>172,62</td>
</tr>
<tr>
<td>10%</td>
<td>13</td>
<td>0</td>
<td>9,94E3</td>
<td>525,06</td>
<td>145,63</td>
</tr>
</tbody>
</table>

| DF | Sum of Squares Mean Square F Value Prob>F |
|----|-----------------------------------------|-----------------|---------|------------------|----------|
| Model | 2 | 2,12E6 | 1,06E6 | 2,38 | 0,11 |
| Error | 33 | 1,47E7 | 4,44E5 |       |       |
| Total | 35 | 1,68E7 |         |       |       |
In Figure 4, it is shown that 5 wt% CNC content increased the modulus of elasticity with +5.9%. Surprisinglly the 3-point bending test suggests a decrease in modulus of elasticity between the 5 wt% CNC samples and the 10 wt% CNC samples at -1.5%, however no statistic difference between categories was found. Not a single one of the samples failed in the glueline, however the fact that there is a reduction in strength between the 5 wt% and 10 wt% CNC suggests that the higher content of CNC in the glueline could result in a rolling shear stress with local points reciving the highest stress and thus breaks, then together with springback effect, reduces strength back towards the original resin.(Atta-Obeng 2011). Very High content of CNC could cause brittle bonds, but there is no litterature on this. It should be pointed out that the 10 wt% CNC samples still had a higher strength than the control samples.
4.3 Thickness swelling

As shown in figure 6, the increase in CNC content reduced swelling and mass increase. Loading of 5 wt% CNC decreased thickness with -4.8% and 10 wt% CNC decreased thickness with -4.1%. Mass deceased -4.9% with 5 wt% CNC compared with the reduction of -3.7% within the 10 wt% CNC panels. However, these categories were not proven statistically different and could therefore be considers random variation (Table 7 & 8). The differences could suggest that there is an optimum amount of CNC when it comes to reducing swelling and water uptake, and it is likely related to the reduction of MOE in Figure 5. But the differences are too small to support this. And again there is no studies or literature on the topic.

![Figure 5: Average thickness swelling and mass increase (72h) of PF-glued and CNC reinforced plywood with categories of 0, 5, 10% (wt) CNC.](image-url)
### Mass Analysis

<table>
<thead>
<tr>
<th>Treatments</th>
<th>0% wt CNC</th>
<th>5% wt CNC</th>
<th>10% wt CNC</th>
<th>4</th>
<th>5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>78</td>
<td>80</td>
<td>80</td>
<td></td>
<td></td>
<td>238</td>
</tr>
<tr>
<td>$\sum X$</td>
<td>13582</td>
<td>20136</td>
<td>18759</td>
<td></td>
<td></td>
<td>52477</td>
</tr>
<tr>
<td>Mean</td>
<td>174.1282</td>
<td>251.7</td>
<td>234.4875</td>
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<td>220.492</td>
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<tr>
<td>$\sum X^2$</td>
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<td>12699094</td>
<td>11152961</td>
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<td></td>
<td>30997601</td>
</tr>
<tr>
<td>Std.Dev.</td>
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<td>310.7945</td>
<td>292.3976</td>
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<td></td>
<td>286.3038</td>
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**Result Details**

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between-treatments</td>
<td>261253.9777</td>
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<td>130626.9889</td>
</tr>
<tr>
<td></td>
<td>$F = 1.60169$</td>
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<td></td>
</tr>
<tr>
<td>Within-treatments</td>
<td>19165609.5054</td>
<td>235</td>
<td>81555.7851</td>
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<tr>
<td>Total</td>
<td>19426863.4832</td>
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</tr>
</tbody>
</table>

Table 7: Analysis of mass increase during 72h water bath. No significant difference between categories. (ANOVA, $a = 0.05$).

### Thickness Analysis

<table>
<thead>
<tr>
<th>Treatments</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>78</td>
<td>80</td>
<td>80</td>
<td></td>
<td></td>
<td>238</td>
</tr>
<tr>
<td>$\sum X$</td>
<td>15572</td>
<td>15629</td>
<td>17478</td>
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<td></td>
<td>48679</td>
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<tr>
<td>Mean</td>
<td>199.641</td>
<td>195.3625</td>
<td>218.475</td>
<td></td>
<td></td>
<td>204.534</td>
</tr>
<tr>
<td>$\sum X^2$</td>
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<td>10370275</td>
<td>11475744</td>
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<td></td>
<td>31840781</td>
</tr>
<tr>
<td>Std.Dev.</td>
<td>299.0451</td>
<td>304.3348</td>
<td>311.3311</td>
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<td></td>
<td>303.873</td>
</tr>
</tbody>
</table>

**Result Details**

<table>
<thead>
<tr>
<th>Source</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between-treatments</td>
<td>24144.8449</td>
<td>2</td>
<td>12072.4224</td>
</tr>
<tr>
<td></td>
<td>$F = 0.12978$</td>
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<tr>
<td>Within-treatments</td>
<td>21860144.3862</td>
<td>235</td>
<td>93021.891</td>
</tr>
<tr>
<td>Total</td>
<td>21884289.2311</td>
<td>237</td>
<td></td>
</tr>
</tbody>
</table>

Table 8: Analysis of swelling during 72h water bath. No significant difference between categories. (ANOVA, $a = 0.05$).
Formaldehyde release was at its highest with the 5 wt% CNC with an increase from control panels at +3%. The 10 wt% CNC samples on the other hand showed a greater reduction at -9.5%. It is likely that the long pressing time and lack of filler could have made the control samples useless by increased emissions of the control boards while pressing. And as such, the formaldehyde from the 5 wt% and 10 wt% would be capable of locking more formaldehyde into the panels for a longer period. Thereby emitting it back out at different slower ratios and speeds. The time of testing was 3 weeks after pressing and could potentially also have influenced the emissions of formaldehyde. In this case, the data suggests that the 10 wt% CNC panels can reduce emissions but the 5 wt% panels cannot or even increase them slightly. But data from the control panels with 0 wt% CNC are only indicative due to the different approach in producing them.

Figure 6: Average steady state formaldehyde emissions
Conclusions

- CNC can greatly boost shear strength of plywood boards. Although 10% CNC showed the highest average shear stress values, other mechanical qualities such as bending strength and resistance to swelling and water uptake will up to a degree also increase. 10wt% CNC also showed considerable viscosity, forming an obstacle for high content boards.

- Statistical difference in shear tests was only observed in room condition pretreatment. In the other pretreatments, the control category had too few samples and reduced statistical relevance. There was also a higher spread in values in the 10% CNC category, this is suggested to be caused by uneven, unnoticeable variations of applying the resin with a roller.

- 10wt% CNC might increase the boards brittleness in dry conditions and have a less pronounced mechanical improvement in resistance to deformation (MOE) compared to 5wt% CNC boards. However, results were not significantly different and more studies would be needed.

- CNC improved bonding within the glue line considerably.

- Formaldehyde emissions will be reduced by the reduction of formaldehyde being used, also boards could potentially lock formaldehyde in them for a longer duration. More studies are needed.

- Results indicate that between 5wt% and 10wt% there is an optimum amount of CNC that balances shear strength gains with bending strength gain and resistance to water. However, if only shear strength is needed, then even higher CNC content may be considered.

- Viscosity increases substantially with increased mass of CNC used.
• Curing time of resins with CNC must be optimized and can no longer follow old norms of pressing. The right combination of time and heat greatly affects the results.
Acknowledgements
Many thanks go to the people at the department of “Wood technology and wood-based composites” at Georg August Universität, Göttingen, Germany for enabling me to do this study. Special thanks go to Dr. André Klüppel and Dieter Varel. I also want to thank Prof. Stergios Adamopoulos for leading me in on this topic.
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