

Polymerised Lignin as a Reinforcing Agent in Microfibrillated Cellulose/Wood Composites

Master's thesis
by
Lukas Kamis



Carried out at the Laboratory of Natural Materials Technology, Åbo Akademi University under the supervision of Prof. Chunlin Xu and Prof. Martti Toivakka at Åbo Akademi University, and Prof. Mehdi Tajvidi and Prof. Douglas Bousfield at the University of Maine.

Abstract

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Lignin is an abundant structural material found in lignocellulosic biomass in various configurations. It is a complex natural polymer, and being an environmentally friendly material, it has much potential for improving the mechanical properties of various products. Lignin can be extracted using different pulping methods, and each method produces lignin with a different structure. The lignin used for various applications must, therefore, be studied to find the optimal lignin fraction for each end-use. In composite materials, lignin can be useful for its many properties, which include antibacterial, retention ability, and mechanical property enhancement. In this thesis, two types of lignin were polymerised with several types of cellulosic materials to see how lignin would affect the properties of natural composites and how efficient polymerisation on the materials can be. Microfibrillated cellulose (MFC) and sawdust were used as cellulosic materials to create lignin-polymerised particleboards, in which MFC would function as a binder between the wood particles. Lignin was polymerised to the fibres with laccase treatment to enhance certain composite properties, such as mechanical strength and water resistance. The results reveal that using unbleached MFC with additional lignin added, enhances the mechanical properties of particleboards when compared to those produced with MFC alone.

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“Natura artis magistra”

Lukas Kamis
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Abbreviations

ANOVA	Analysis of variance
AL	Alkaline lignin
CaO	Lime
CMC	Carboxymethyl cellulose
DI	Deionised
DS	Dry solids content
G unit	Guaiacyl unit
H unit	<i>p</i> -hydroxyphenyl unit
IB	Internal bond
KL	Kraft lignin
LDP	Low density particleboard
L-MFC	Lignin-containing MFC
M _n	Number average molar mass
MFC	Microfibrillated cellulose
MOE	Modulus of elasticity
MOR	Modulus of rupture
NaOH	Sodium hydroxide
OL	Organosolv lignin
P-SD	Pine Sawdust
RH	Relative humidity
SD	Sawdust
SEM	Scanning electron microscope
S unit	Syringyl unit
T _g	Glass transition temperature
TS	Thickness swell
TSE	Twin-screw extrusion
UMaine	the University of Maine
UMFC	Unbleached microfibrillated cellulose
WA	Water absorption
WP	Wood particles
ÅAU	Åbo Akademi University

Table of Contents

Abstract.....	i
Acknowledgement	ii
Abbreviations.....	iii
Table of Contents	iv
List of Figures	vi
List of Tables.....	viii
1 Introduction	1
2 Theory	3
2.1 Components in Lignocellulosic Biomass.....	3
2.1.1 Cellulose	3
2.1.2 Hemicellulose	4
2.1.3 Lignin.....	5
2.2 Lignin Fractionation Techniques.....	7
2.3 Properties of Microfibrillated Cellulose	8
2.4 Carboxymethyl Cellulose	9
2.5 Particleboard Manufacturing and Advancements.....	9
3 Experimental.....	12
3.1 Materials and methods	12
3.1.1 Characterisation of MFC & UMFC	12
3.1.2 Characterisation of Sawdust	14
3.2 Lignin Polymerisation for Film Formation	16
3.2.1 Characterisation with Microscopy and Scanning Electron Microscope	18
3.3 Methodology for Particleboard Production and Testing	18
3.3.1 ÅAU Particleboard.....	19
3.3.2 ÅAU Particleboard Manufacturing.....	21
3.3.3 UMaine Particleboard Manufacturing.....	22

3.3.4	Testing of UMaine Particleboard	25
4	Results and Discussion.....	29
4.1	Characterisation of MFC and U-MFC	29
4.1.1	Morphology.....	29
4.1.2	SEM Imaging of MFC Composites.....	31
4.2	Film Formation of L-MFC Films	32
4.2.1	MFC films contact angle.....	35
4.2.2	The Effect of Polymerisation.....	36
4.3	Particleboard Results	37
4.3.1	ÅAU Particleboards	37
4.3.2	UMaine Particleboard	38
	Contact Angle	40
	Water Absorption and Thickness Swelling	41
	Internal Bond Strength.....	43
	SEM Imaging of Particleboard.....	44
5	Conclusions	47
6	Summary in Swedish – Svensk sammanfattning	48
7	References	50
	Appendix A	54
	Appendix B	56

List of Figures

<i>Figure 1. Schematic figure of how cellulose polymers build up microfibrils and fibrils in the cell wall. Adapted from (Fröhlichová et al., 2014).....</i>	<i>3</i>
<i>Figure 2. Sugar units of hemicelluloses found in wood. Modified from (Rowell, Pettersen & Tshabalala, 2012).</i>	<i>4</i>
<i>Figure 3. The tree monolignols (left) and common linkages found in lignin (right). Adapted from Garedeew et al. (2020).....</i>	<i>6</i>
<i>Figure 4. SEM images of lignin nanoparticles obtained with different ultrasound intensity treatments (Wang et al., 2018).</i>	<i>7</i>
<i>Figure 5. MFC with dry solids content from the left 15.8%, 3% and 0.5%.....</i>	<i>12</i>
<i>Figure 6. From the left, kraft board used for U-MFC, unrefined kraft pulp and Masuko setup used for making U-MFC.....</i>	<i>13</i>
<i>Figure 7. Increase of fines with increased passes through Masuko grinder.</i>	<i>13</i>
<i>Figure 8. Sawdust composition, A) Sawdust from UPM Kymmene, B) Sieving station, C) fractions from sieving, D) from the left WP size over 2mm, $\leq 2\text{ mm} > 1.4\text{ mm}$, and $\leq 1.4\text{ mm} > 710\text{ }\mu\text{m}$, and E) sawdust particles $\leq 710\text{ }\mu\text{m}$.</i>	<i>14</i>
<i>Figure 9. Captured images with optical microscopy of pine sawdust, with both larger and smaller size distribution (Images captured by Maryam El Hajam)</i>	<i>15</i>
<i>Figure 10. Width and length distribution of pine sawdust. PF=pine flour. (Data collected by Maryam El Hajam)</i>	<i>15</i>
<i>Figure 11. In situ polymerisation steps.....</i>	<i>17</i>
<i>Figure 12. From the top left, particle mixture in the mould with the wire mesh sticking out the sides, the dewatering station with vacuum pump and hydraulic press, hot pressing setup, hot press used.....</i>	<i>19</i>
<i>Figure 13. Large batch polymerisation, a) the setup for lignin polymerisation and b) the mixer used for mixing L-MFC with SD before manufacturing boards.</i>	<i>20</i>
<i>Figure 14. Board production process at UMaine. A) Laccase reaction in water bath, B) Mixing after reaction, C) Mould and pressure plate, D) Particle mixture in mould, E) Dewatering station, F) Dewatered particleboard, G) Aluminium plate with mesh wire, H) Hot-pressing, and I) Hot pressed particleboard.....</i>	<i>24</i>
<i>Figure 15. Cups with formulations 3, 4 and 5, polymerisation at 22 °C without aeration.</i>	<i>25</i>
<i>Figure 16. Particleboards cut for 3-point mechanical testing.....</i>	<i>26</i>

Figure 17. Round particleboard pieces for testing IB, TS and WA. In the top right corner IB testing and in the bottom two pictures, boards submerged in water. 27

Figure 18. Samples for CA and SE testing and sandpaper used to sand down them down. 28

Figure 19. Microscopy images of MFC, a), b), and c), and U-MFC, d), e), and f). a), b) d), and e) with 100 μm scale, c) and f) with 50 μm scale. 30

Figure 20. SEM image of U-MFC, showing lignin nanoparticles attached to the fibrils a) and b), as well as crystallised mineral structure c). 31

Figure 21 SEM images of MFC polymerised with AL a, b) and KL c, d). Scale bar: 200 nm. 32

Figure 22. MFC films polymerised 5h with 10% lignin, a) KL, b) AL. MFC films polymerised 6h, c) KL and d) AL, and polymerised 24h e) KL and f) AL. 33

Figure 23. MFC films polymerised for 24h with 15% a) KL, b) AL, 20% c) KL, and d) AL. 34

Figure 24. MFC films with CMC 10 wt%. From the left AL 20%, AL 10%, KL 10%, KL 20% and MFC 100% without CMC. 34

Figure 25. Mean contact angle for polar and nonpolar liquids on LDP panels. 41

Figure 26. Water absorption on UMaine LDPs, presenting the value of the initial weight and weight after 24 h. 42

Figure 27. Thickness swelling on UMaine LDPs, presenting the value of the initial thickness and thickness after 24 h. 43

Figure 28. Internal bond strengths (MPa) for UMaine LDP samples 1-12. Demonstrating that inclusion of lignin does not significantly change the IB strength. 44

Figure 29. SEM images of SD/MFC [80/20] composite, showing MFC bonded to P-SD fibres in cryo-cracked sample. 45

Figure 30. SEM images of SD/MFC/lignin [80:20:4] composite, showing MFC bonded to P-SD fibres in cryo-cracked sample. Polymerisation 24h with a, b) AL added and c, d) KL added. 46

List of Tables

<i>Table 1. Composition of pulp used for MFC and U-MFC. Data acquired from UMaine personnel.</i>	<i>14</i>
<i>Table 2. Length, width, and aspect ratio of Pine sawdust with standard deviation. (Data acquired from Maryam El Hajam)</i>	<i>15</i>
<i>Table 3. Formulations and ratios of material used for ÅAU boards.</i>	<i>20</i>
<i>Table 4. Dry solids content for materials used, measured with IR moisture analyser.</i>	<i>22</i>
<i>Table 5. Formulations and reference number for UMaine boards. HP (number indicating minutes of hot-pressing), T22 (polymerisation at 22 °C with limited aeration), T39 (polymerisation at 39 °C), and NP (no laccase added and no polymerisation).....</i>	<i>23</i>
<i>Table 6. Characteristics of MFC and U-MFC used for films and LDP.....</i>	<i>29</i>
<i>Table 7. Average contact angle after 3.48 s, 9.2 s, and 19.2 s, on top and bottom surface of MFC films with standard deviation. Values given in [Å°].....</i>	<i>36</i>
<i>Table 8 Mechanical strength of MFC based films with added 10% and 20% alkaline lignin or kraft lignin. Standard deviation is in parenthesis.</i>	<i>37</i>
<i>Table 9. Average mechanical properties with standard deviation as result from the flexural test on ÅAU LDPs. The formulation is an addition to SD.</i>	<i>38</i>
<i>Table 10. Average mechanical properties with standard deviation as result from flexural test on UMaine LDPs. HP (number indicating minutes of hot-pressing), T22 (polymerisation at 22 °C, with minimal aeration), T39 (polymerisation at 39 °C), and NP (no laccase added and no polymerisation).</i>	<i>39</i>

1 Introduction

Stronger materials, such as composites made from natural fibres and polymers, have been a prioritised topic lately due to the environmental crisis we are experiencing. The goal is to be able to replace synthetic materials and polymers with bio-based alternatives to help save the environment, as well as to produce materials that conserve energy, decrease weight, and can be recycled. The appealing factor for natural fibre composites is the specific properties and the low prices the materials have. Today, many industry sectors such as furniture, packaging, construction, and the automobile sector are pursuing naturally made composite materials due to their advantages over synthetic fibres. Materials that already consist of natural fibres include various building materials, such as particleboard and insulation, foods for both humans and animals, and medicine and chemicals. Fossil fuels, including oil, are estimated to only last another 50 years, which makes it important to find new materials that can replace the products based on fossil fuels. Additionally, problems with landfills decline with materials that can easily be recycled or are biodegradable (Sanjay et al., 2016; Ho et al., 2012).

Lignin is seen as a material that can be used to replace fossil-based chemicals and resins used in many composite applications. However, lignin is not yet utilised as well as it could be, which is because lignin has a heterogeneous structure that complicates its utilisation. Most of the lignin produced is burnt in recovery boilers to produce energy for pulp mills. Lignin has a high energy content (~25.5 kJ/g), which is higher than carbohydrates (~17.0 kJ/g) and cellulose (17.2 kJ/g), although, lower than for coal. The production of lignin is expected to increase in the coming years, due to the increased biofuels production. Lignin characterisation and purification have been done on the laboratory scale, and the problem in focus now is scaling it up for industrial uses. However, even with upscaling, lignin is complex, and purification of substantial amounts may result in low yields since lignin's structure varies depending on the used raw material sources and the pulping process. (Wang et al., 2019; Yoo & Ragauskas, 2021).

The goal of this master's thesis was to produce high-performance MFC/lignin composites and to understand the effect polymerised lignin has on different properties in the composites. To make lignin compatible as a matrix, lignin needs to be modified by laccase-mediation. The properties in focus in this thesis are mechanical properties, thermal stability, and wettability of MFC and fibre composites. Furthermore, this thesis focuses on which type of lignin best is suited for different applications and the value the final product can add. To achieve the results, two types of lignin, two types of MFC and two types of sawdust were used. These materials were combined, and laccase was mediated in diverse ways to try to understand the effect of in situ polymerisation and the effects of lignin in the composites.

The hypotheses of the thesis were the following:

- If fibres contain lignin, in situ polymerisation of lignin in fibres will make fibres stronger
- If lignin is added and polymerised, then the polymerised lignin will enhance the mechanical properties of fibre-based composites
- If lignin is partially hydrophobic, then adding lignin will decrease the wettability of lignin-containing composites

The goals of the thesis were the following:

- To successfully produce MFC films
- To successfully polymerise lignin with MFC dispersions
- To find the optimal lignin concentration for the composites
- To produce lignin-mediated MFC-Sawdust composites
- To test the properties of the composites
- To evaluate the best formulations and enhancements of lignin in composites

2 Theory

2.1 Components in Lignocellulosic Biomass

Cellulose, hemicelluloses, and lignin found in wood are distributed unevenly throughout the wood cells. Each component plays a distinct role in the structure and function of wood. Depending on the age and the region in which the tree is growing, the mass proportions of the components are widely varying (Willför, et al., 2011).

2.1.1 Cellulose

Cellulose is a natural, fibrous polysaccharide that forms the primary component of the cell wall in biomass. It is one of the most abundant biopolymers found in wood, accounting for 40–50% of its composition, and even higher proportions in non-wood materials (70–90%). Cellulose is composed of D-anhydroglucopyranose units linked by β -1, 4-glycosidic bonds, which provide exceptional structural stability in wood. In wood, the arrangement of cellulose provides high structural stability. Microfibrils, which are composed of both amorphous and crystalline regions, are formed by cellulose chains. The crystalline regions are a result of hydroxyl groups in the cellulose chains, forming hydrogen bonds. Larger fibrils are formed by bundles of microfibrils, and these in turn make up the cell wall, see Figure 1. The formation of microfibrils gives cellulose its strength and stiffness, with microfibrils measuring several micrometres in length and 2-30 nm in width, depending on the cellulose source (Fröhlichová et al., 2014; Börjesson & Westman, 2015; Brigham, 2018).

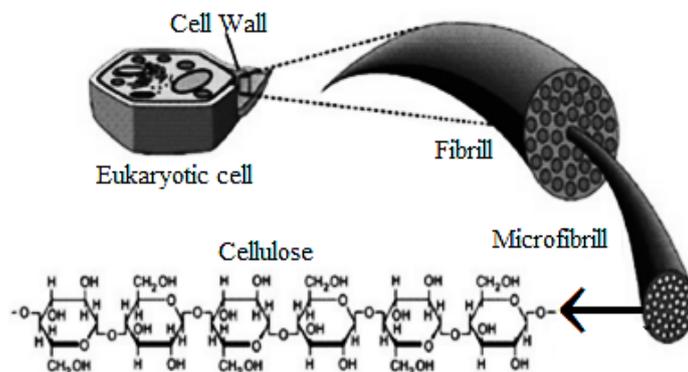


Figure 1. Schematic figure of how cellulose polymers build up microfibrils and fibrils in the cell wall. Adapted from (Fröhlichová et al., 2014)

2.1.2 Hemicellulose

One of the larger components in wood is hemicellulose, which functions with cellulose as a structural component. Substantial amounts of hemicellulose are usually present in the area where a tree is under stress. Hemicellulose is a polysaccharide polymer composed of hexoses (D-galactose, D-glucose, and D-mannose), pentoses (D-arabinose, L-arabinose, and D-xylose), deoxyhexoses (L-rhamnose and L-fucose), and small amounts of uronic acids (D-galacturonic acid and 4-O-methyl-D-glucuronic), as shown in Figure 2. Hemicellulose usually contains multiple types of sugar units which can be referred to as individual sugar units discussing hemicellulose (Willför et al. 2011; Rowell et al. 2012). The presence of multiple sugar units in hemicellulose makes the polymer chemically heterogeneous. Xylans are the most prevalent type of hemicellulose found in hardwood, while glucomannans are the most common type found in softwood (Saha, 2003).

Hemicelluloses are found in different proportions in hardwood and softwood. While some tropical hardwood species contain more lignin than hemicellulose. Hardwood and softwood also have differences in individual hemicellulose content. Hardwood and softwood also differ in their individual hemicellulose content, with hardwood containing between 25% and 35% hemicellulose and softwood containing between 20% and 30%, as measured by wood dry solids content. Hardwood typically contains more xylose and acetylated hydroxyl groups, while softwood contains more galactose and mannose units (Willför, et al., 2011)

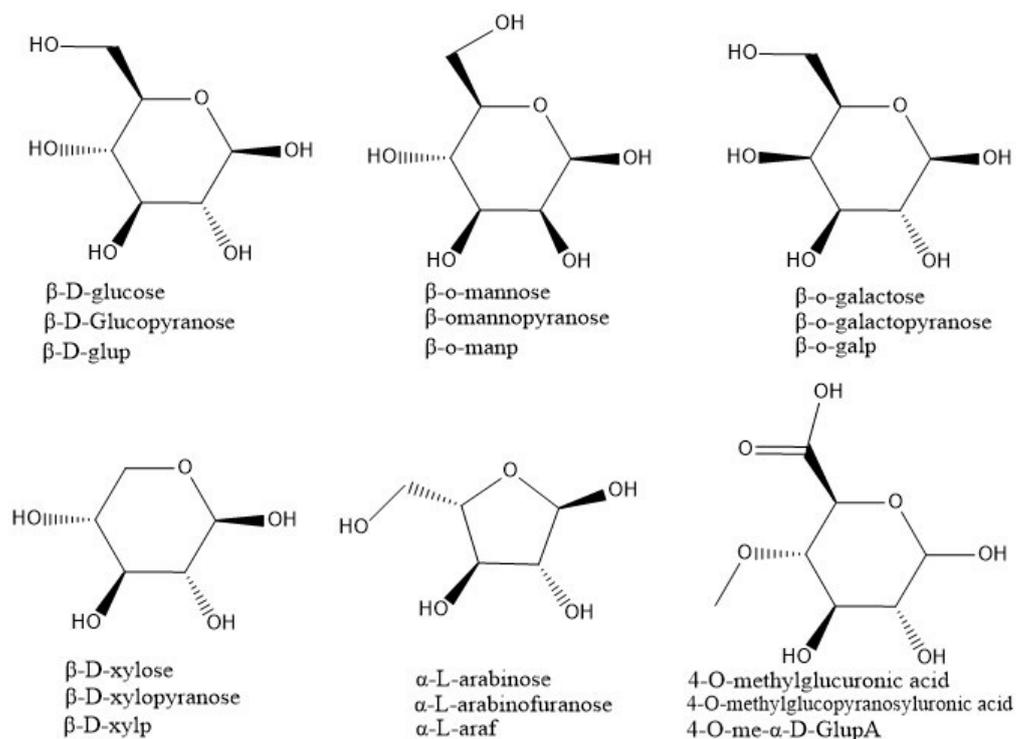


Figure 2. Sugar units of hemicelluloses found in wood. Modified from (Rowell, Pettersen & Tshabalala, 2012).

2.1.3 Lignin

Lignin is bonded closely to cellulose and hemicellulose and its function is to strengthen the cell walls and improve structural integrity. In cellulose, lignin works as a matrix between the fibres, making it a naturally occurring polymer that strengthens the cell walls by acting as a glue. Lignin also protects the tree against enzymatic degradation and from pathogens and insects. (Faruk & Sain 2016; Mandlekar et al., 2018; Antunes et al., 2022).

Lignin is a complex, heterogeneous three-dimensional polymer that is composed of phenylpropane units, such as sinapyl-, coniferyl-, and *p*-coumaryl alcohols. These units, also known as C9 units, possess a hydroxyl group bonded to C4 and may have one or two methoxyl groups bonded to C3 and C5. The aromatic rings of these monolignols are referred to as syringyl (S-unit), guaicyl (G-unit), and *p*-hydroxyphenyl (H-unit). When the aromatic rings are unmethoxylated and have one or two methoxyl groups, the side chain carbons are named α , β and γ , with α located at C1 on the aromatic ring. Additionally, the aromatic ring is numbered clockwise from 1 to 6, starting from the side chain (Antunes et al., 2022; Lourenço & Pereira 2017). The bonds between lignin monomers consists of ether and carbon-carbon bonds. The carbon-carbon bond consists of 5–5, β -5, β - β , β -1, and ether bonds consisting of β -O-4, 4-O-5, 1-O-4, with β -O-4 being the most prevalent. In softwood, the β -O-4 linkage accounts for nearly 50% of all linkages, while in hardwood it accounts for approximately 60% (Lourenço & Pereira 2017; Ralph, Lapierre, & Boerjan, 2019). The monolignols and common linkages can be seen in Figure 3.

Lignin is found in various forms, depending on the source it is extracted from and the type of extraction process. Softwood has the highest lignin content of about 25-35% and consists of H and G units, however, the H units are only found in smaller quantities, compared to G units. Hardwood contains about 15-28% lignin, and it consists of G and S units, so-called GS lignin. For hardwood, the S unit varies between distinct species. Non-woods have a lower concentration, between 9 and 20% of lignin than woody materials. The lignin is of type HGS, and it is characterised by its high number of H units (Lourenço & Pereira, 2017).

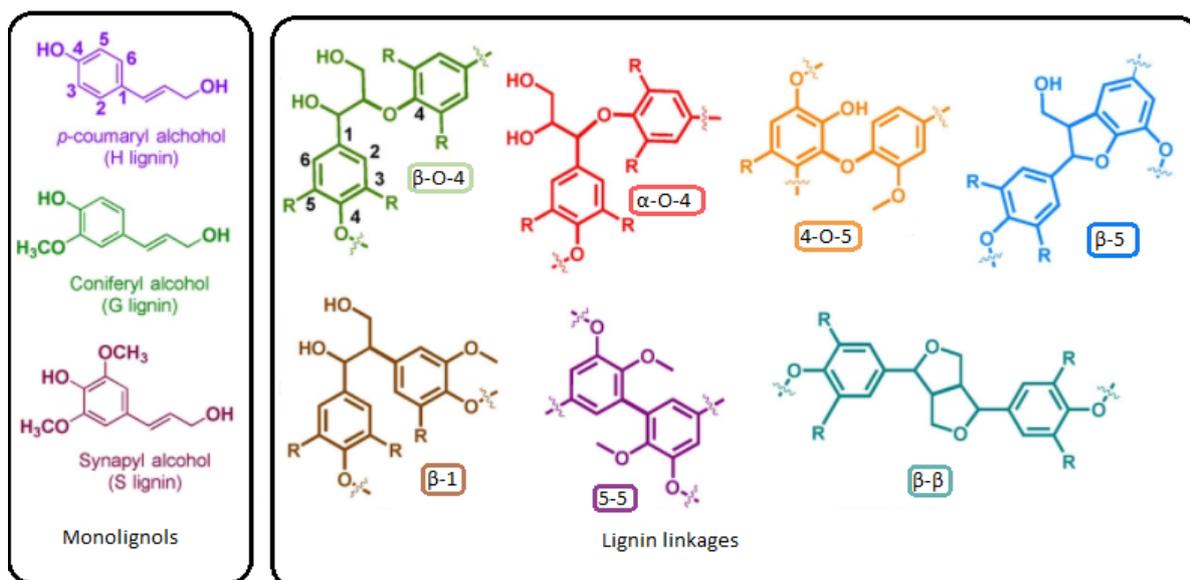


Figure 3. The tree monolignols (left) and common linkages found in lignin (right). Adapted from Garedeew et al. (2020).

Lignin exhibits antimicrobial properties against both Gram-positive and Gram-negative bacteria. This function is most effective at temperatures higher than 35 °C, between 0 and 7 °C lower than the ambient temperature (20 °C). Organosolv lignin derived from softwood demonstrates higher antimicrobial properties than Kraft lignin derived from softwood, making it a more suitable option for applications requiring antimicrobial properties (Alzameem, et al., 2019).

Lignin nanoparticles (LNPs) can be obtained from dissolving lignin in tetrahydrofuran (THF) and by dialysis slowly adding water to the system. Nanoparticles are formed as the water is reducing the lignin's degree of freedom, resulting in segregation and hydrophobic regions. Lignin nanoparticles usually have a spherical shape and size between 21 and 139 nm with a narrow size distribution (Leivonen et al., 2016; Ma et al., 2020). As shown in Figure 4, the LNPs have a spherical structure, and comparable size distribution, either small or large, however, the smaller LNPs can be seen in larger quantities.

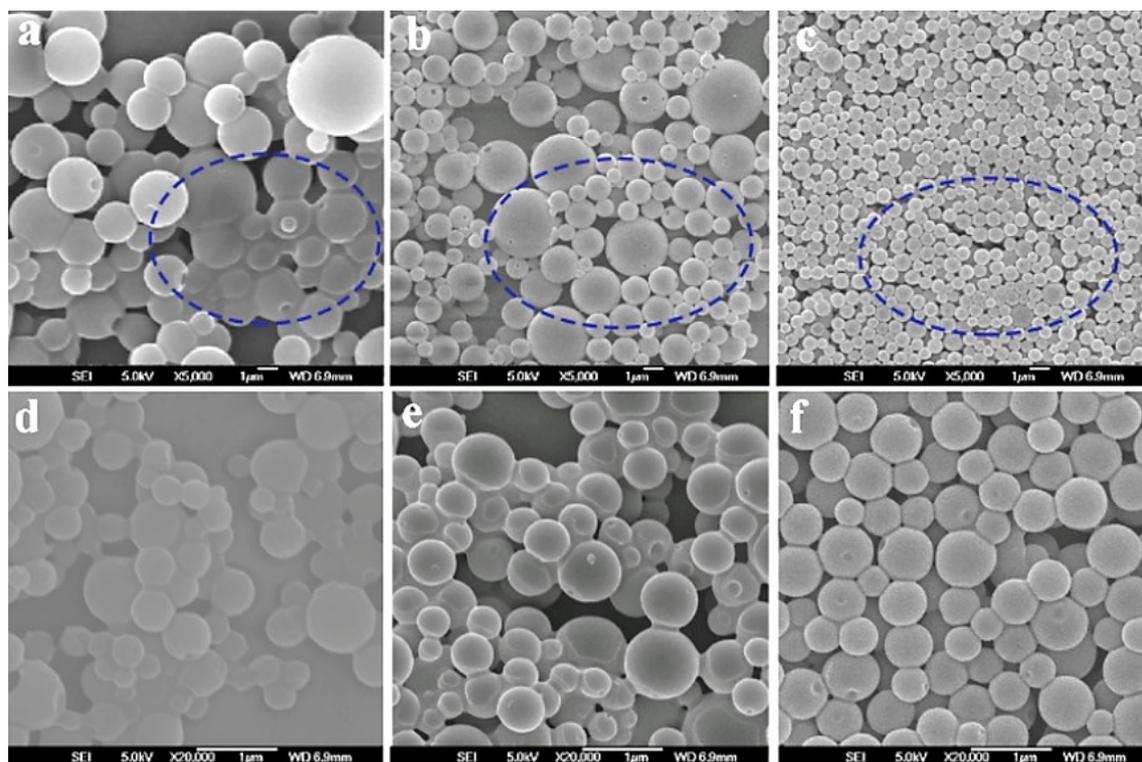


Figure 4. SEM images of lignin nanoparticles obtained with different ultrasound intensity treatments (Wang et al., 2018).

2.2 Lignin Fractionation Techniques

Lignin can be extracted from its lignocellulosic biomass by physical or chemical treatment. The pulping process used in the industry focuses on breaking down the ester and ether bonds, which results in different lignin than the lignin found in the plants. This lignin is called technical lignin and can either be sulphur-containing or sulphur-free. The main sulphur-containing processes are Kraft pulping and sulphite pulping, from which kraft and lignosulphonate lignin can be extracted. The sulphur-free processes are solvent pulping and soda pulping, from which organosolv lignin and soda lignin can be extracted. In this section, the focus is on kraft lignin, organosolv lignin, and pressurised hot water extraction (PHWE)

The kraft process use white liquor, which contains NaOH (sodium hydroxide) and Na₂S (sodium sulphide). The white liquor breaks the bonds between lignin and cellulose in the cooking process at temperatures of 150–180 °C. The cellulose can be separated by filtration, leaving the lignin and hemicelluloses as black liquor. To recover the lignin, the black liquor is acidified. The sulphur content in the extracted lignin is typically below 2–3% and the number-average molar mass (M_n) is usually between 1000 and 3000 g/mol. After the cook, the black liquor can be concentrated and combusted to reduce the sulphate to sulphide to produce green liquor. Lime (CaO) is then added to react with sodium

carbonate, which after reaction, results in NaOH and calcium carbonate precipitate. The CaCO₃ present in the green liquor can then be removed to create new white liquor.

Organosolv pulping is a pulping process in which only organic solvents are used. Usually methanol, ethanol, acetone, THF, ethylene glycol, or other organic acids can be used. In addition to solvents, water, high pressure, and an elevated temperature between 100 and 250 °C are used in the process. The cooking time varies between 30 and 90 min. In the cooking process, lignin is broken down and dissolved in an organic solvent, and hemicelluloses are depolymerised and turn into saccharides, which make up the black liquor. Cellulose is left as an insoluble material. Comparing organosolv pulping to other pulping methods, organosolv pulping has less pollution, all biomass fractions can be isolated, and all solvents used can be recovered. To precipitate lignin, water and a strong acid are added, and lignin in its pure form can be obtained through centrifugal filtration. The lignin obtained from an alcell process has a low molecular weight (Mw) < 900, low ash content, low polydispersity and is sulphur free (Xu et al., 2020; Mboowa, 2021; Lagerquist, 2022).

PHWE is a method that can be used to extract pure and highly reactive lignin. The method uses water, reduced pressure (0.8 bar) and elevated temperature (150 °C) for 2 hours to extract the components in the biomass. The water to wood ratio in the extraction process is set to 5:1. The extract is then circulated 10 times through the biomass, to extract the hemicelluloses. The chips can further be cooked with NaOH, to produce black liquor, furthermore, the black liquor can be recirculated in other batches, where it can act as an extraction chemical as well as increase the lignin concentration in the liquor, to minimise the costs of lignin evaporation. The lignin extraction process is held at reactor temperatures between 15 and 70 °C, under a typical 6-7 bar pressure, for 15-60 min. The black liquor produced is then concentrated, precipitated with HCL (pH 2.5), filtrated, and washed to obtain lignin, referred to as BLN (Von Schoultz, 2014, 2015; Lagerquist et al., 2018).

2.3 Properties of Microfibrillated Cellulose

Microfibrillated cellulose (MFC) is highly refined, often de-lignified pulp material that exhibits high strength, stiffness, relatively low density and is a renewable and biodegradable biopolymer. Due to its unique microfibril structure, MFC has been studied as a potential material for use in nanocomposites. Additionally, MFC has attracted interest in other applications, such as barrier properties in films and paper coatings. At high concentrations, MFC is gel-like and displays a highly shear thinning behaviour. (Siró & Placket, 2010; Lavoine et al., 2012; Rantanen et al., 2015).

MFC can be produced at varying concentrations, however, high concentrations are typically preferred to conserve energy. Methods for producing high concentration MFC include mechanical treatment, enzyme-aided fibrillation, and twin-screw extrusion (TSE), or their

combinations. Mechanical treatment is the most energy-consuming process (5-30 MWh/t), where cellulose pulp is grinded between grinding stones. However, the energy consumption can be reduced to 1-2 MWh/t by pre-treating cellulose with chemical methods such as TEMPO oxidation, carboxymethylation, and enzymatic hydrolysis. By combining enzymatic hydrolysis and TSE, MFC can be produced at ~20 wt% with low energy consumption, making it more suitable for industry use (Rol et al., 2020; Koppolu et al., 2022).

MFC can be made from lignin-containing pulp and sawdust, however, the fibrillation rate is slower than for delignified pulp, and the energy uptake is lower during disintegration. The use of lignin-containing materials leads to a more heterogeneous material with fewer individual microfibrils when compared to starting from delignified material. Pre-treating the material used for making MFC by sulfonation increases the bonding capacity of lignin-containing MFC made from softwood (Ämmälä, et al., 2019). In comparison, MFC films have been reported to have approximately 2.5 times higher tensile strength than printing paper, although the type of paper and basis weight were not specified (Syverud & Stenius, 2009).

2.4 Carboxymethyl Cellulose

Carboxymethyl cellulose (CMC) is a cellulose derivative composed of polysaccharides of anhydro-glucose linked by β -1, 4 bonds. CMC share a similar structure to cellulose, apart from OH groups partially being substituted by anionic carboxymethyl groups linked to carbon. CMC is widely used in various products and function as a thickening agent, emulsifier, stabiliser, or regulator of viscoelastic behaviour. In packaging materials, CMC can improve film stability, thermal stability, and impart antimicrobial and antioxidant properties when blended with other substances (Rahman, et al., 2021). The addition of CMC to MFC suspensions can increase the water retention and reduce the water removal, depending on the degree of substitution and molecular weight of the CMC (Kokol, 2022).

2.5 Particleboard Manufacturing and Advancements

Particleboards are a type of wood panel made from smaller wood particles such as sawdust and are commonly bound using urea-formaldehyde (UF) or phenol-formaldehyde (PF) resins. These resins are synthesised from petroleum-based resources, but with the increasing concerns over UF's carcinogenic properties and rising oil prices, there has been a push to find alternatives. Particleboards are produced by mixing wood chips with resin and forming the boards with a hot-press under heat and pressure. Particleboard can be used as base materials for surfaces and furniture; however, it is not as strong and durable as solid wood. Particleboards are prone to absorb more moisture and swell more than solid wood. (Çetin & Özmen, 2002; Euring, et al., 2016). Lignin, a natural binder, has been proposed as a potential substitute due to its resemblance to PF. Laccase mediation of lignin can assist

in the in-situ polymerisation of free radical reactions, binding the lignin to the fibres and acting as a glue between them (Nasir, et al., 2014).

In 2019, 358 million m³ of wood-based panels were produced, 28% of which was particleboard, 29% medium-density fibreboard, and 30% plywood. Sawdust is not the only type of wood used in particleboards, alternative raw materials such as wood trimmings, old furniture and waste from secondary wood processing can be used to save wood resources. Recycled and post-consumer material is used at an average of 30% in the industry. The total market value worldwide for particleboard in 2021, was at USD 21.3 Billion.

According to standard (EN 309:2005), particleboard is defined as panel material manufactured from wood under pressure and heat. The type of wood used in the production of particleboard influences the resulting properties significantly, with softwood demonstrating better mechanical properties than hardwood. Long and small wood chips are desired for production, as they provide better contact between the fibres. Smaller chips are needed to fill in the hollow gaps, created by the larger chips, making the panels more uniform. Specific dimensions of wood chips are difficult to define. The different grades of particleboard include standard grade, utility grade, moisture-resistant grade, fire-resistant grade, and high-density grade. The most common methods used to evaluate the board include modulus of rupture (MOR), modulus of elasticity (MOE), internal bond (IB), thickness swell (TS), density, and fire resistance. Particleboard production follows standards ASTM D1037-12 and ASTM D5055 for medium-density fibreboard (Pędzik, et al., 2021, IMARC, 2022).

Utilisation of MFC as binder in particleboard is still mainly at the research and development state. A study by Amini et al. (2017) found that using southern pine wood particles and MFC, the MOE (Modulus of Elasticity) does not change significantly with added MFC between 15 and 20%, while the MOR (Modulus of Rupture) had a significant increase at increased density levels. The study also found that WA decreases with higher densities, while TS increases. It also stated that moisture removal is important for developing high strength and adhesion between the wood particles and MFC (Amini et al., 2017).

Another study by Hafez & Tajvidi, found that increasing the wt% of MFC from 10-20%, can further enhance mechanical properties such as specific strength, modulus, and strain at break (Hafez & Tajvidi, 2020). In other studies, MFC has been added to UF to improve the mechanical bonding strength. A combination of UF-MFC is shown to have higher viscosity and shear thinning compared to UF, leading to better size distribution of adhesive to larger particles. As a result, particleboards with UF-MFC can be seen to have better mechanical performance than particleboards with just UF (Mahrtdt, et al., 2016).

A study conducted by Felby, et al., in 2002 and 2004, used native lignin in beech fibres that were laccase-treated as an adhesive in the production of particleboards. The study found that laccase-treated boards had higher strength properties than untreated boards, with the significant strength improvements that were seen in dry particleboard. The improved

bonding strength might have been a result of increased interfacial compatibility, and the increased wet strength a result of precipitated lignin, that created covalent bonds. However, in general, it is difficult to study the bonding mechanisms in particleboards. (Felby, et al., 2002; 2004).

Another study conducted by Widsten & Kandelbauer, in 2008, attempted to manufacture particleboard without binders by using enzymatic pre-treatment of lignin acting as a binder, using laccase and peroxidase enzymes. The results showed that binderless particleboard is difficult to manufacture, as the cost of technical lignin as adhesive might be too high. The manufacturing methods were also found to be incompatible with existing industrial processes, as the incubation of particles needed to be conducted in separate steps (Widsten & Kandelbauer, 2008).

3 Experimental

3.1 Materials and methods

BioPiva™ 300 Softwood Kraft lignin (KL) was obtained from UPM, while alkaline birch lignin (AL) was acquired from CH Bioforce (CHB). Microfibrillated cellulose (MFC) and unbleached microfibrillated cellulose (U-MFC) were produced and supplied from the University of Maine. Sawdust from spruce was sent from UPM Kymmene and sawdust from pine was obtained from the University of Maine. MetZyme Laccase L371 was shipped from MetGen Oy. Cationic starch (C135) was acquired from Chemigate and Carboxymethyl cellulose (CMC) used was FinnFix 4000G.

3.1.1 Characterisation of MFC & UMFC

Microfibrillated Cellulose was obtained from the University of Maine and characterised. The dry solids content of the filter cake was measured using a RADWAG MA 50 R IR moisture analyser and found to be 15.82%. The MFC was then diluted with distilled water to 3% dry solids using a pulp disintegrator and further reduced to 0.5% with magnetic stirring for 2 h. The resulting samples of different dry solids content are shown in Figure 5. Additionally, the MFC was analysed using a Valmet Fibre Image Analyser (Valmet FS5) to measure fibre length, width, coarseness, curl, opacity, and fines. The University of Maine's Process Development Centre produced the high-fines (90%) content pulp (MFC) by refining bleached softwood kraft pulp using specialised plates in a refiner. The fines content was measured using a MorFi fibre analyser (Koppolu et al., 2019).



Figure 5. MFC with dry solids content from the left 15.8%, 3% and 0.5%.

Unbleached Microfibrillated Cellulose (U-MFC) was produced using a Masuko Super Mass Collider at the University of Maine (UMaine). The process involved mixing dried softwood Kraft pulp sheets with water to reach a consistency of 3% and passing it through the Masuko grinder in a batch process, as shown in Figure 6. The grinding gap was set to -100, and the unrefined pulp was analysed after every 10 passes using a MorFi Compact Fibre Analyser (Software R10.07). The fines content was also analysed at 57 passes and 58 passes.



Figure 6. From the left, kraft board used for U-MFC, unrefined kraft pulp and Masuko setup used for making U-MFC.

The relationship between the number of passes through the Masuko and the fines content is visualised in Figure 7. After 58 passes, the fines content was 95% and the dry solids content was measured to be 3% using an IR moisture analyser. Prior to utilisation, the U-MFC was thoroughly mixed, and the solids content was re-assessed.

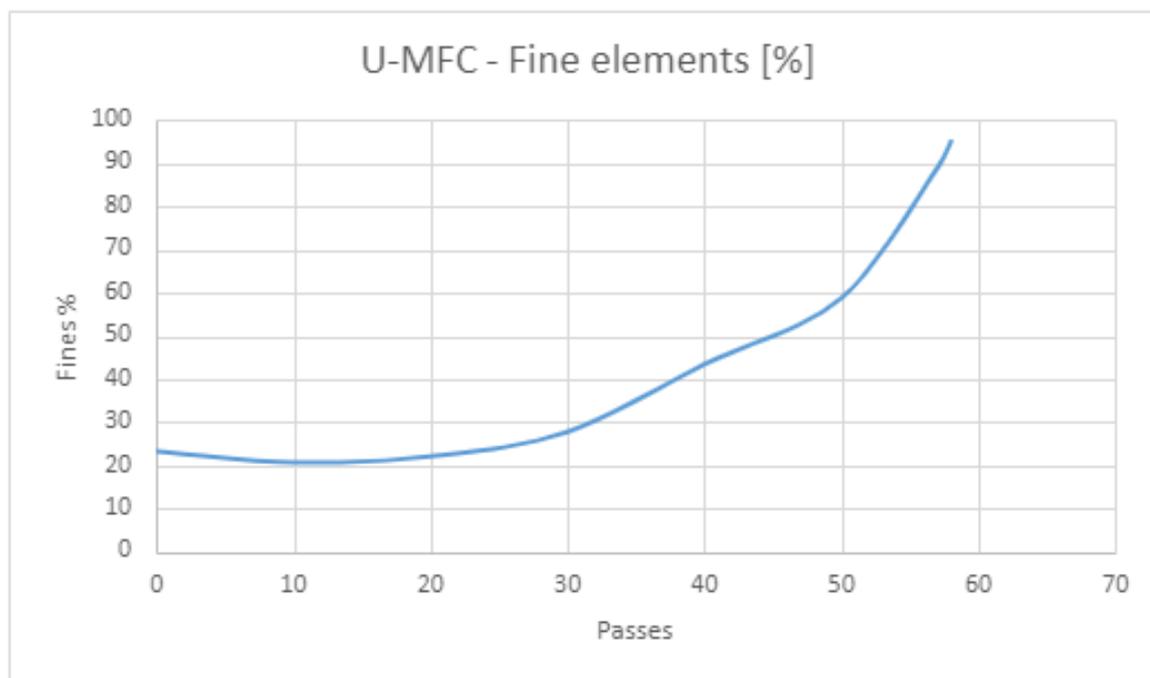


Figure 7. Increase of fines with increased passes through Masuko grinder.

The composition of MFC and U-MFC used was analysed by the personnel at UMaine, as presented in Table 1. The hypothesis was that the composition of MFC from UMaine and Åbo Akademi University (ÅAU) should be consistent, as the MFC used at ÅAU was sourced from UMaine. The results indicate that the content of Klason lignin in the U-MFC sample was lower than anticipated. Furthermore, both MFC and U-MFC samples displayed similar concentrations of xylan. In contrast, the concentration of glucan in bleached kraft pulp was found to be significantly higher.

Table 1. Composition of pulp used for MFC and U-MFC. Data acquired from UMaine personnel.

Sample	Glucan (%)	Xylan (%)	Klason Lignin (%)
Bleached kraft pulp	79.33 (1.65)	18.4 (0.67)	-
Unbleached kraft pulp	41.62 (0.19)	15.84 (0.63)	5.42

3.1.2 Characterisation of Sawdust

The sawdust used in the study was sourced from UPM Kymmene and was derived from spruce. Prior to use, the sawdust was sieved to remove larger fragments of wood particles (WP). The sieves used had wire mesh sizes of 2 mm, 1.4 mm, 1 mm, 710 μm , and 500 μm . Most of the sawdust particles were found to be below 710 μm in size, and all particles below this size were mixed, as illustrated in Figure 8.

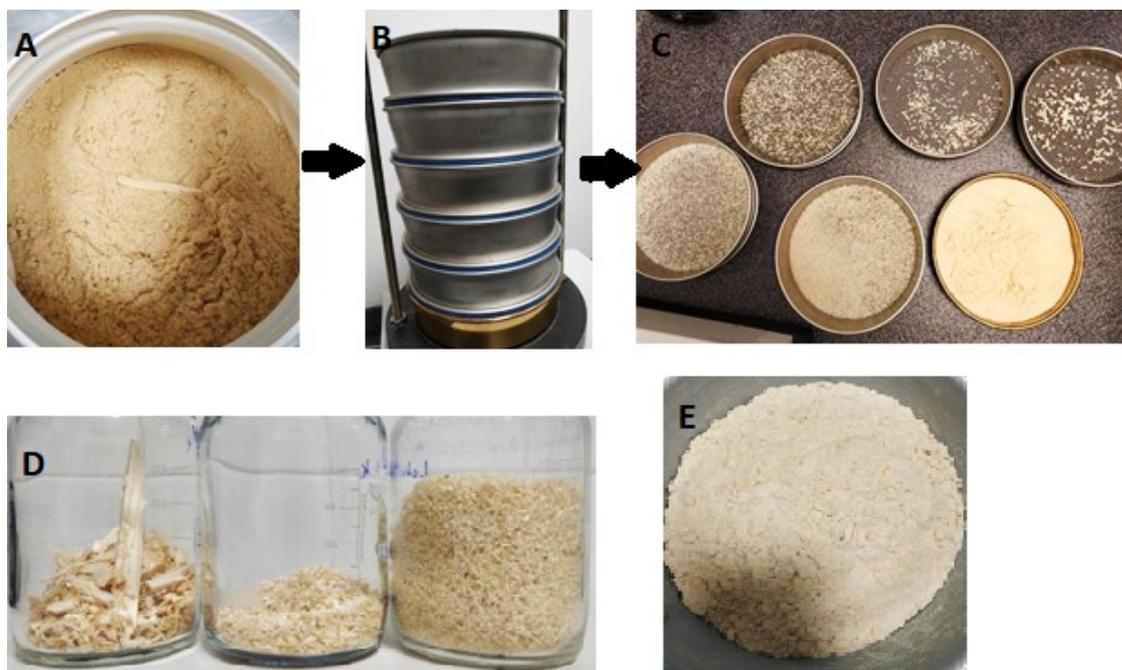


Figure 8. Sawdust composition, A) Sawdust from UPM Kymmene, B) Sieving station, C) fractions from sieving, D) from the left WP size over 2mm, $\leq 2 \text{ mm} > 1.4 \text{ mm}$, and $\leq 1.4 \text{ mm} > 710 \mu\text{m}$, and E) sawdust particles $\leq 710 \mu\text{m}$.

Sawdust used at UMaine originated from pine wood and is referred to as P-SD (Pine Sawdust). It had a much smaller average size and was flour-like in appearance compared to the sawdust used at ÅAU. As shown in Figure 9, although larger particles were present, the smaller particles dominated in terms of quantity. Analysis of the P-SD revealed that most of the particles had a width of 25 to 50 μm and a length of 0 to 200 μm , as depicted in Figure 10.

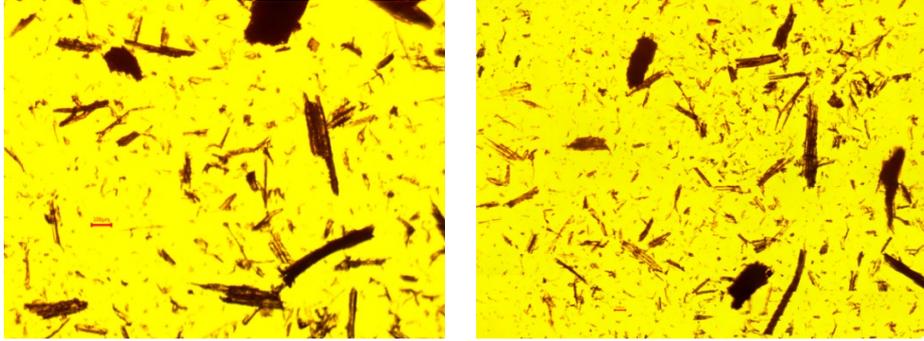


Figure 9. Captured images with optical microscopy of pine sawdust, with both larger and smaller size distribution (Images captured by Maryam El Hajam)

The high standard deviation in the size distribution of P-SD is attributed to the small number of larger particles present in the mixture. Most of the particles found in P-SD have a width of less than 100 μm and a length of less than 200 μm .

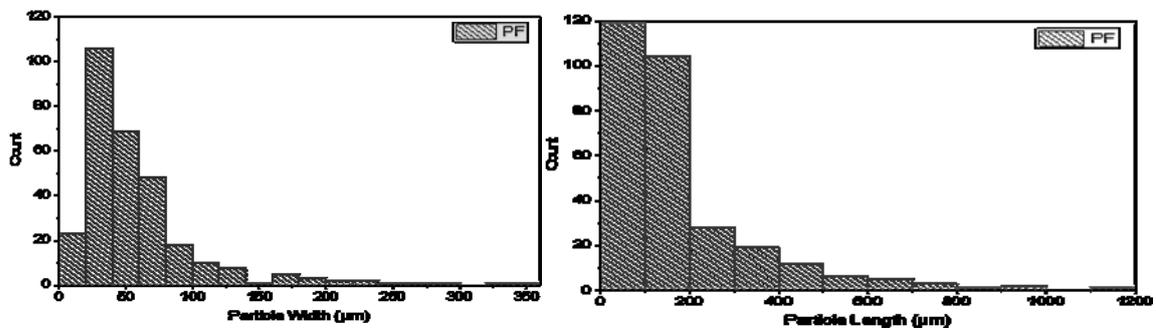


Figure 10. Width and length distribution of pine sawdust. PF=pine flour. (Data collected by Maryam El Hajam)

The parameters presented in Table 2 indicate that most of the particles have a width of approximately 10 μm in width and a length of 7 μm when standard deviation is negative. The smaller the particles are, the larger the surface area available for binding with MFC, U-MCF, and lignin is. However, the mechanical strength of the wood can suffer.

Table 2. Length, width, and aspect ratio of Pine sawdust with standard deviation. (Data acquired from Maryam El Hajam)

Parameters	Mean value (Standard deviation)
Length (μm)	179.9 (172.7)
Width (μm)	59.1 (49.7)
Aspect ratio	3.2 (1.8)

3.2 Lignin Polymerisation for Film Formation

Lignin was first dissolved in water under alkaline conditions for a period of 24 hours. The pH value was adjusted to 11 with 0.5 M NaOH solution for the Alkali Lignin (AL) and 11.5 for the Kraft Lignin (KL) at the initiation of the process. The pH value subsequently decreased to 10 over time. Prior to usage, the alkaline lignin was placed in a vacuum desiccator for 30 minutes to remove any excess solvent and to dry the lignin. The KL sample had a solid dry content of approximately 66 wt%, which was measured using an infrared moisture analyser. To dissolve the lignin, 200 mg and 300 mg were weighed respectively and distilled water was added to obtain a total volume of 20 g. After 24 hours, the solution was centrifuged using a HERMLE Z36HK centrifuge to separate the undissolved lignin from the solution. The undissolved lignin was then freeze-dried to cross-reference the amount of dissolved lignin with the amount that remained undissolved. The amount of dissolved lignin was measured by drying 1 g of solution in an oven at 105 °C for 4 hours. The results for each batch varied between 7 and 11.6 mg/g for AL and 4 to 13.6 mg/g for KL dissolved.

The in-situ polymerisation of lignin and Microfibrillated Cellulose (MFC) was carried out using a 6-reactor Radley carousel. MFC was measured and added to a round bottle that was placed on a scale. For each reaction, 100 or 150 g of MFC (0.5%) was used. The MFC was heated to a temperature of 39°C within the bottle, while the external temperature was maintained at 45°C. The pH was adjusted to 10 with 0.5 M NaOH. The carousel, which was equipped with a magnetic stirrer, was rotated at 650 rpm during the reaction, and aeration was added. Laccase (515 U/ml) was added to the MFC suspension according to equation 1. Lignin was added at a rate of 8 ml/min, the amount of lignin needed was directly proportional to the amount of dissolved lignin in mg/g. Lignin was added according to equation 2, where the MFC/lignin ratio was 90:10, 85:15, 80:20 and 50:50 and equation 3. The reaction times were 5 h, 6 h and 24 h. Once the reaction had reached its time limit, the contents were placed in a glass bottle and then placed in a water bath for 5 minutes at a temperature of 90-96°C to inactivate the laccase and end the reaction (see Figure 11). The bottles were cooled down to room temperature and stored in a cold room.

The bottles containing the MFC/lignin mixture were shaken using an SKF20500 lab companion for 30 minutes to ensure thorough mixing of the MFC and lignin. The mixture was then transferred to petri dishes (Ø 8.75 cm) and aluminium cups (Ø 10 cm) using a 30 ml syringe. The use of aluminium cups was evaluated as an alternative to petri dishes as the films were found to be difficult to remove from the latter.

The target grammage for the films was 30 g/m², which was achieved by adding a dry weight of 180 mg fibres per petri dish. The Lignin-containing Microfibrillated Cellulose (L-MFC) mixture was then dried at a controlled temperature of 23°C and 50% relative humidity (RH) for 4 to 5 days.

In addition, the MFC/lignin mixture was mixed using a FlackTek DAC 330-100 L Speed Mixer® for 90 seconds at 1500 rpm, to investigate the potential effects of mixing on lignin migration during the formation of the films.



Figure 11. In situ polymerisation steps.

$$\text{Equation 1} \quad \text{Laccase amount (g)} = \frac{\text{Lignin amount (g)} \times 10}{\text{Enzyme activity (U/ml)}} \times 3$$

$$\text{Equation 2} \quad \frac{\text{MFC ratio}}{\text{Lignin ratio}} = \frac{\text{MFC consistency}}{\text{Lignin needed (mg)}}$$

$$\text{Equation 3} \quad \text{Lignin amount (g)} = \frac{\text{Lignin needed (mg)}}{\text{Lignin solids content (mg/g)}}$$

To accelerate the drying time of the L-MFC 10% films, some test samples were placed in an oven for 2 hours at 105 °C, after which the samples were left to dry under ambient conditions. Additionally, some samples were dried using an infrared moisture analyser to evaluate the effects of faster drying on the films. The L-MFC 10% and 50% mixture was also placed on aluminium foil, both on the glossy and non-glossy side, and put in the oven at 105°C to dry for 4 hours to evaluate how well the films would release from the surface.

To enhance the viscosity of the L-MFC mixture, carboxymethyl cellulose (CMC) was added to the L-MFC mixture at a dry weight ratio of MFC/CMC (90:10). This increased viscosity was expected to mitigate lignin migration when casting the film in petri dishes.

The CMC used was FinnFix 4000G dissolved to a dry solids content of 2.5%. L-MFC and CMC were mixed with magnetic stirring at approximately 1000 rpm for 60 minutes before casting in petri dishes. The films were left to form in a conditioned room for 4 days at 23°C and 50% RH.

3.2.1 Characterisation with Microscopy and Scanning Electron Microscope

Visually, U-MFC has a deep brown colour that is distinct from the pure white colour of bleached MFC. A light microscope was utilised to examine the fibres more closely, with the most effective results obtained using lenses with magnifications of 5X, 10X, and 20X.

Scanning electron microscopy imaging was used for MFC, U-MFC, and MFC polymerised samples. The objective was to investigate whether lignin is attached to the MFC fibrils, and to determine if lignin could be seen as a substrate. The samples examined were MFC, U-MFC, MFC polymerised with AL and MFC polymerised with KL. The magnifications used ranged from 5 KX to 13.01 KX and negative staining was used to charge the samples for improved image quality.

3.3 Methodology for Particleboard Production and Testing

The objective of the fibre board production was to create low-density particleboard (LDP) with a density of approximately 0.6 g/cm³. According to ASTM D1554-10, low-density particleboards have a density of less than 0.64 g/cm³. All particleboards were produced using the same dewatering station and hot-pressing technique, as illustrated in Figure 12.

MFC was diluted from 3% to ~1.5%, by adding distilled water and stirring until uniform. Sawdust particles (spruce) used had a particle size $\leq 710 \mu\text{m}$. An IR moisture analyser was used to measure the exact dry weight values for all components used. The AL solution used had a lignin content of 20.7 mg/g and the KL solution had a lignin content of 19.0 mg/g.

The composite materials were prepared by mixing the lignin and cellulosic components in a specified ratio. The mixture was then placed in a custom-made plastic mould with the volume of 864 cm³ (12 cm x 12 cm x 6 cm), which was CNC-machined to the desired shape and equipped with 500, 1.0 mm holes drilled in the bottom. The mould was positioned on an aluminium plate with a central aperture to facilitate vacuum-assisted dewatering. To ensure proper solid retention, a 100 μm mesh filter was placed around the mixture in the mould. The dewatering process was aided by applying a vacuum with a pump and pressure with a hydraulic press, with emphasis on the use of more vacuum than pressure for optimal dewatering. The dewatering process was carried out using a hydraulic press, which could exert a maximum pressure of 2 metric tonnes (1.36 MPa) on the composite mixture (area = 0.0144 m²). The pressure was then reduced to 1 metric tonne (0.68 MPa) to facilitate the removal of water by vacuum. The process was repeated until the composite material

reached a thickness of 1-1.5 cm. The partially dewatered composite was then placed between 100 μm mesh filters, which were sandwiched between aluminium foil and metallic plates. Five (5) spacers with a thickness of 5 mm were inserted between the metal plates to ensure a consistent board thickness. The composite was then hot-pressed for 7 minutes at 180 °C. To release any excess steam, the pressure was briefly released every minute for the first 4 minutes of the hot-pressing.



Figure 12. From the top left, particle mixture in the mould with the wire mesh sticking out the sides, the dewatering station with vacuum pump and hydraulic press, hot pressing setup, hot press used.

3.3.1 ÅAU Particleboard

At Åbo Akademi University (ÅAU), particleboard was made by mixing sawdust (spruce), MFC and lignin at different ratios. In some experiments, MFC was polymerised with lignin. These boards were made to see how MFC would affect the mechanical properties and to see if lignin could be implemented to enhance the mechanical properties even further.

At ÅAU, boards with pure sawdust were made as a control unit for mechanical properties, to measure against SD/MFC in dry weight ratio [90:10] and [80:20]. To see if polymerised lignin could improve the mechanical properties of the boards, lignin was polymerised with MFC at a dry weight ratio of MFC/lignin [80:20] and then Mixed with SD at a ratio of SD/(MFC/lignin) [80:20:4], see Figure 13. To see if CMC would improve properties CMC was added at 10% dry weight on top of MFC, at the ratio: SD/MFC/lignin/CMC [80:20:4:2]. Cationic starch (C135) was also tested to see if it could help retain more lignin and improve the mechanical properties. C135 was also added on top of MFC at 10%, at the ratio

SD/MFC/lignin/C135 [80:20:4:2]. One sample containing both CMC and C135 was also tested; the ratio for this sample was SD/MFC/AL/C135/CMC [80:20:4:2:1.4], and AL was used for this sample, all of which is shown in Table 3.

Table 3. Formulations and ratios of material used for ÅAU boards.

Sample formulation	Ratio
Sawdust (SD)	100
SD/MFC	90:10
SD/MFC	80:20
SD/MFC/AL	80:20:4
SD/MFC/AL/CMC	80:20:4:2
SD/MFC/AL/C135	80:20:4:2
SD/MFC/AL/C135/CMC	80:20:4:2:1.4
SD/MFC/KL	80:20:4
SD/MFC/KL/CMC	80:20:4:2
SD/MFC/KL/C135	80:20:4:2

To produce medium-density particleboards (0.65 g/cm³), 46.8 g of dry weight material is required. However, as the materials used contain water and moisture, the actual weight may vary. Two boards were made from each sample, as one board is typically cut into three test pieces.



Figure 13. Large batch polymerisation, a) the setup for lignin polymerisation and b) the mixer used for mixing L-MFC with SD before manufacturing boards.

3.3.2 ÅAU Particleboard Manufacturing

To understand the mechanical properties of unbound SD particleboard, 56.16 g SD with a dry solids content of 83.33% was mixed with 500ml water in a beaker, to make a thick mixture that could be pressed in a dewatering station. When the water stopped flowing, the boards were removed from the dewatering station, and hot-pressed. The moisture content after dewatering was not analysed.

Since the mould can only fit 0.72 dm³, the dry solids content of MFC had to be limited to a minimum of 1.5% DS. To make sure that the mixtures would fit in the mould, the dry solids content of MFC had to be 1.5%. When mixing SD and MFC [90:10] together, 50.54 g SD (DS 83.33%) was mixed with 314.516 g MFC (DS 1.488%). The two components were mixed in a beaker, using a spatula. SD/MFC [80:20] was mixed using the same principle as before, 37.44 g SD was mixed with 582.45g MFC (DS 1.607%).

Particleboards containing added lignin have the ratio MFC/lignin [80:20]. For AL, 3600g MFC (DS 1.6%) was added to a 5L beaker. The beaker was placed in a hot water bath with the temperature set to 45 °C and a Heidolp RZR 2020 stirrer was added to stir the mixture in the water bath. After 12.7 ml Laccase was added, followed by slowly adding 217.4 g lignin solution (20.7 mg/g). Aluminium foil was placed on top to eliminate moisture loss through evaporation. The stirring was set to such rpm that air would mix in. The polymerisation time was 24 h, after which the mixture was heated to +90 °C, to stop the enzyme activity. The mixtures were let to cool to room temperature and later put in cool storage prior to use. For the KL mixture, 3800g MFC (DS 1.5%), 14.6 ml Laccase and 250 g lignin (19 mg/g) were used. The same principles as for AL were used.

The first lignin-containing particleboards were made with (80:20:4) SD/MFC/lignin ratio. First, 1251 g polymerised AL mixture was added to a kitchen mixer bowl and then 89.54 g SD (DS 83.99%) was added. The mixture was mixed for 4 minutes, using a silicone-coated stirrer, see Figure 13. The mixture was then divided evenly into two beakers. The mixtures were then made into boards, with the same technique as described earlier.

In the second experiment, 70.5 g CMC (DS 2.5%) was added to the polymerised L-MFC mixture. The mixture was mixed for 2 minutes in the kitchen mixer, 89.54 g SD was then added to the mix and mixed for 4 minutes. The CMC was added in a ratio of SD/MFC/lignin/CMC [80:20:4:2].

In the third experiment, 2.313 g C135 (DS 81.25%) was added to the SD and mixed properly. Cationic starch was added in ratio SD/MFC/lignin/C135 [80:20:4:2]. Polymerised MCF-L was then added and mixed for 4 minutes and divided evenly into beakers. Boards were made with the same technique as before. All boards were stored in a room with RH 50% and a temperature of 23 °C for at least 24 h, before cutting and testing.

3.3.3 UMaine Particleboard Manufacturing

At the University of Maine (UMaine), a different approach was taken in which SD, MFC, and lignin were all polymerised together, to investigate whether the lignin present in the wood particles (pine wood) combined with added lignin would affect the board properties. Also, a test was conducted where only sawdust and MFC were polymerised with laccase to examine how the enzyme would work on the lignin present in the wood. The target density for the boards was the same as at ÅAU, low-density particleboard with 0.60 g/cm³. The boards ended up being around 0.50 to 0.55 g/cm³, which classifies the boards as low-density boards. For low-density boards, it is relatively easy to achieve the standards set.

Unbleached MFC (U-MFC) containing lignin was used to investigate if the lignin present in the fibrils could be utilised to improve the mechanical properties of the boards. Typically, the mechanical properties of unbleached softwood kraft pulp would be lower than those of bleached pulp. U-MFC was mixed with pine SD as a control, to evaluate how the lignin present in U-MFC and P-SD would affect the mechanical properties. U-MFC was produced from unbleached kraft pulp, by using a Masuko super mass collider. The same batch of material was used for all boards produced at UMaine. The dry solids content of each material is shown in Table 4.

Table 4. Dry solids content for materials used, measured with IR moisture analyser.

Material	Dry solids content (%)
Pine sawdust	92.23
MFC	2.81
U-MFC	2.82

The lignin solutions used at UMaine were prepared the same way and from the same lignin as used at ÅAU. The AL solution had a lignin content of 24.9 mg/g, and the KL solution had a lignin content of 36.1 mg/g.

Two parallel samples were produced for each formulation (Table 5), except for the samples polymerised at 22 °C. All formulations had the P-SD/MFC or P-SD/U-MFC ratio at [80:20] and MFC/U-MFC ratio to lignin [80:20]. The first two formulations were made to see the difference between the hot-pressing times. The room-polymerised samples were made to see how temperature and lack of mixing would affect the final properties and the non-polymerised samples were made as reference samples to the other samples. Each polymerisation carried out over 24 h, in a fume hood, as shown in Figure 14 A). The mould had a volume of 960 cm³ (12.5 cm × 12.8 cm × 6 cm).

Table 5. Formulations and reference number for UMaine boards. HP (number indicating minutes of hot-pressing), T22 (polymerisation at 22 °C with limited aeration), T39 (polymerisation at 39 °C), and NP (no laccase added and no polymerisation).

SD/MFC-NP-HP(7)	1
SD/MFC-NP-HP(15)	2
SD/MFC-T22	3
SD/MFC/AL-T22	4
SD/MFC/KL-T22	5
SD/MFC-T39	6
SD/MFC/AL-T39	7
SD/MFC/KL-T39	8
SD/U-MFC-NP	9
SD/U-MFC-T39	10
SD/U-MFC/AL-T39	11
SD/U-MFC/KL-T39	12
SD/U-MFC-NP Medium Density	13

To produce boards with formulations 1, 2, 9, and 13, P-SD and MFC or U-MFC were measured and mixed in the ratio [80:20] and mixed in the kitchen aid mixer for 4 minutes. The particle mixture was then placed in the dewatering station, which had a metal wire mesh at the bottom. To minimise waste and achieve a mould size closer to 12 x 12 cm, two metal plates were placed on the inside of the mould to make the presser head fit tighter. The pressure was added up to approximately 250 kg (170 kPa) over an area of 0.0144 m². This modification was deemed effective in achieving the desired dimensions of the mould while also minimising the amount of material needed.

When the pressure plate reached its target position in the mould and the water stopped sipping out, the board was taken out from the mould and placed between two metal wire meshes and two metal plates covered in aluminium. The aluminium back parts were sprayed with silicon coating to prevent them from sticking in the hot press. The samples were then placed in the hot press at 356 °F (180 °C) and tightened until the boards were flattened to 5 mm. To evaluate the effect of pressing time on the mechanical properties of the composites, two different formulations were used. The first formulation was exposed to a hot-pressing temperature of 180°C for 7 minutes, while the second formulation was subjected to the same temperature for 15 minutes.



Figure 14. Board production process at UMaine. A) Laccase reaction in water bath, B) Mixing after reaction, C) Mould and pressure plate, D) Particle mixture in mould, E) Dewatering station, F) Dewatered particleboard, G) Aluminium plate with mesh wire, H) Hot-pressing, and I) Hot pressed particleboard.

Formulations 3, 4, and 5, one board each, were all produced the same way. The materials needed (P-SD, MFC, lignin and laccase) for one board were measured. First, P-SD and MFC were mixed, then 8 ml laccase was added, and finally, the lignin was added. After stirring thoroughly, the mixtures were placed into plastic beakers. Plastic straws were added to allow some aeration, as shown in Figure 15. However, they were quickly filled up with liquid. Lids were placed on the beakers to prevent evaporation, and between the lid and beaker, a straw was placed to allow air into the beakers. After 24 h, the reaction time was up, and the mixtures were made into boards. In this case, the mixtures were not heated to 90 °C to stop the enzyme reaction, since hot-pressing the samples at 180 °C could be used to stop the enzyme activity.

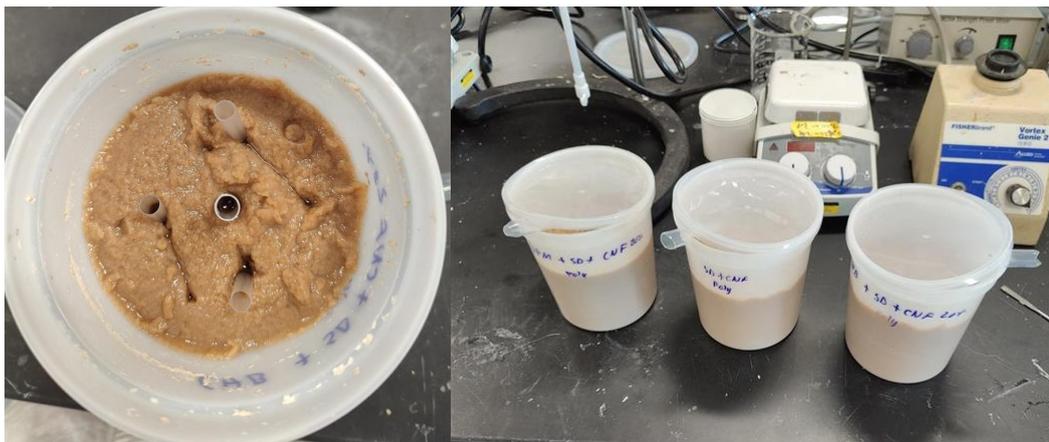


Figure 15. Cups with formulations 3, 4 and 5, polymerisation at 22 °C without aeration.

Formulations 6, 7, 8, 10, 11, and 12 were all made the same way, the only difference was that formulation 6 and 7 used MFC and formulations 10–12 used U-MFC. First, P-SD and MFC or U-MFC were added and mixed, then laccase was added (formulations 6 and 10). Laccase and lignin were added for formulations 7, 8, 11, 12. The mixtures were placed in a 3L Erlenmeyer beaker with an added stirrer. To make stirring easier, 300 to 500 ml water was added to the mixtures. A green rubber gasket was placed between the top of the beaker and the stirrer to avoid evaporation of water. The polymerisation reaction was kept for 24 h in a water bath at 42 °C outside temperature, which resulted in an inside temperature of 39 to 40 °C.

3.3.4 Testing of UMaine Particleboard

Prior to conducting any testing, the particleboards were conditioned in a standard conditioning room for 24 h. The humidity level was set at 50% and the temperature was maintained at 23 degrees Celsius. A FLS Muse 3D Autofocus Desktop CO2 Laser Cutter was utilised to cut each board into three specimens, as depicted in Figure 16. Each specimen and board were labelled with a unique identification number to facilitate the identification of any failures that may occur within specific points of the board. The boards were cut into pieces measuring 30 mm in width and 110 mm in length, providing ample material for subsequent testing of contact angle and surface energy. The cutting parameters used were a speed of 60%, power of 80%, and current of 80%, with the laser making three passes over the same area.

After cutting, the samples were returned to the humidity chamber for an additional 24 hours to ensure that any drying caused by the laser-cutting process was reversed. Once the samples had been in the chamber for 24 hours, they were weighed using a laboratory scale and their dimensions were measured with digital callipers for precision. The samples were then tested using a 6800 series Instron mechanical tester, which had pre-programmed measurements for 3-point bending. The support span was set to 80mm, and the load rate

was set to 3mm/min. The samples were tested until failure, and data was collected from the Instron's 3-point bending measurements, including flexural strength (MPa), flexural strain (%), and modulus (Automatic Young's) (MPa).

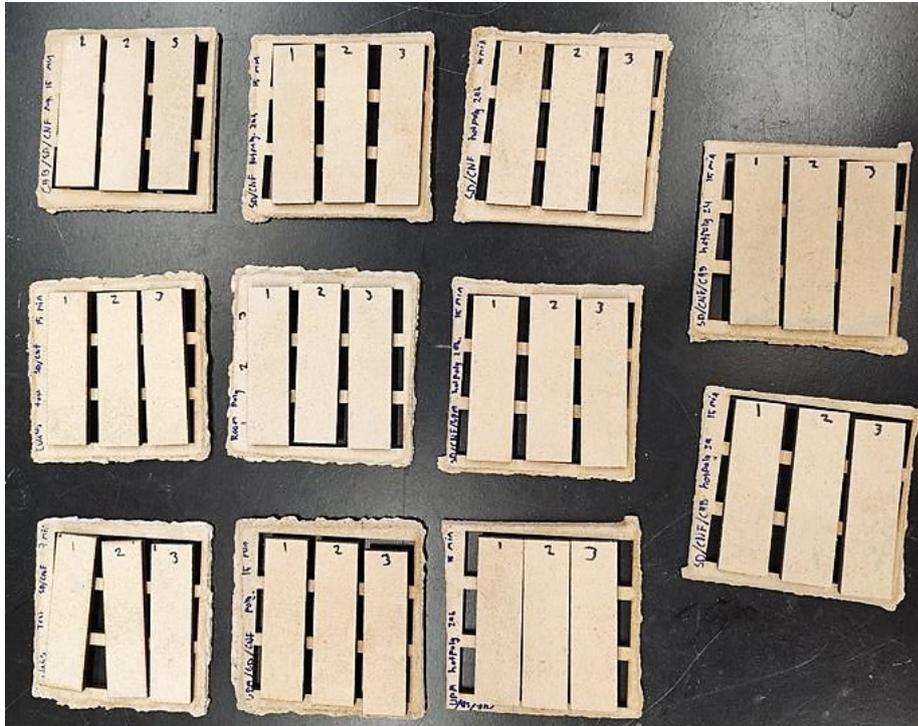


Figure 16. Particleboards cut for 3-point mechanical testing.

The cracked samples were then cut with the same laser cutter into smaller round pieces (\varnothing 2, 6 cm) from both sides of the crack, as shown in Figure 17. It was possible to obtain 12 pieces from each sample, with two boards per formulation. These round pieces were used for measuring internal bonding (IB), water absorption (WA), and thickness swelling (TS).

Internal bond strength is a critical characteristic of particleboard, as it determines the ability of the board to withstand loads and resist breaking or delaminating when subjected to stress. The stronger the internal bonds, the more durable and structurally sound the board will be, making it more resistant to wear and tear over time. A higher IB value indicates that the particles are more tightly bonded together, resulting in a superior quality particleboard. The resin, in this case MFC, acts as the adhesive between the fibres and polymerised lignin is used to enhance the strength of the composite.

Internal bond was tested by securely attaching the samples to metal plates using hot glue with a strength rating of A+. The samples were then placed a standard humidity room at 50% relative humidity and 23 °C for 24 h. Samples with the closest densities to each other and other formulations were chosen for testing. Six samples per formulation were used for IB testing. The samples were tightly clamped between two anti-slip material-fitted clamps for measurement. Wing nuts were also fitted with silver tape to prevent slipping. Samples glued and inserted between the clams is shown in Figure 17.

Thickness swelling and water absorption were tested by submerging six labelled samples that had been weighed and measured beforehand. The samples were submerged in water for 2 hours and 24 hours. Initially, the samples floated, to ensure they were fully submerged, weights in the form of lids were placed on top. After 2 hours, all the samples stayed under the water surface without additional weights on top, and the samples could be measured and weighed. Before measuring water absorption and thickness swelling, the excess water on the surfaces was wiped off. The same method was used when measuring the samples again after 24 hours. Water absorption is given as a weight increase of the sample in percentage according to Equation 4. Thickness swelling is calculated according to ASTM D 3502-76 (ASTM 1999) with Equation 5.



Figure 17. Round particleboard pieces for testing IB, TS and WA. In the top right corner IB testing and in the bottom two pictures, boards submerged in water.

Sample results were run through SPSS program with analysis of variance (ANOVA) normalisation according to density for all samples after testing.

Equation 4
$$WA (\%) = [(W_w - W_i) / W_i] \times 100$$

Above, W_w is the wet weight (g), and W_i is initial dry weight (g).

Equation 5
$$TS (\%) = [(T_0 - T_i) / T_i] \times 100$$

Above, T_0 is the wet thickness (mm), and T_i is the oven dry thickness (mm).

Contact angle and surface energy were measured with a Krüss mobile surface analyser (MSA). The samples used for testing were the widest pieces left from the first laser-cutting, as shown in Figure 18. One side of the samples was first sanded down with P150 grid sandpaper to remove the rough surface created by the metal wire mesh. The samples were then dusted and sanded again with P400 grid sandpaper. Finally, the samples were cleaned again with compressed air and paper hand sheets. The MSA was filled with deionised (DI) water (polar) and diiodomethane (non-polar) liquid. The goal was to obtain at least 12 measurements of each liquid on the surfaces. However, due to some internal problems, the MSA did not give constant readings. Outlier measurements were excluded from the mean value calculation.

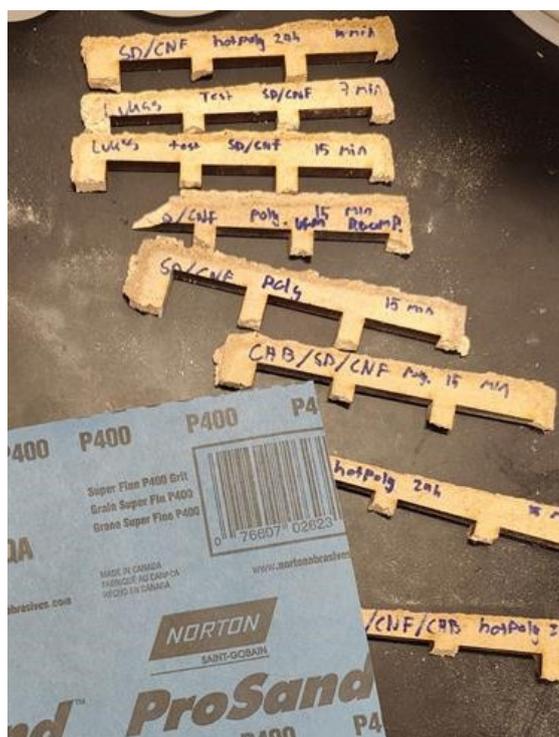


Figure 18. Samples for CA and SE testing and sandpaper used to sand down them down.

SEM images were taken using a (Zeiss NVision 40 FIB/SEM) on cracks in the lignin-polymerised boards, SD/MFC, SD/MFC/AL, and SD/MFC/KL. The cracks were created by freezing samples in liquid nitrogen and cracking them while still frozen. Negative staining was used on the samples as preparation for imaging and a conductive coating was applied on the sides to prevent charging on the specimens. SEM imaging was conducted to see how well MFC binds to the wood particles, as well as to see if lignin could be spotted in the composite. The highest quality images were captured with 1.74 KX and 10 KX magnification. To gain insight into individual fibres, images were captured using both Signal A = SE2 and Signal A = InLens lenses.

4 Results and Discussion

The results of the tensile testing and contact angle measurements of the MFC films can be found in Appendix A, along with the results of the particleboards produced at ÅAU. The results of the mechanical testing, internal bond, thickness swelling, and water absorption tests, as well as ANOVA normalised values for the composites produced at UMaine, can be found in Appendix B.

4.1 Characterisation of MFC and U-MFC

The characteristics of MFC and U-MFC should not differ significantly from each other, as can be seen in Table 6. What differentiates the two is the lignin content in U-MFC (5.4%) and that they were not produced the same way. As shown in Table 6, the length and curl are similar, however, the width, kink angle, and fines content differ between the two. The fines and kink angle are a result of longer grinding time of the fibrils in Masuko. The more fibres are grinded, the wider they also become, since they are flattened by the pressure applied, resulting in the fibres/fibrils breaking and producing more fines. The fines content in MFC could be studied to determine how the fines affect the mechanical strength properties and bonding properties of MFC to wood particles.

Table 6. Characteristics of MFC and U-MFC used for films and LDP.

	Length (mm)	Width (μm)	Kink angle ($^{\circ}$)	Curl (%)	Fines (%)
MFC	0.367	18.39	38.7	9.89	85.19
U-MFC	0.397	27.0	128.0	9.5	95.1

4.1.1 Morphology

MFC and U-MFC were both studied under microscopy to identify any differences between the two. As shown in Figure 19, they both appear fairly similar to each other. In both materials, larger fragments of fibres can be observed mixed with the fibrils.

Upon comparing the two 5X magnification figures, it can be observed that MFC has more distinct fibrils than U-MFC, and U-MFC has some darker spots along the fibrils, which is due to the presence of lignin. At 10X magnification, U-MFC (fines content ~95%) have shorter fibrils than MFC (fines content ~90%). Lastly, at 20X magnification, it can be seen that U-MFC have individual fibrils that have darker spots on them. This is due to the presence of lignin, which makes up about 5% of U-MFC, resulting in the material being darker in colour. Microscopy also shows that the degree of fines can be observed to differ in the way the fibrils interact with each other. The longer the fibrils are, the more they

tangle around the fibrils. This also means that when preparing samples and working with a lower degree of fines MFC, the suspension made must be thoroughly mixed to ensure that the fibrils are separated from each other.

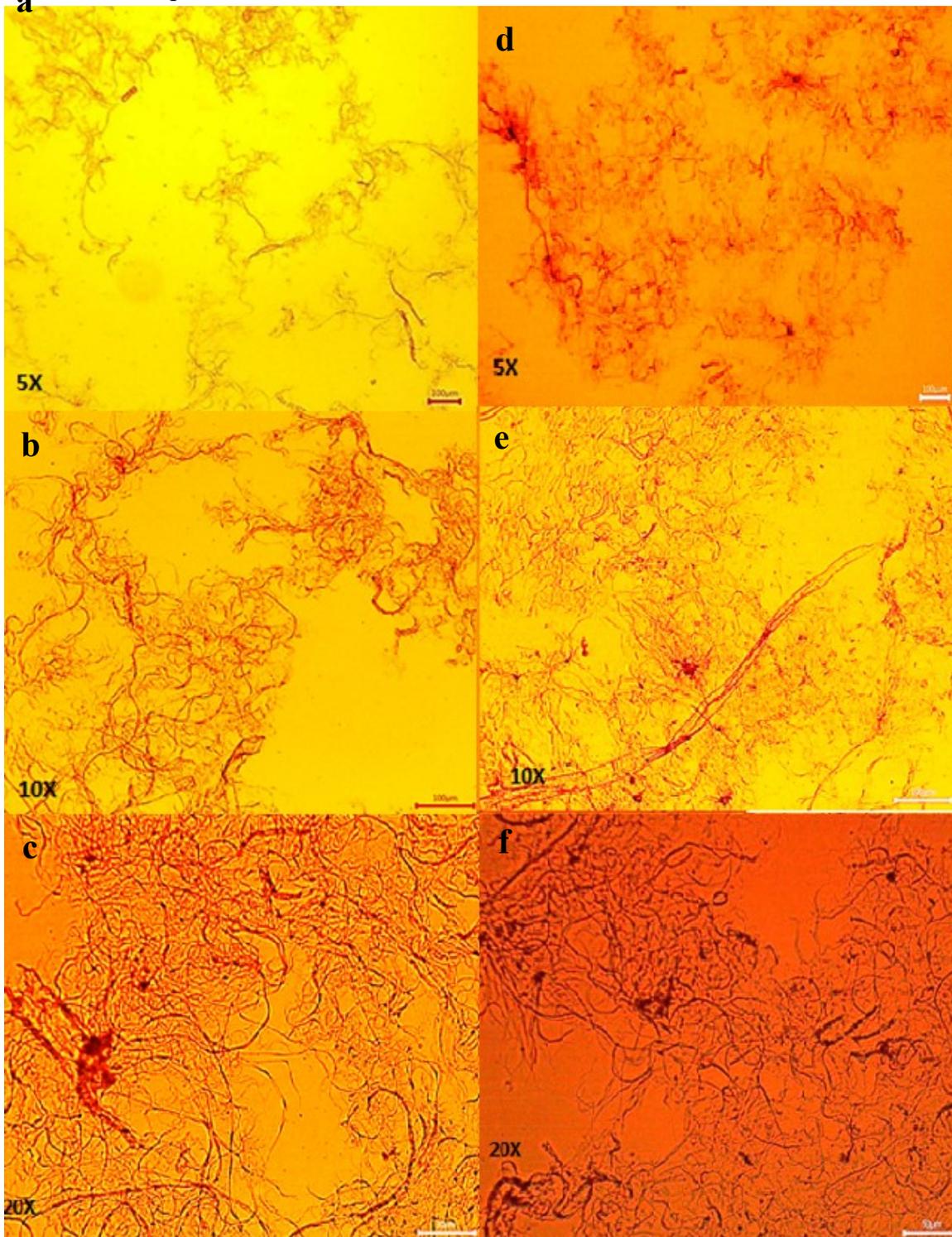


Figure 19. Microscopy images of MFC, a), b), and c), and U-MFC, d), e), and f). a), b) d), and e) with 100 μm scale, c) and f) with 50 μm scale.

4.1.2 SEM Imaging of MFC Composites

Scanning electron microscopy (SEM) was used to examine the fibrils in more detail and to determine how lignin is attached to the fibrils. In Figure 20 a, b), nanoparticles can be seen on the fibrils. These nanoparticles are typical precipitations of lignin. As discussed in 2.1.3, the nanoparticles have comparable size and spherical structure, showing small size distribution of either large or small LNP, as shown in Figure 4. It is expected to see these LNPs on the fibrils, since the U-MFC contains about 5% lignin. Figure 20c depicts a structure with 90° angles, which is suspected to be a crystallised mineral found in the tap water used to prepare the U-MFC. SEM imaging of pure MFC was not possible due to extensive crystallisation that obscured all fibrils.

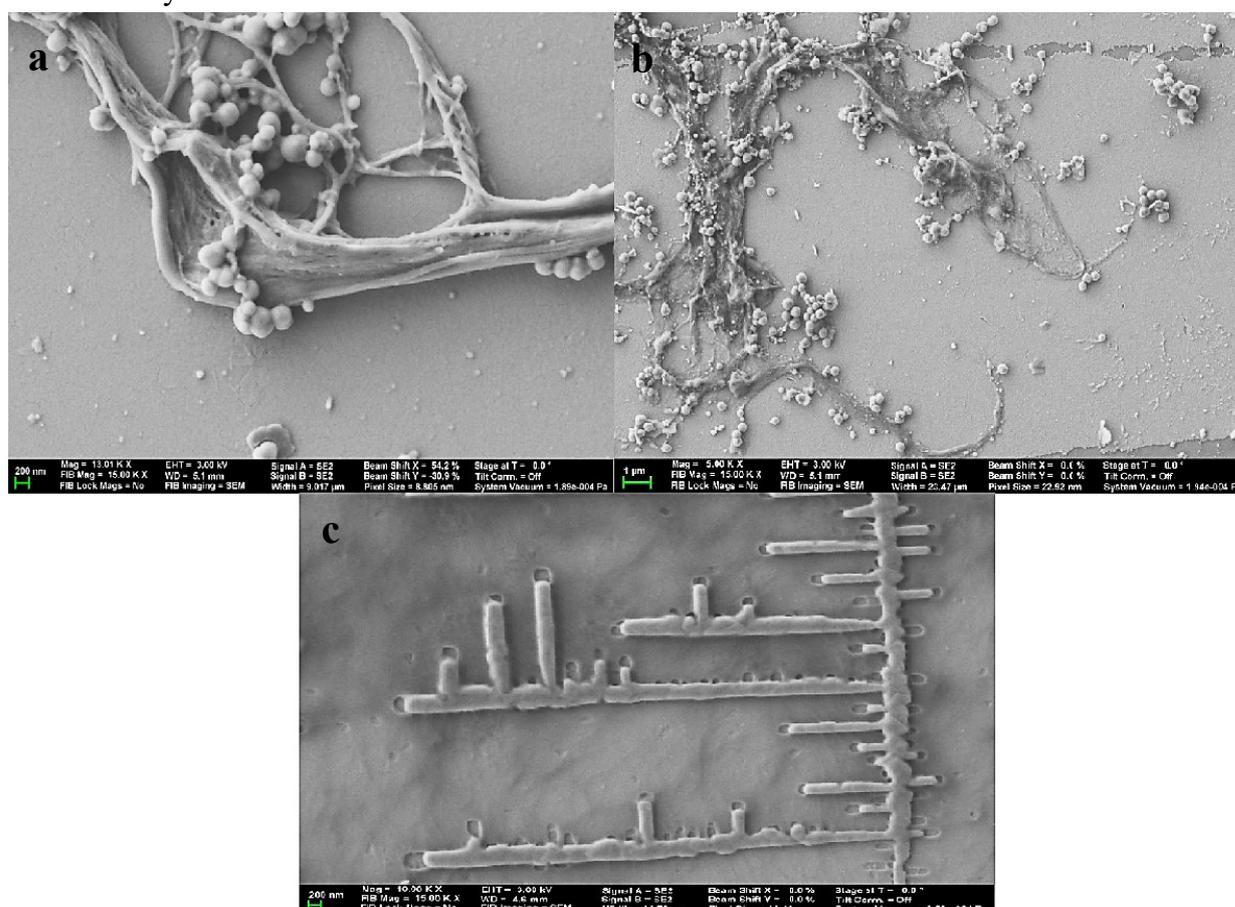


Figure 20. SEM image of U-MFC, showing lignin nanoparticles attached to the fibrils a) and b), as well as crystallised mineral structure c).

MFC was polymerised with KL and AL to assess the visibility of polymerised lignin on the fibrils. The samples were polymerised for 24 h under continuous stirring on a hot plate, with a MFC to lignin ratio of [80:20]. Figure 21 demonstrates reduced presence of crystalline particles and the presence of small LNPs. In this case, AL lignin is present on the fibrils, however, in a limited amount compared to KL. The first image of AL exhibits some charging, making it difficult to observe the lignin particles. KL appears to have produced better results, with lignin particles adhering to the fibrils and a shape similar to dried lignin.

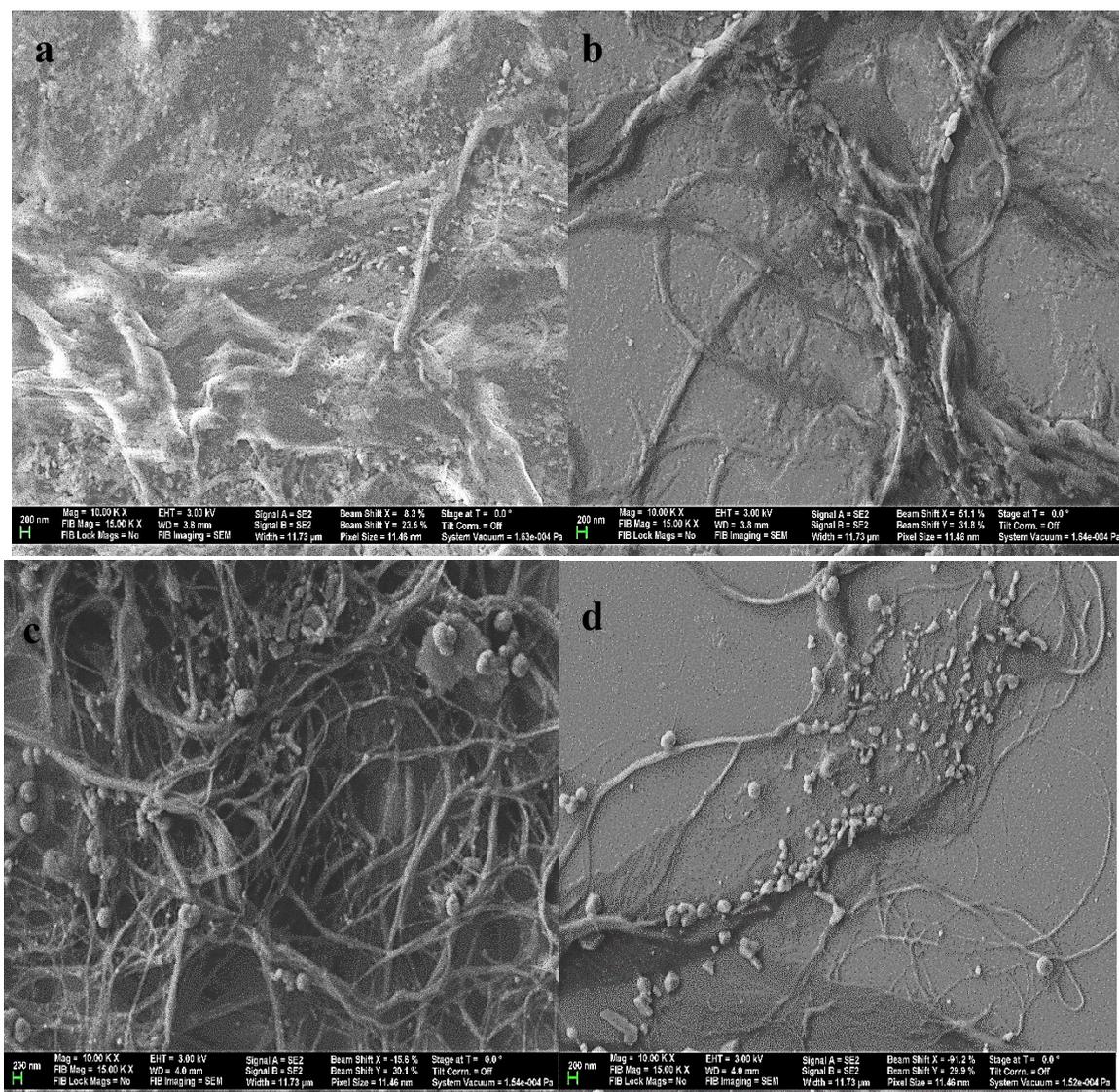


Figure 21 SEM images of MFC polymerised with AL a, b) and KL c, d). Scale bar: 200 nm.

In conclusion, the results suggest that polymerisation of lignin with laccase is partially effective. Further optimisation through studies to determine the extent of polymerisation, and the impact of time and temperature, are necessary to fully understand the process.

4.2 Film Formation of L-MFC Films

Pure MFC films were made as a control to ensure the films could be produced in petri dishes. The challenge in making the films is that the films are drying along the edges first, which causes some shrinkage. This shrinkage may result in uneven films. To ensure that all samples were suitable for testing, extra films were produced.

In the first polymerisation attempt, in-situ polymerisation time was set to 5 h, with a lignin content of 10%. It can be seen in the images that the lignin has migrated to the sides. The

drying surface was checked with a level to ensure that the drying would be as even as possible. The reaction time was increased to 6 h, to see if longer polymerisation would change the outcome. As shown in Figure 22, there are some darker spots in the brown area. This is likely due to KL being difficult to dissolve at first, which can indicate that pH was too low, and that the polymerisation time was too short.

The KL films in Figure 22 can be seen to have darker spots in them, which is due to the lignin not being fully dissolved in the water. AL is much easier to dissolve in water, while KL needs a pH of 11.5 to dissolve completely. The slow drying of the films may have contributed to the agglomeration of lignin particles during drying, and the drying surface may not have been completely level. Another reason for the uneven lignin distribution could be that the polymerisation time was too short or that the 10% lignin content is too low. The in-situ polymerisation reaction time was set to 6 h.

When films with 10% lignin were polymerised for 24 h and let to dry, the lignin migration still caused problems in the film. The problem could still be due to a too-low lignin concentration, as increased polymerisation time did not help. As seen in Figure 22, the smaller petri dishes with KL have the lignin concentrated in the middle, while the others have it alongside the edge. The samples speed mixed shows no improvement in lignin migration. No further tests were made on these samples. The conclusion from this experiment indicated that the lignin concentration needed to be higher or that the solution needed to be stabilised to prevent the migration of lignin.

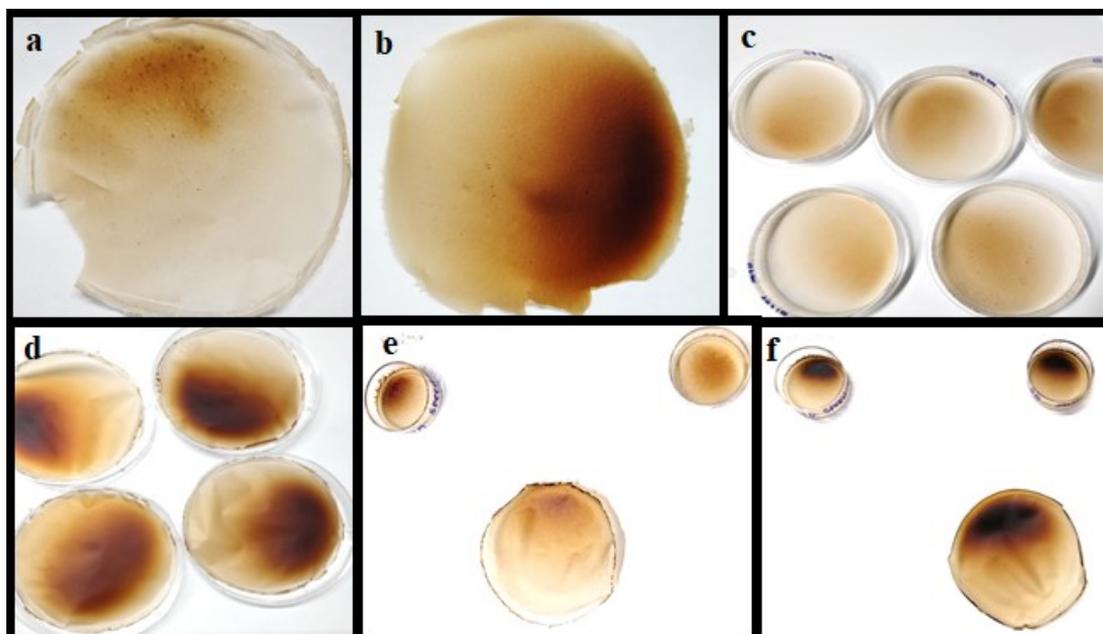


Figure 22. MFC films polymerised 5h with 10% lignin, a) KL, b) AL. MFC films polymerised 6h, c) KL and d) AL, and polymerised 24h e) KL and f) AL.

The result from increasing the lignin concentration to 15% and 20%, show that it did not restrict lignin migration, as shown in Figure 23. Lignin is still concentrated on one side of the film and both KL and OL films have lignin particles present. Although the higher lignin concentration made the films darker in appearance, the films were not uniform. Further methods were needed to stabilise the suspension and prevent lignin migration.

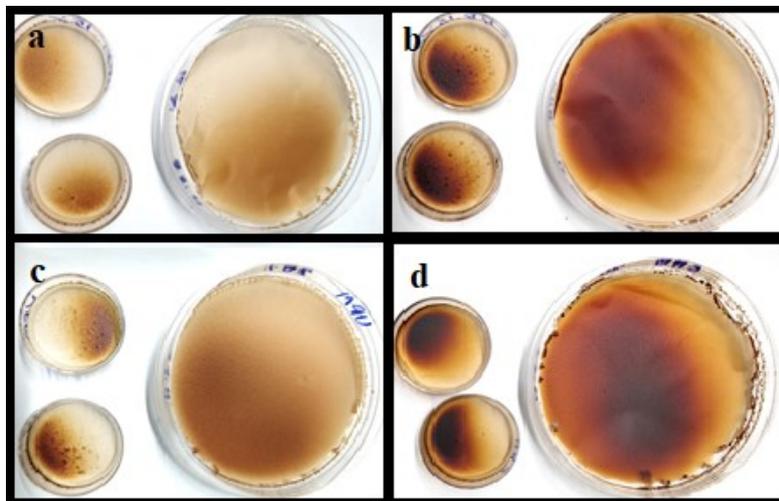


Figure 23. MFC films polymerised for 24h with 15% a) KL, b) AL, 20% c) KL, and d) AL.

Adding CMC to the L-MFC mixture prevents the lignin from migrating to one area, as shown in Figure 24. The films exhibit a uniform distribution of lignin. CMC, as a thickening agent, reduces the tendency of particle migration compared to its absence. However, incorporation of CMC alters the film properties, resulting in easier detachment from the petri dish and reduced shrinkage at the edges.



Figure 24. MFC films with CMC 10 wt%. From the left AL 20%, AL 10%, KL 10%, KL 20% and MFC 100% without CMC.

In conclusion, the objective of this study was to examine the impact of in-situ polymerisation of lignin on the properties of MFC films. The experiment results indicate that producing L-MFC films through in-situ polymerisation of lignin is challenging due to lignin migration. However, the addition of a stabilising agent, enables the creation of homogeneous films with improved peeling properties. Overall, the study suggests that further research is needed to optimise the in-situ polymerisation process of lignin in MFC films to improve their properties.

4.2.1 MFC films contact angle

To evaluate the wettability of the MFC films, contact angle (CA) measurements were conducted. The top surface of each film, characterised by its rough texture, and the bottom surface, which exhibited a glossy appearance due to contact with a smooth petri dish during drying, were analysed. The CA was measured at 3.48 seconds, 9.20 seconds, and 19.2 seconds, with the average value being a result from three measurements.

As expected, the initial CA was observed to be higher at the onset of the measurement and gradually declined over time. This reduction in CA can be ascribed to the natural phenomenon of surface spreading, absorption, and swelling, indicating that the results should be interpreted with caution as the drop volume initially decreases, but later fluctuates over time. Additionally, the glossy side of the films exhibited a slightly higher CA than the rough side, which may be a result of a smoother surface.

The data indicated that the pure MFC film exhibited similar CA to the rest of the films. However, the high standard deviation observed in the measurements highlights the variability in contact angle among different samples. According to Kolar, et al., 2021, MFC film should have an average CA of $\sim 43^\circ$, while the data show that MFC (top) has the highest CA. Lignin, which is a hydrophobic substance, should increase the contact angle when more lignin is added. Comparing the 10% lignin with the 20% lignin added in the films, the CA slightly increases, as shown in Table 7.

It is important to note that the addition of CMC can also influence the contact angle of the films. As CMC acts as a stabilising agent, it is likely that its inclusion in the films resulted in a lower contact angle as compared to the pure MFC film. Furthermore, the data suggest that CMC increases the water retention of the films. As mentioned in section 2.4, CMC should increase the water retention, which can be seen as the water retention increases with added CMC. To understand the wettability of the film better, more films need to be tested and more research on the subject is needed.

Table 7. Average contact angle after 3.48 s, 9.2 s, and 19.2 s, on top and bottom surface of MFC films with standard deviation. Values given in [Å°].

Sample	CA Top	CA Top	CA Top	CA Bottom	CA Bottom	CA Bottom
	3.48 s	9.2 s	19.2 s	3.48 s	9.2 s	19.2 s
MFC 100%	85.1 (6.2)	66.5 (2.0)	61.8 (3.1)	63.8 (27.1)	59.2 (24.6)	55.22 (21.42)
MFC + AL 10%	44.1 (3.6)	37.5 (2.3)	35.6 (2.2)	61.4 (8.2)	58.3 (7.7)	52.3 (3.4)
MFC + AL 20%	59.6 (5.3)	56.5 (3.3)	55.1 (1.5)	63.6 (3.4)	60.5 (2.2)	59.0 (2.8)
MFC + KL 10%	65.4 (12.3)	57.5 (6.7)	54.5 (7.5)	54.6 (2.3)	52.2 (2.6)	51.1 (2.6)
MFC + KL 20%	59.1 (4.9)	57.5 (4.4)	56.0 (4.3)	67.4 (3.4)	65.1 (3.0)	64.1 (3.1)

4.2.2 The Effect of Polymerisation

Adding lignin to MFC film enhances its mechanical properties. The polymerised lignin can increase maximum load, tensile stress, and MOE by 34-53%, 36-59% and 38-61% respectively, as shown in Table 8.

With 10 or 20 wt% lignin, the mechanical properties are improved, but samples with 10 wt% have higher tensile strength. Samples with 20 wt% have better strength and elongation. The formulation of 20 wt% lignin was set for particleboards based on results from lignin polymerised MFC films.

The MFC films had a consistent fibre content, resulting in increased density with additional lignin. Further analysis of the impact of lignin on the films' properties could be achieved by decreasing the MFC content while maintaining density with increased lignin. The addition of CMC to the MFC film matrix would facilitate a more accurate evaluation of the strength characteristics among different formulations.

Table 8 Mechanical strength of MFC based films with added 10% and 20% alkaline lignin or kraft lignin. Standard deviation is in parenthesis.

Sample	Maximum Load (N)	Tensile Stress (MPa)	MOE (MPa)
MFC 100%	13.9 (3.5)	85.7 (21.9)	4206.5 (585.7)
MFC + AL 10%	18.6 (1.5)	120.3 (9.7)	5819.3 (887.8)
MFC + AL 20%	20.4 (2.2)	109.2 (9.8)	6459.2 (386.9)
MFC + KL 10%	20.5 (1.8)	136.7 (12.3)	6418.5 (578.6)
MFC + KL 20%	21.3 (1.2)	116.4 (5.0)	6766.6 (410.9)

4.3 Particleboard Results

4.3.1 ÅAU Particleboards

The properties of LDPs are highly dependent on the type of wood particles and binder used. Sawdust, for example, exhibits resilient properties when used as an individual material, but as a compressed composite, it lacks sufficient internal bonding properties and can be considered a fragile material. To promote a better understanding of how binders affect the mechanical properties of composites, it is important to study different formulations.

Table 9 presents the mechanical properties of the initial LDPs. The addition of 10 wt% MFC binder to sawdust (SD) has been found to almost double the mechanical strength properties of the composite. Increasing the MFC content to 20 wt% further enhances the mechanical strength properties. These values presented were not normalised by density and should only be used as indicative values for different formulations.

It is also important to note that some specimens were discarded from the results due to signs of shear failure and insufficient bonding in the middle, which may have been a result of poor moisture removal and short hot-pressing time, as discussed in section 2.5. The densities and weights of the boards can be found in Appendix A.

From testing the mechanical strength of the films with added lignin, the best mechanical strength was obtained from films with 20 wt% lignin added. Therefore, only 20 wt% was tested. The addition of AL improves the maximum load, stress, and flex modulus, indicating that alkaline lignin can be used to improve mechanical properties in particleboards. However, soluble lignin can still be found in wastewater during the dewatering process. Therefore, the lignin concentration is lower than 20 wt% in the final product. KL used in the composite did not significantly improve the mechanical properties, except for increasing the flex modulus.

Table 9. Average mechanical properties with standard deviation as result from the flexural test on ÅAU LDPs. The formulation is an addition to SD.

Sample Formulation	Maximum load (N)	Flexural strength (MPa)	Modulus (MPa)
SD 100%	2.3 (0.5)	0.3 (0.1)	132.2 (74.7)
MFC 10%	16.0 (6.0)	2.0 (0.5)	184.1 (23.1)
MFC 20%	33.8 (4.2)	5.2 (0.7)	558.5 (68.2)
AL 20%	39.1 (3.1)	6.2 (0.5)	740.9 (63.5)
AL 20% + CMC	23.7 (4.4)	3.8 (0.7)	363.2 (49.7)
AL 20% + C135	43.0 (4.7)	6.9 (0.6)	1051.9 (189.4)
AL 20% + CMC + C135	40.3 (4.0)	6.4 (0.5)	846.3 (108.5)
KL 20%	34.7 (2.1)	5.6 (0.5)	649.2 (96.5)
KL 20% + CMC	34.3 (2.6)	5.3 (0.4)	673.4 (45.9)
KL 20% + C135	38.3 (5.0)	5.9 (0.8)	763.6 (95.3)

The addition of CMC was tested as a way to retain the lignin particles in the particle mixture. However, the result showed that the addition of CMC resulted in slower dewatering of the fibre mixture, and for the mixture with added AL, the mechanical properties were lower than of MFC 20 wt%. For the boards with added KL, the addition of CMC only improved the flex modulus, still being in the same range as the composite with 20 wt% added KL.

The addition of cationic starch (C135) to the composite board improves all the mechanical properties, which is expected since it can be used in the paper industry for this reason. However, it should be noted that the effluent of these composites still had the same dark colour, indicating that lignin still is in its soluble form and is being filtered away with the effluent. The additional board with CMC and C135 added had the same problem with poor dewatering and lignin in the effluent, and with 3 wt% less CMC added.

Based on the results, the formulation where 20 wt% lignin had been added to MFC was used for further experiments. However, it should be noted that lignin in the effluent meant that the final lignin concentration was lower than 20 wt%. Additionally, the lignin present in the wood had not been polymerised in these experiments. The cutting technique used may also have caused cracks in the samples, therefore, all possible reasons for the occurrence of cracks were addressed in the following experiments.

4.3.2 UMaine Particleboard

To prevent slip failure and cracking in the boards made at UMaine, measures were taken to increase the dewatering and hot-pressing time to 15 min. As to further prevent failure within the board, the samples were cut with a laser cutter. The moisture content was not analysed after dewatering. Table 10 presents the formulations used and their corresponding

reference number. Normalised values and initial values for the experiment can be seen in Appendix B.

The type of sawdust used (P-SD) had a smaller size than the SD. Therefore, samples with MFC 20 wt% were made to compare the composites. The pressing time was set to 7 min and 15 min respectively to see how the pressing time influences the properties of the board. The results of the mechanical testing of the UMaine boards are shown in Table 10. The increased hot-pressing time (7–15 min), seen in formulation 2, was found to have inferior mechanical properties. The composite with the shorter pressing time (7 min) has better mechanical strength values than formulations 3 to 8. It can be concluded that the hot-pressing time plays a significant role in determining the mechanical properties of the LDPs.

The mechanical results from formulations 3, 4, and 5 indicate that the polymerisation reaction at room temperature causes the composite material to lose some of its mechanical strength. This may be an indication that laccase is breaking down the lignin within the sawdust, making the fibres weaker. A similar result can be seen in formulation 6, where laccase is reacting with SD and MFC.

Table 10. Average mechanical properties with standard deviation as result from flexural test on UMaine LDPs. HP (number indicating minutes of hot-pressing), T22 (polymerisation at 22 °C, with minimal aeration), T39 (polymerisation at 39 °C), and NP (no laccase added and no polymerisation).

Formulation	Formulation No.	Flexural Strength (MPa)	Flexural Strain (%)	Modulus (Young's) (MPa)
SD/MFC-HP7	1	7.4 (0.8)	1.1 (0.07)	996.1 (109.5)
SD/MFC-HP15	2	5.8 (0.2)	1.1 (0.05)	764.2 (54.8)
SD/MFC-T22	3	4.5 (0.1)	1.3 (0.08)	564.4 (34.8)
SD/MFC/AL-T22	4	4.7 (0.2)	1.6 (0.04)	537.8 (34.0)
SD/MFC/KL-T22	5	5.4 (0.3)	1.3 (0.04)	687.9 (31.6)
SD/MFC-T39	6	4.6 (0.5)	1.3 (0.1)	581.3 (68.0)
SD/MFC/AL-T39	7	5.9 (0.8)	1.4 (0.3)	701.7 (140.8)
SD/MFC/KL-T39	8	5.6 (0.7)	1.5 (0.3)	642.7 (152.2)
SD/U-MFC-NP	9	7.1 (0.3)	1.0 (0.03)	939.4 (41.8)
SD/U-MFC-T39	10	7.2 (1.0)	1.0 (0.07)	969.4 (143.9)
SD/U-MFC/AL-T39	11	9.8 (0.6)	1.0 (0.05)	1295.9 (88.1)
SD/U-MFC/KL-T39	12	8.7 (0.9)	1.0 (0.06)	1157.9 (114.2)

Formulations 7 and 8 show similar mechanical strength properties as the LDPs made at ÅAU with 20 wt% added lignin. This indicates that in-situ polymerisation can be conducted with or without the SD present in the reaction. It also suggests that the particle size distribution does not play a significant role and that both pine and spruce function similarly as a reinforcement in the composite. The formulations that use U-MFC (9–12) can be seen to have higher mechanical strength properties than the ones with MFC. It is believed that the improved mechanical properties are due to the presence of roughly 5% lignin in the U-MFC, which can be utilised in the polymerisation process of lignin. The addition of further lignin may result in additional improvement in properties. The strong bonding properties of lignin within composites contribute to improved mechanical strengths, but at the cost of decreased flexibility.

Contact Angle

The effects of treated MFC and U-MFC with and without polymerised lignin on LDP panels can be seen in Figure 25, which represents the contact angles of polar and non-polar liquids on the panel surfaces. Comparing samples 1 and 2, it can be observed that increased hot-pressing time decreases the surface energy as detailed in Appendix B. This decrease in surface energy results in an increase in the contact angle of both polar and non-polar liquids. Lignin can lower surface tension, which can be seen in samples 4 and 5, where lignin should be in its free depolymerised form and increase the contact angles of the liquids; however, the contact angles are similar to sample 2.

The reason for this may be that laccase activates the lignin present in the P-SD, the additional added lignin and laccase can have been acting as a catalyst to accelerate the process of creating fibre-to-fibre bonds when hot-pressed, resulting in a more potent adhesion and lower surface tension (Euring et al., 2016). This phenomenon should also be visible in samples where lignin is added to lignocellulosic materials mediated by laccase; however, in other samples, the contact angles are lower. This can be caused by there being too low amount of the laccase mediator in the mixtures to account for the lignin present in the wood and U-MFC. Samples 6–11 have similar contact angles for both polar ($> 90^\circ$) and non-polar liquids. This indicates, whether lignin is present or not, the contact angle and surface energies are not as much affected by the presence of lignin.

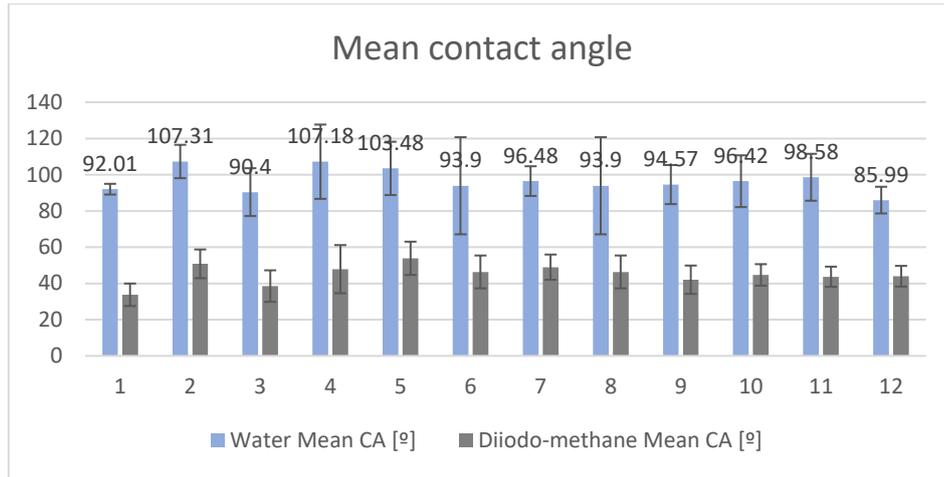


Figure 25. Mean contact angle for polar and nonpolar liquids on LDP panels.

All the samples were prepared and sanded in the same manner to ensure that the surfaces had the same roughness. However, the differences in contact angles indicate that some sample surfaces might have been smoother than others, which may have led to differences in contact angles. Another likely reason for the difference in contact angle may be measurement errors, as the Krüss surface analyser had problems with dispensing the liquids and reading the contact angles. Therefore, the sample sizes are not equal, and the standard deviation is either too high or too low, as larger differences could not be distinguished and rejected.

Water Absorption and Thickness Swelling

The increase in water absorption (WA) and thickness swelling (TS) of particleboard samples can be observed in Appendix B, showing higher values after 24 hours of submersion than after 2 hours. The different formulations were found to have varying properties in terms of WA and TS, as revealed by the normalisation analysis (ANOVA), which was conducted to eliminate the effect of density on the results.

The highest water absorption can be seen in sample 1, which is the only sample hot-pressed for 7 min (Figure 26). The result after ANOVA shows that sample 1 performed the worst, with a 129.3% weight increase after 2h and a total of 150% weight increase after 24 h. This indicates that hot-pressing the composite longer will make the LDP denser, which can decrease water absorption. The sample with the lowest water absorption after 2h, was sample 10, with only 103.9% weight increase and 114.7% after 24 h, thus being equally resistant as samples 9 (117.6%), 6 (134.0%) and 12 (108.3%) after 24 h, within sig. ($p=0.127$).

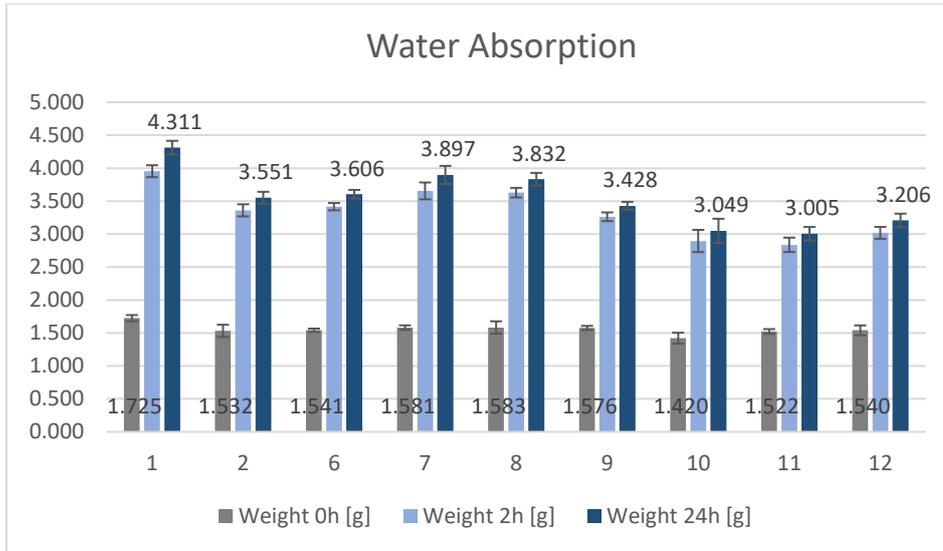


Figure 26. Water absorption on UMaine LDPEs, presenting the value of the initial weight and weight after 24 h.

The size of the samples can have affected the results, as the samples used were smaller than the standard method used and, therefore, the water can have penetrated more along the edges. The samples were also cut with a laser cutter (burned edges), which can have affected how well the water can penetrate through the sides.

Thickness swelling was only measured in one dimension (thickness), and the diameter of the samples was only measured before submersion. Representative thickness swelling over time can be seen in Figure 27. After ANOVA, the samples that had the highest thickness swelling were sample 1, with 38.9% (2h) and 47.1% (24 h), sample 7, with 21.8% (2h) and 24.8% (24 h) and sample 8, with 24.7% (2 h) and 28.0% (24 h). Sample 11 had significantly less swelling than other samples, with only 19.8% (2h) and 21.9% (24 h). Other samples that performed well were sample 10 with 15.6% (2h) and 18.8% (24 h) and sample 12 with 18.8% (2 h) and 21.1% (24 h).

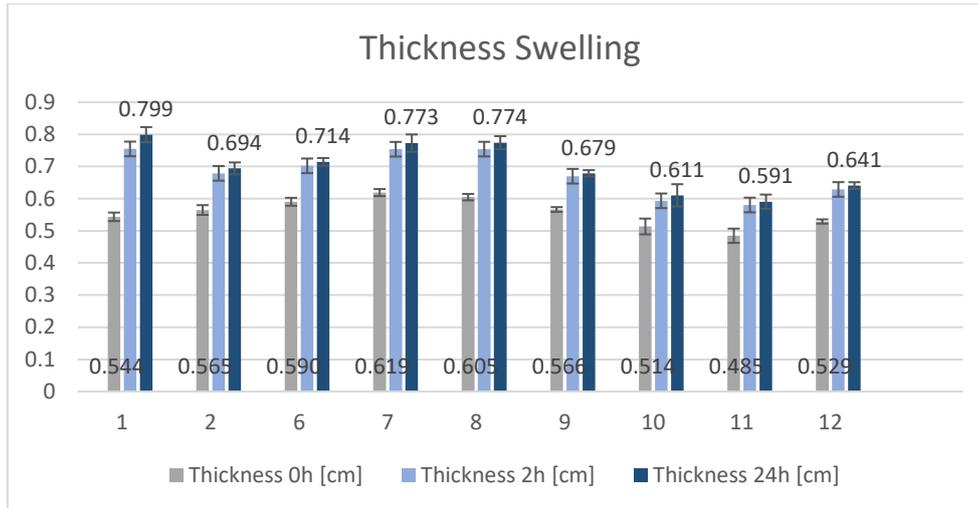


Figure 27. Thickness swelling on UMaine LDPs, presenting the value of the initial thickness and thickness after 24 h.

According to (TS EN 312, 2005), particleboard used in load-bearing and heavy-duty applications requires the maximum thickness swelling to be 14–15% after 24 h submersion in water. The LDPs do not meet the Turkish standard requirements. However, by increasing the density and binder, the boards could meet the standards (Güler & Büyüksarı, 2011). These LDPs are appropriate only for indoor use, where they will not be impacted by moisture.

Internal Bond Strength

The internal bond strengths, after normalisation, show samples with and without added lignin being equally strong. Samples in order from the highest performing are 10, 2, 1, 11, 9, 4, and 8, and they all fit in the same group within sig. ($p = 0.135$), as seen in Figure 28. However, the results indicate that polymerisation of natural lignin present in the U-MFC works better than polymerisation of added technical lignin in the composites. For samples 1 and 2, it can still be seen that increased hot-pressing time gives the samples better IB strength, although not on a significant level. The samples polymerised at room temperature show weaker IB strength than samples that were polymerised at ideal conditions. However, sample 12 with U-MFC and added KL lignin is in the same lower group as samples 7, 5, 3, and 6. Samples only containing MFC or U-MFC have the highest IB strength.

Formulation	N	1	2	3	4	5
6	6	.4017				
3	6	.4300	.4300			
5	6	.4400	.4400	.4400		
12	6	.4400	.4400	.4400		
7	6	.4567	.4567	.4567	.4567	
8	5		.4820	.4820	.4820	.4820
4	6		.4900	.4900	.4900	.4900
9	6			.5000	.5000	.5000
11	6			.5017	.5017	.5017
1	6				.5117	.5117
2	6				.5167	.5167
10	6					.5350
Sig.		.109	.085	.081	.090	.135

Figure 28. Internal bond strengths (MPa) for UMaine LDP samples 1-12. Demonstrating that inclusion of lignin does not significantly change the IB strength.

SEM Imaging of Particleboard

Scanning electron microscopy images were taken of three samples, to see whether lignin present in the composite could be spotted. Additionally, SEM images can be used to analyse the adhesion between the particles and the binding agent, as this can impact the overall quality and performance of the particleboard.

For MFC to function as a binder in the particleboard, it must be added in a wet state. The addition of MFC to SD results in the creation of hydroxyl (-OH) groups through free energy, which bond with hydrogen (-H), and spontaneous dewatering occurs. The MFC fibrils bind the SD particles together to form the composite. Figure 29 illustrates how the MFC fibrils have created a web-like structure to hold the SD particles in place. The SD particles can still be seen without MFC bonded to them, indicating inadequate mixing and weak spots present in the composite layer. The mixing of SD and MFC should have been enough. Therefore, the mixture could have contained too much water in the dewatering process. The mixture should have been re-mixed after some dewatering to ensure that MFC would cover all SD particles in the composite.

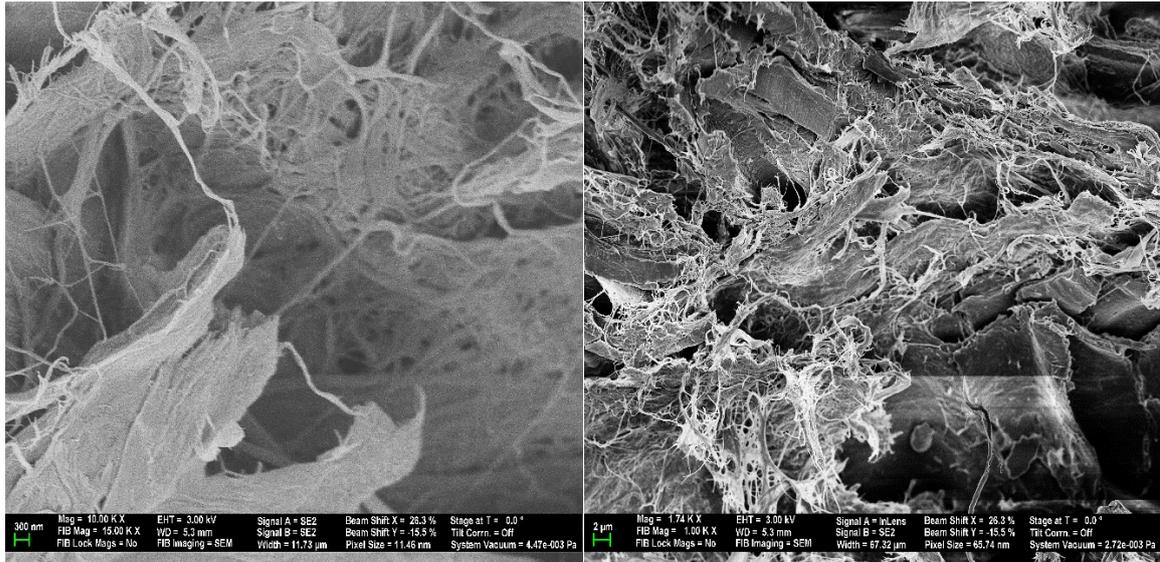


Figure 29. SEM images of SD/MFC [80/20] composite, showing MFC bonded to P-SD fibres in cryo-cracked sample.

Samples which were mixed for 24 h before dewatering and pressing show more uniform MFC across the cryo crack, as shown in Figure 30. The space between the SD particles is filled with MFC fibrils that form a network of fibrils. With increased mixing time, the uniformity is better within the composite, even though a shorter mixing time would indicate a better internal bonding strength, as the fibrils are more present in the gaps between the SD particles. With negative staining, no lignin nanoparticles could be seen in the cracked composite samples. This absence of lignin nanoparticles could indicate that the LNPs have melted and become incorporated in the wood particles and MFC during the hot-pressing process. When 20 wt% lignin is added to MFC, it is challenging to identify any lignin nanoparticles on the fibrils in the network.

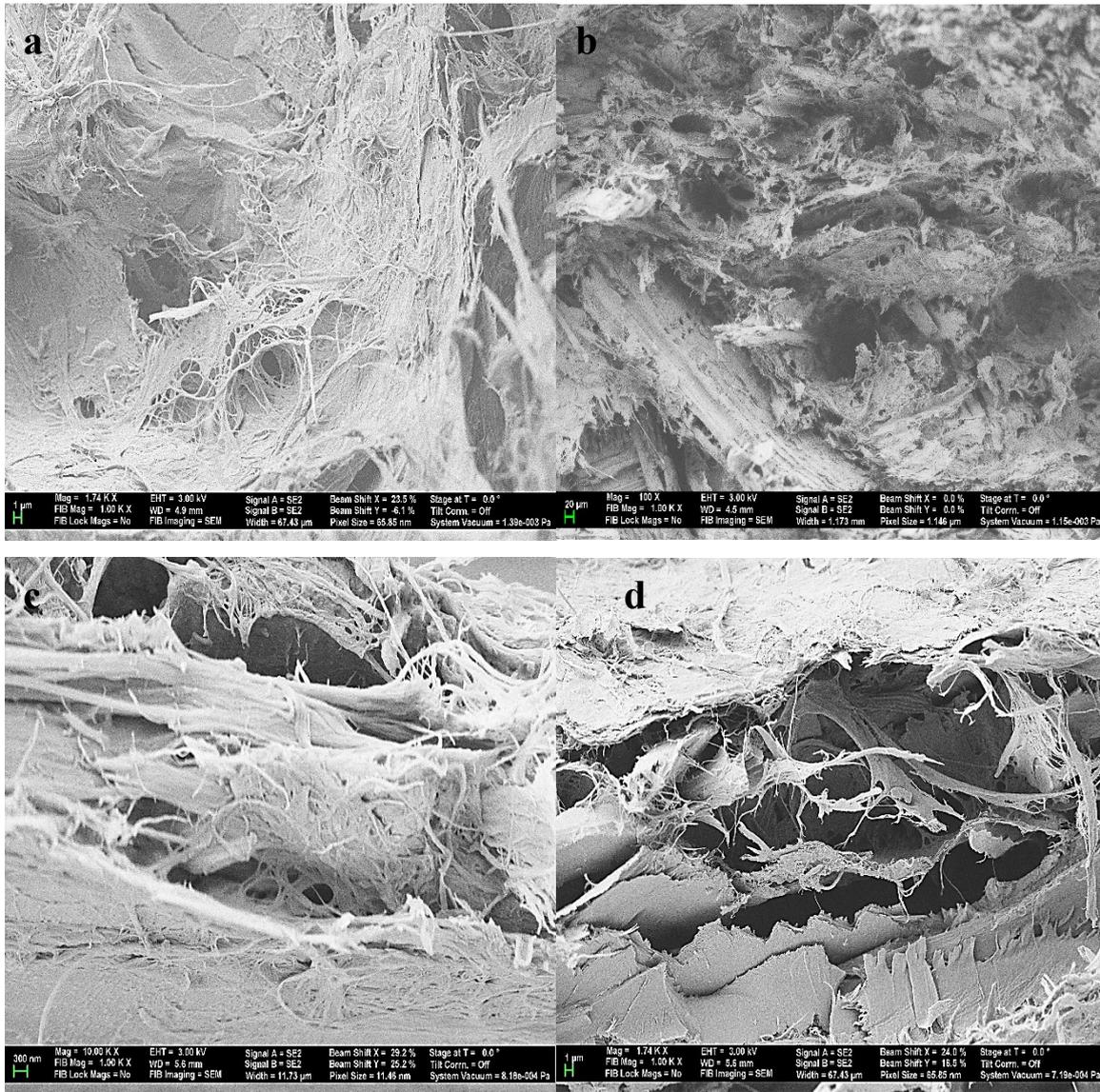


Figure 30. SEM images of SD/MFC/lignin [80:20:4] composite, showing MFC bonded to P-SD fibres in cryo-cracked sample. Polymerisation 24h with a, b) AL added and c, d) KL added.

5 Conclusions

The use of microfibrillated cellulose as an additive in fibre-based products has received substantial attention due to its potential to enhance strength. The properties of MFC and U-MFC can vary depending on the fines level and presence of lignin, offering opportunities for optimisation of specific composite characteristics. In line with the trend towards replacing fossil-based products with renewable alternatives, fibre-based materials are becoming increasingly relevant. Recent advancements in technology have facilitated the increased production of MFC, however, the lignin component has yet to be fully utilised. The objective of this study is to investigate the impact of incorporating lignin into MFC composite materials and to assess the resulting improvement in mechanical properties, thermal stability, and water resistance.

The formation of films incorporating lignin into MFC dispersions was investigated through treatment with laccase. The results show that prolonged drying times resulted in migration of lignin to a singular area. The utilisation of CMC as a stabilising agent prevented this migration, however, it also increased the wettability of the films. To maintain the enhanced mechanical properties provided by the addition of lignin, without increasing wettability, it is necessary to use a stabilising agent that decreases the wettability, to achieve a uniform film. To attain transparent films, the optimal lignin content was found to be 20 wt% or lower; however, higher lignin content can result in a stiffer, less transparent film.

In the context of particleboard composite materials, the incorporation of CMC resulted in increased water retention, making production more difficult and resulting in lower-quality properties compared to boards produced without CMC. Utilising laccase-mediated MFC or an addition of cationic starch (C135) further enhanced the mechanical properties. The use of U-MFC was found to be a more favourable alternative to MFC, as it provided improved properties and was produced with fewer chemicals, leading to a lower cost and more environmentally friendly process. The type of lignin utilised was also found to impact the properties of the particleboard composites.

In the utilisation of U-MFC, the lignin on the fibrils can be mediated with laccase, as well as an additional 20% lignin added to the MFC ratio, resulting in a composite composition that closely resembles an actual 10–20% lignin content. Additionally, the lignin present in the effluent generated by the process can be reused in the production of further particleboards, by incorporating it to the desired lignin ratio and pH level.

Further research is needed to better compare the laccase-treated composites with pure lignin composites, but in situ polymerisation of lignin has been shown to enhance the mechanical properties of particleboard when compared to non-polymerised particleboard.

6 Summary in Swedish – Svensk sammanfattning

Polymeriserat lignin som förstärkningsmedel i mikrofibrillerade cellulosa/träkompositer

Kompositmaterial gjorda av naturliga fibrer har blivit ett prioriterat område inom forskning. Detta beror på den globala krisen med global uppvärmning, som har fått oss att vilja ersätta fossila material med mera naturvänliga och naturligt nedbrytbara material. Detta skulle inte bara hjälpa att motverka den globala uppvärmningen, utan även göra det möjligt att producera material som förbrukar mindre energi, minimerar vikten och som kan återvinnas. Det finns redan många företag som har övergått till naturbaserade material i sina innovationer, såsom i möbler, förpackningar, byggkonstruktioner och i bilbranschen. Naturliga fibrer har också en del bättre egenskaper än syntetiska fibrer. Produkter som i dag består av naturliga fibrer är partikelskivor, mat för både djur och människor, medicin och läkemedel. Råolja räknas endast finnas tillgängligt under de kommande 50 åren, vilket gör det allt viktigare att hitta hållbara lösningar (Sanjay et al., 2016; Ho et al., 2012).

Lignin ses som ett lämpligt substitut för fossilbaserade kemikalier och används redan inom vissa områden. Dessvärre används inte lignin till sin fulla potential, vilket kan bero på ligninets heterogena struktur, som gör det svårt att omvandla ligninet till rent tekniskt lignin. Därför bränns en stor del av ligninet i sodapannor för att ta till vara energi som gått åt vid massafabriker. Det är förväntat att produktionen av lignin kommer öka under de kommande åren på grund av den höga efterfrågan på biobränslen, men att få tekniskt lignin som kan användas är ännu ett problem (Wang et al., 2019; Yoo & Ragauskas, 2021).

Målet med detta diplomarbete var att producera kompositmaterial av mikrofibrillerad cellulosa (MFC), lignin och sågspån för att bättre förstå hur polymeriserat lignin påverkar kompositmaterialens egenskaper. För att göra ligninet användbart, behöver ligninet modifieras med ett oxiderande enzym, lackas. Avsikten med att använda lignin är att förbättra mekaniska och termiska egenskaper, samt minimera vätkomponenten av kompositmaterialen. Två typer av lignin, mikrofibrillerad cellulosa och sågspån kommer användas för att göra MFC-filmer och partikelskivor.

MFC, oblekt MFC (U-MFC) och sågspån av tall tillhandahölls av the universitetet i Maine. Sågspån av gran tillhandahölls av UPM Kymmene, kraftlignin av UPM och renat björklignin av CH Bioforce Oy. Alla material karakteriserades enligt torrsvikt, som mättes med en infraröd fuktighetsmätare. För att kunna använda ligninet, som var i pulverform, löstes det upp i en vattenlösning med tillsatt natriumhydroxid för att höja pH-värdet till (pH 10–11). MFC hade en torrsvikt på 15 % och späddes ut med vatten till 0,5 % för filmer och 3 % för kompositer.

MFC-filmer tillverkades genom att väga upp 30 g MFC 0,5-procentig massa i en petriskål, och låta massan torka till en film i 23 °C och relativ luftfuktighet 50 %, i 3 till 5 dagar. Ligninpolymerisering skedde i en reaktionskarusell, där 0,5-procentig MFC-massa

blandades med laccaseenzym och lignin. Rektorstiderna som testades var 5 h, 6 h, och 24 h, där omrörningshastigheten var 650 rpm och temperaturen i kärlet var 39 °C. Koncentrationer av lignin som testades var 10, 15, och 20 vikt %. Eftersom lignin migrerade till kanterna under torkningsprocessen, var tanken att koncentrationen var för låg eller att reaktionstiden var för kort. Med hjälp av karboximetylcellulosa (CMC) kunde ligninets migration i filmerna hävas och filmerna fick en jämnt fördelad ligninkoncentration.

Vid Åbo Akademi gjordes även partikelskivor med MFC och polymeriserat lignin. Tanken var att hitta recept för den starkaste partikelskivan med det bästa förhållandet lignin. Eftersom 20 vikt % lignin i MFC-filmerna hade den högsta mekaniska styrkan, användes även 20 vikt % lignin för partikelskivor. I dessa skivor polymeriserades lignin med MFC i 24 h och blandades sedan med sågspån i förhållande sågspån/MFC/lignin [80:20:4]. Ur blandningen pressades sedan extra vatten ut med hjälp av en tryckpress och bildade en våt skiva. Den våta skivan pressades sedan i en varmpress i 7 minuter och 180 °C. Förhållandet av MFC testades i 10 och 20 vikt %, samt genom att lägga till katjonisk stärkelse och CMC, vilket resulterade i att 20 vikt % MFC med tillsats av katjonisk stärkelse hade den högsta mekaniska styrkan.

Vid universitetet i Maine, fortsatte testningen av partikelskivor. Här polymeriserades lignin i en blandning av sågspån och MFC/U-MFC. Tekniken som användes var densamma, som tidigare nämnt, men med andra redskap, samtidigt som tiden för het pressning ökades från 7 minuter till 15 minuter. U-MFC innehöll 5,4 % lignin, vilket inverkar på den slutgiltiga ligninkoncentrationen i partikelskivorna samt på att mängden lackas enzym som användes. Stärkelse fanns inte tillgängligt, och testades därmed inte. Dessa partikelskivor användes för att testa mekanisk styrka (3-point bending) och intern bindningsstyrka med hjälp av en Instron mätapparat, kontaktvinkel (vätbarhet) med både polär och opolär vätska och genom att mäta hur vatten absorberades och tjockleken svällde.

Mätningar som gjordes vid universitetet i Maine, analyserades med hänsyn till varians för att det fanns densitetsskillnader mellan proverna. Det visade sig i de mekaniska proverna att proven med U-MFC hade bättre styrka än proven med MFC. Även proven med U-MFC och tillsatt lignin 20 vikt% hade bättre mekanisk styrka. Dessa prov klarade sig bra även i vattenabsorption och i svälltestet, vilket gör partikelskivorna med U-MFC med tillsatt lignin 20 vikt% till de överlägga bästa skivorna. Kontaktvinkeltestet visade ingen stor skillnad på om lignin fanns med eller inte.

Som slutsats kan sägas att lignin kan användas för att förbättra de mekaniska egenskaperna, både i MFC-film och i partikelskivor. Genom att använda laccase för att oxidera lignin kan egenskaperna förbättras ännu mer. Vätbarheten av MFC-film kan förbättras genom att använda bindemedel som är vattenavstötande, medan partikelskivorna påverkas lika mycket av lignin.

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Appendix A

The raw data found in the table below needs to be normalised. The data only shows raw data output from Instron, and therefore is not fully correct, thus beginning of data points are not the same for every sample. Specimen 5 can be seen to incorrect data points, which is a result of a failed test.

Table A-1. Raw data from tensile testing of films with added CMC. Specimen 5 is neglected in the results. CHB refers to alkali lignin and UPM refers to kraft lignin, number indicating percentage of lignin added.

	Specimen label	Maximum Load [N]	Tensile stress at Maximum Load [MPa]	Tensile strain (Extension) at Maximum Load [%]	Load at Break (Standard) [N]	Tensile stress at Break (Standard) [MPa]	Tensile strain (Extension) at Break (Standard) [%]	Tensile stress at Yield (Zero Slope) [MPa]	Modulus (E-modulus) [MPa]
1	CHB10-2-1	18,59	126,64	5,79	0,64	4,35	6,10	-----	6379,32
2	CHB10-2-2	17,82	121,37	6,29	-0,39	-2,63	10,54	121,37	5124,43
3	CHB-3-1	19,00	120,57	6,16	1,26	8,00	6,44	120,57	7350,28
4	CHB10-3-2	20,02	127,01	7,34	0,94	5,99	7,55	127,01	4564,18
5	CHB10-4-1	0,28	1,77	0,01	0,09	0,57	0,27	1,77	43058,11
6	CHB10-4-1	20,20	126,55	6,80	0,53	3,30	6,95	-----	5708,05
7	CHB10-4-2	15,87	99,47	4,29	1,00	6,27	4,54	99,47	5789,70
8	UPM10-2-1	20,39	139,27	6,90	0,37	2,51	7,05	139,27	6541,15
9	UPM10-2-2	19,20	131,15	7,73	0,21	1,46	7,87	124,71	6218,82
10	UPM10-3-1	17,14	112,45	6,18	-0,53	-3,51	6,33	-----	5521,98
11	UPM10-3-2	21,95	144,03	8,44	0,64	4,23	8,57	-----	7084,21
12	UPM10-4-1	21,58	143,50	8,09	1,26	8,38	8,24	-----	5997,95
13	UPM10-4-2	22,55	149,96	9,19	0,89	5,91	9,32	-----	7146,63
14	CHB20-2-1	20,74	112,72	5,73	0,48	2,62	5,94	-----	6874,92
15	CHB20-2-2	19,70	107,04	4,92	0,12	0,65	5,05	-----	6580,99
16	CHB20-3-1	20,74	107,82	6,51	-0,26	-1,36	6,65	-----	5904,58
17	CHB20-3-2	24,45	127,05	7,00	0,29	1,51	7,06	-----	6583,40
18	CHB20-4-1	17,16	94,10	4,33	-0,57	-3,13	4,45	-----	5960,93
19	CHB20-4-2	19,47	106,73	6,05	-1,01	-5,56	6,26	103,58	6850,48
20	UPM20-2-1	19,49	108,78	5,52	0,22	1,24	5,72	-----	6407,77
21	UPM20-2-2	21,36	119,22	6,71	-1,06	-5,92	6,80	-----	6642,90
22	UPM20-3-1	21,54	118,35	4,90	0,70	3,83	5,04	118,35	7455,81
23	UPM20-3-2	20,09	110,40	5,09	-0,31	-1,73	5,21	110,40	6242,35
24	UPM20-4-1	22,36	118,93	6,00	-0,07	-0,39	6,16	-----	7110,51
25	UPM20-4-2	23,07	122,70	5,83	0,44	2,33	5,92	-----	6740,11
26	MFC100-2-1	11,12	70,37	5,32	-0,51	-3,25	5,87	70,37	3918,83
27	MFC100-2-2	11,49	72,71	5,45	-0,52	-3,31	5,75	72,71	3280,19
28	MFC100-3-1	10,04	66,73	8,96	-0,50	-3,33	9,09	-----	3974,87
29	MFC100-3-2	13,98	74,37	6,08	1,65	8,76	6,30	-----	4205,34
30	MFC100-4-1	16,39	103,19	8,13	-0,21	-1,35	8,38	-----	5022,27
31	MFC100-4-2	20,14	126,82	8,95	1,44	9,07	9,07	-----	4837,42
Coefficient of variation		26,30235	26,48910	28,20514	306,62281	293,87734	28,69260	37,22186	94,74630
Maximum		24,45	149,96	9,19	1,65	9,07	10,54	139,27	43058,11
Mean		18,32	110,06	6,28	0,23	1,47	6,60	100,80	7131,57
Median		19,70	118,35	6,16	0,22	1,46	6,33	114,38	6242,35
Minimum		0,28	1,77	0,01	-1,06	-5,92	0,27	1,77	3280,19
Range		24,16	148,19	9,18	2,71	14,99	10,27	137,50	39777,92
Standard deviation		4,81857	29,15310	1,77122	0,71280	4,31516	1,89241	37,51869	6756,89394
Mean + 1 SD		23,14	139,21	8,05	0,95	5,78	8,49	138,32	13888,46
Mean - 1 SD		13,50	80,90	4,51	-0,48	-2,85	4,70	63,28	374,67

In Table A-2 can be seen that some data points are missing for KL 20 and MFC 100. This is due to equipment measurement failure. No values near on the time stamp or near the time stamps were measured for those samples.

Table A-2. Average contact angles for MFC films with added lignin and CMC.

AL-10%	Bottom 1	Bottom 2	Bottom 3	AVERAGE	STDV	Top 1	Top 2	Top 3	AVERAGE	STDV
3.48s	49.89	66.57	67.87	61.44	8.187	39.22	45.48	47.68	44.13	3.584
9.25s	49.21	57.74	67.95	58.30	7.661	33.91	38.92	39.65	37.49	2.551
19.20s	48.39	56.72	51.83	52.31	3.418	32.55	36.7	37.67	35.64	2.221
44.88s	46.16	54.87	49.65	50.23	3.579	31.98	34.74	35.34	34.02	1.463
AVERAGE	48.4125	58.975	59.325			34.415	38.96	40.085		
AL-20%	Bottom 1	Bottom 2	Bottom 3	AVERAGE	STDV	Top 1	Top 2	Top 3	AVERAGE	STDV
3.48s	67.54	63.96	59.14	63.55	3.442	56.82	67.09	55	59.64	5.322
9.25s	63.46	59.93	58.16	60.52	2.203	55.61	60.86	53.01	56.49	3.265
19.20s	62.74	58.23	55.94	58.97	2.825	54.08	59.18	51.93	55.06	3.040
44.88s	60.68	55.62	53.96	56.75	2.858	52.05	56.46	50.03	52.85	2.685
AVERAGE	63.605	59.435	56.8			54.64	60.897	52.492		
KL-10%	Bottom 1	Bottom 2	Bottom 3	AVERAGE	STDV	Top 1	Top 2	Top 3	AVERAGE	STDV
3.48s	56.55	55.91	51.45	54.64	2.268	49.08	78.91	68.29	65.43	12.345
9.25s	54.85	53.04	48.73	52.21	2.567	48.19	63.77	60.4	57.45	6.693
19.20s	53.78	51.94	47.63	51.12	2.577	44.08	61.89	57.61	54.53	7.591
44.88s	52.29	49.64	45.38	49.10	2.846	40.91	58.75	55.04	51.57	7.686
AVERAGE	54.367	52.632	48.297			45.565	65.830	60.335		
KL-20%	Bottom 1	Bottom 2	Bottom 3	AVERAGE	STDV	Top 1	Top 2	Top 3	AVERAGE	STDV
3.48s	64.04	70.81		67.43	3.385	52.29	63.69	61.38	59.12	4.921
9.25s	62.1	68.08		65.09	2.990	51.29	61.3	59.75	57.45	4.399
19.20s	60.96	67.24		64.10	3.140	49.9	59.83	58.16	55.96	4.341
44.88s	58.95	63.5		61.23	2.275	48.57	57.63	56.9	54.37	4.110
AVERAGE	61.512	67.407				50.512	60.612	59.047		
MFC-100%	Bottom 1	Bottom 2	Bottom 3	AVERAGE	STDV	Top 1	Top 2	Top 3	AVERAGE	STDV
3.48s	36.75	90.95		63.85	27.100	76.66	91.27	87.33	85.09	6.172
9.25s	34.61	83.86		59.24	24.625	64.46		68.55	66.51	2.045
19.20s	33.79	76.64		55.22	21.425	58.59		64.92	61.76	3.165
44.88s	32.37	70.18		51.28	18.905	53.89	49.62	55.99	53.17	2.650
AVERAGE	34.380	80.407				63.4	70.445	69.197		

Appendix B

Table B-1. Normalised strength for particleboard formulation made at UMaine.

Homogeneous Subsets

		NStrength					
Duncan ^{a,b}		Subset for alpha = 0.05					
Formulation	N	1	2	3	4	5	6
6	6	8.9656					
5	3	9.3369	9.3369				
3	3	9.7917	9.7917	9.7917			
2	6		10.4023	10.4023			
8	6			10.9727	10.9727		
4	3			10.9762	10.9762		
7	6			11.1475	11.1475		
1	6				12.1000	12.1000	
9	6					13.1078	
10	6					13.1912	
12	6						15.3275
11	6						16.5001
Sig.		.235	.126	.066	.118	.117	.076

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 4.800.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table B-2. Normalised modulus for particleboard made at UMaine.

		NModulus			
Duncan ^{a,b}		Subset for alpha = 0.05			
Formulation	N	1	2	3	4
3	3	1120.486			
6	6	1139.029			
5	3	1183.710	1183.710		
8	6	1256.516	1256.516		
7	6	1320.599	1320.599		
2	6		1377.908		
4	3		1394.144		
1	6			1638.234	
9	6			1723.571	
10	6			1774.271	
12	6				2034.016
11	6				2172.765
Sig.		.094	.078	.228	.192

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 4.800.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table B-3. Homogenous subsamples for internal bonds of particleboards made at UMaine.

InternalBond

Duncan^{a,b}

Formulation	N	Subset for alpha = 0.05				
		1	2	3	4	5
6	6	.4017				
3	6	.4300	.4300			
5	6	.4400	.4400	.4400		
12	6	.4400	.4400	.4400		
7	6	.4567	.4567	.4567	.4567	
8	5		.4820	.4820	.4820	.4820
4	6		.4900	.4900	.4900	.4900
9	6			.5000	.5000	.5000
11	6			.5017	.5017	.5017
1	6				.5117	.5117
2	6				.5167	.5167
10	6					.5350
Sig.		.109	.085	.081	.090	.135

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 5.902.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

Table B-4. Water absorption after 2h on UMaine particleboards.

WA2h

Duncan^a

Formulation	N	Subset for alpha = 0.05				
		1	2	3	4	5
10	6	15.6375				
9	6		18.2753			
12	6		18.8453			
6	6		18.9539			
11	6		19.7649	19.7649		
2	6		20.2088	20.2088		
7	6			21.7654		
8	6				24.6853	
1	6					38.9361
Sig.		1.000	.141	.107	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 6.000.

Table B-5. Water absorption after 24 h on UMaine particleboards

WA24h

Duncan^a

Formulation	N	Subset for alpha = 0.05					
		1	2	3	4	5	6
10	6	18.8471					
9	6	19.8939	19.8939				
6	6	21.0166	21.0166	21.0166			
12	6	21.1455	21.1455	21.1455			
11	6		21.9196	21.9196			
2	6			22.9545	22.9545		
7	6				24.8258		
8	6					28.0138	
1	6						47.0775
Sig.		.127	.178	.198	.172	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 6.000.

Table B-6. Thickness swelling after 2h on UMaine particleboards

TS2h

Duncan^a

Formulation	N	Subset for alpha = 0.05					
		1	2	3	4	5	6
11	6	86.3600					
12	6		96.1396				
10	6		103.9374	103.9374			
9	6			107.0721			
2	6				119.9265		
6	6				121.7018	121.7018	
1	6					129.2759	129.2759
8	6					129.7666	129.7666
7	6						131.1994
Sig.		1.000	.054	.431	.655	.059	.650

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 6.000.

Table B-7. Thickness swelling after 24 h on UMaine particleboards

TS24

Duncan^a

Formulation	N	Subset for alpha = 0.05				
		1	2	3	4	5
11	6	97.3870				
12	6		108.3073			
10	6		114.7161	114.7161		
9	6			117.5722		
2	6				132.4687	
6	6				134.0273	
8	6					142.6178
7	6					146.5669
1	6					149.9936
Sig.		1.000	.133	.499	.712	.103

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 6.000.

Table B-8. WA and TS increase in per cent.

Sample	Sample	Diameter	Density	Thickness	Weight	Thickness	Weight
Name	Number	[cm]	[g/cm ³]	increase 2h	increase 2h	increase 24h	increase 24h
				[%]	[%]	[%]	[%]
SD/MFC-HP7	1	2.58	0.61	38.9 %	129.3 %	47.1 %	150.0 %
SD/MFC-HP15	2	2.57	0.52	20.2 %	119.9 %	23.0 %	132.5 %
SD/MFC-T39	6	2.57	0.50	19.0 %	121.7 %	21.0 %	134.0 %
SD/MFC/AL-T39	7	2.61	0.48	21.8 %	131.2 %	24.8 %	146.6 %
SD/MFC/KL-T39	8	2.58	0.50	24.7 %	129.8 %	28.0 %	142.6 %
SD/U-UMFC-NP	9	2.58	0.53	18.3 %	107.1 %	19.9 %	117.6 %
SD/U-MFC-T39	10	2.57	0.53	15.6 %	103.9 %	18.8 %	114.7 %
SD/U-MFC/AL-T39	11	2.57	0.61	19.8 %	86.4 %	21.9 %	97.4 %
SD/U-MFC/KL-T39	12	2.57	0.56	18.8 %	96.1 %	21.1 %	108.3 %
SD/U-MFC-MD	13	2.58	0.71	27.7 %	76.9 %	29.6 %	87.8 %

Table B-9. Average contact angles and standard deviation of surface energy for polar and non-polar solvents used on particleboards made at UMaine. MD = medium density.

Sample name	Water Mean CA [°]	Steps water	Diiodo-methane Mean CA [°]	Steps Diiodo-methane	Surface free energy mN/m	Disperse mN/m	Polar mN/m
SD/MFC-HP7	92.01 (2.97)	5	33.74 (6.20)	5	43.02 (3.18)	42.60 (2.79)	0.42 (0.39)
SD/MFC-HP15	107.31 (9.20)	5	50.81 (7.94)	11	33.87 (4.82)	33.82 (4.45)	0.05 (0.36)
SD/MFC-T22	90.40 (13.20)	8	38.52 (8.72)	7	41.17 (6.46)	40.35 (4.29)	0.83 (2.17)
SD/MFC/AL-T22	107.18 (20.50)	7	47.88 (13.27)	9	35.54 (8.37)	35.45 (7.29)	0.09 (1.08)
SD/MFC/KL-T22	103.48 (14.71)	6	53.84 (9.19)	9	32.15 (5.76)	32.11 (5.23)	0.04 (0.53)
SD/MFC-T39	93.90 (26.80)	2	46.34 (9.07)	10	36.95 (8.80)	36.29 (4.91)	0.66 (3.89)
SD/MFC/AL-T39	96.48 (8.19)	6	48.98 (6.96)	7	35.28 (4.86)	34.84 (3.86)	0.44 (1.00)
SD/MFC/KL-T39	93.90 (26.80)	2	46.34 (9.07)	10	36.95 (8.80)	36.29 (4.91)	0.66 (3.89)
SD/U-UMFC-NP	94.57 (10.78)	4	42.05 (7.81)	6	38.96 (5.28)	38.96 (5.28)	0.40 (1.23)
SD/U-MFC-T39	96.42 (14.28)	9	44.70 (5.93)	18	37.47 (4.54)	37.17 (3.16)	0.29 (1.38)
SD/U-MFC/AL-T39	98.58 (12.95)	7	43.67 (5.58)	24	37.82 (3.68)	37.71 (2.94)	0.10 (0.74)
SD/U-MFC/KL-T39	85.99 (7.36)	10	43.97 (5.72)	20	39.65 (4.97)	37.56 (3.03)	2.09 (1.95)
SD/U-MFC-MD	73.91 (7.86)	11	40.30 (5.21)	15	45.23 (5.93)	39.46 (2.63)	5.77 (3.29)

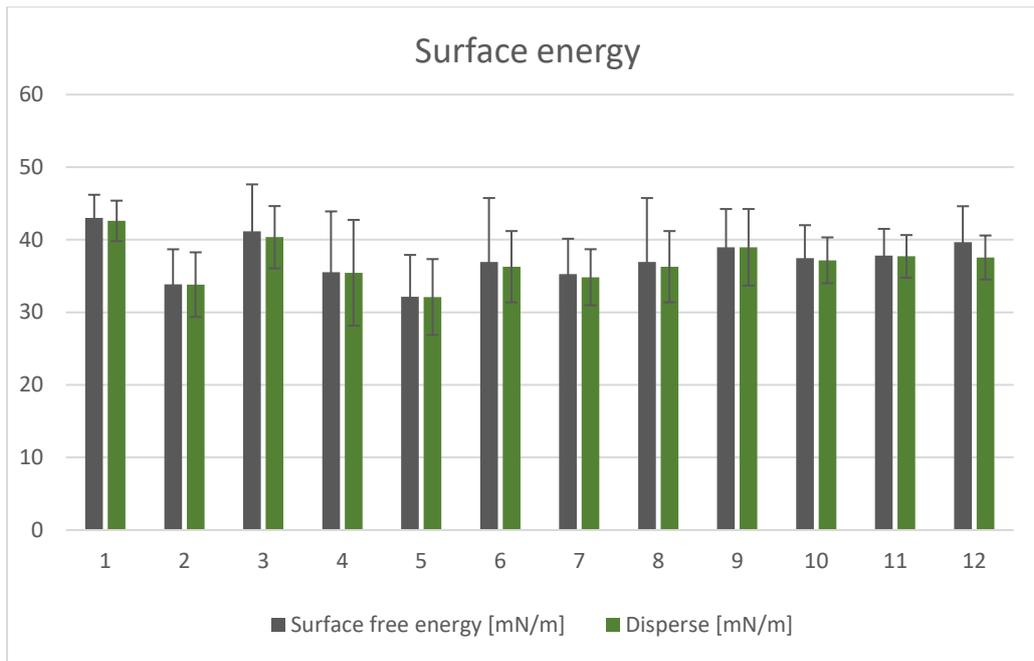


Figure B-10. Surface energy on UMaine particleboard composites.

Table B-11. Average values for weight, volume, density, and mechanical strengths (3-point bending).

Sample	Weight (g)	Volume (cm ³)	Density (g/cm ³)	Flexural Strength (MPa)	Flexural Strain (%)	Modulus (Automatic Young's) (MPa)
SD/MFC-HP7	10.62	17.52	0.61	7.35	1.09	996.06
SD/MFC-HP15	9.95	18.14	0.55	5.77	1.13	764.21
SD/MFC-T22	8.84	18.59	0.48	4.45	1.29	564.40
SD/MFC/AL-T22	8.98	18.67	0.48	4.70	1.55	537.83
SD/MFC/KL-T22	9.09	18.46	0.49	5.42	1.33	687.91
SD/MFC -T39	9.44	18.60	0.51	4.58	1.27	581.33
SD/MFC/AL-T39	9.96	18.89	0.53	5.91	1.44	701.68
SD/MFC/KL-T39	9.77	19.21	0.51	5.59	1.46	642.73
SD/U-UMFC-NP	9.95	18.28	0.54	7.14	1.04	939.37
SD/U-MFC-T39	9.28	17.03	0.54	7.20	1.04	969.44
SD/U-MFC/AL-T39	9.70	16.25	0.60	9.85	1.02	1295.93
SD/U-MFC/KL-T39	9.70	17.07	0.57	8.73	1.02	1157.92
SD/U-MFC-MD	12.83	17.56	0.73	14.4	1.15	1716.19

Table B-12. Standard deviations for weight, volume, density, and mechanical strengths (3-point bending).

Sample	Weight	Volume	Density	Flexural Strength	Flexural Strain	Modulus (Automatic Young's)
	(g)	(cm³)	g/cm³	(MPa)	(%)	(MPa)
SD/MFC-HP7	0.39	0.27	0.02	0.82	0.07	109.48
SD/MFC-HP15	0.51	0.73	0.02	0.23	0.05	54.82
SD/MFC-T22	0.22	0.42	0.05	0.08	0.08	34.75
SD/MFC/AL-T22	0.34	0.66	0.00	0.18	0.04	34.01
SD/MFC/KL-T22	0.21	0.22	0.01	0.33	0.04	31.60
SD/MFC -T39	0.43	0.89	0.01	0.51	0.12	67.96
SD/MFC/AL-T39	0.26	1.25	0.03	0.78	0.25	140.77
SD/MFC/KL-T39	0.55	0.22	0.02	0.65	0.31	152.17
SD/U-UMFC-NP	0.17	0.44	0.01	0.27	0.03	41.26
SD/U-MFC-T39	0.37	0.65	0.01	0.98	0.07	143.88
SD/U-MFC/AL-T39	0.14	0.61	0.02	0.60	0.05	88.09
SD/U-MFC/KL-T39	0.32	0.36	0.02	0.93	0.06	114.18
SD/U-MFC-MD	0.36	0.58	0.02	1.28	0.06	178.01