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COLLOIDAL LIGNIN PARTICLES IN PLYWOOD ADHESIVES

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Fibre and Polymer Engineering

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Abstract

Lignin is a by-product of the pulp production and it is mainly used for energy generation at the pulp mill. Lignin has potential to be used in many more valuable applications, such as in plywood adhesives. Lignin polymer has a phenolic structure and it is a non-toxic natural material, whereas the currently used phenol-formaldehyde (PF) resins in plywood applications are toxic and fossil-based. The goal of this thesis was to produce a lignin-based adhesive without any fossil-based components for plywood applications. The hypothesis was that colloidal lignin particles (CLPs) of lignin fractions would produce a strong adhesive. Also, the effect of a cationic component, such as gelatin and cationic lignin in the adhesion was investigated.

Lignoboost lignin was fractionated to ethanol soluble lignin (ESL) and ethanol insoluble lignin (EIL) fractions. These fractions were characterised with Fourier Transform Infrared Spectroscopy (FT-IR) and differential scanning calorimetry (DSC). The colloidal lignin particles were prepared from these fractions for glue tests. Also, cationic lignin was prepared. These were characterised with particle size and zeta potential measurement. CLPs of different lignin fractions, cationic lignin and gelatin were concentrated to ~30% dry matter content. For gluing tests, ice cream sticks were glued with a lap-shear joint applying cold (CP) or hot pressing (HP). The tensile shear strengths of different glues were determined, and they were compared to polyvinyl acetate (PVA) glue. ABES testing was used in order to test lignin in different pressing temperatures and compare the adhesive strength to PF. Also, moisture resistance testing was done and FESEM images were taken of the glued surface.

The FT-IR analysis of Lignoboost lignin and different lignin fractions showed that the fractionation has not affected the lignin structure. The DSC analysis showed that the glass transition temperature (T_g) decreased with fractionation. T_g for Lignoboost lignin was 178ºC and for ESL 138°C. EIL showed no clear T_g. Zeta potential was negative for CLP fractions and positive for cationic components. Particle sizes of CLPs varied with different fractions. Cationic lignin showed lowest and gelatin coated lignin the highest particle size. In the lap-shear testing, HP samples showed better results than the CP samples and this was because lignin softened in a higher temperature. HP gelatin showed maximum value of 6.4 MPa, followed by gelatin+EIL CLP, gelatin+CLP and gelatin+ESL CLP. Cationic lignin showed lowest adhesive strength. The PVA glue value (7.7 MPa) was not reached. In Automated Bonding Evaluation System (ABES) testing the PF value was exceeded with birch veneer but not with spruce veneers. Spruce veneers showed decreasing adhesive strength with increasing pressing temperature. Moisture resistance for CLPs+gelatin showed stabile bonding therefore indicating that there might be potential for plywood applications. The lignin glues used in this thesis showed good bonding, but did not reach the adhesive strength of commercial glue or PF.

Keywords Lignin, adhesives, lignin fractions, colloidal lignin particles, lap-shear, gelatin, DSC

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Tiivistelmä

Ligniini on selluntuotannon sivuvirta, jota käytetään enimmäkseen sähköntuotantoon sellutehtailla. Ligniinissä on kuitenkin potentiaalia arvokkaampien tuotteiden käyttökohteissa, kuten vaneriliimoissa. Ligniinillä on fenolinen rakenne ja se on myrkytön luonnollinen materiaali, kun taas vaneriapplikaatioissa tällä hetkellä käytetty fenoli-formaldehydi (FF) on myrkyllinen ja valmistettu fossiilisista raaka-aineista. Tämän diplomityön tarkoitus oli valmistaa ligniiniliima vaneriapplikaatioihin ilman fossiilisia lisäaineita. Hypoteesina oli, että ligniinifraktioista valmistetut kolloidiset ligniinipartikkelit (CLPt) muodostaisivat vahvan liiman. Myös kationiset komponentit, kuten gelatiini ja kationinen ligniini, saattaisivat muodostaa vahvan adheesion.

Lignoboost fraktioitiin etanoliin liukenevaan (ESL) ja etanoliin liukenemattomiin (EIL) fraktioihin. Nämä fraktiot karakterisoitiin infrapunaspektrometrialla (FTIR) ja pyyhkäisykalorimetrillä (DSC). CLPt valmistettiin näistä fraktioista liimatestauksia varten. Myös kationinen ligniinijohdannainen valmistettiin kokeita varten. Näistä mitattiin partikkelikoko ja zeta potentiaali ja ne konsentroitiin ~30% kuiva-ainepitoisuuteen. Liimatestaus suoritettiin vetolujuuskokeella, jossa näytteet kylmä- tai kuumapuristettiin ja niitä verrattiin kaupalliseen polyvinyyliasetaatti(PVA)-liimaan. Eri lämpötilojen vaikutusta ligniiniin tutkittiin ABES-testauksella ja verrattiin FF:n arvoihin. Myös kosteudenkestävyyttä tutkittiin ja liimojen pinnoista otettiin elektronimikroskooppikuvat.

Lignoboostin ja ligniinifraktioiden FT-IR-kuvaajat vastasivat ligniinin kuvaajaa, joten fraktiointi ei vaikuttanut merkittävästi ligniinin rakenteeseen. DSC-analyysin perusteella ligniinifraktioissa havaittiin erilaisia termisiä ominaisuuksia. Fraktiointi pienensi lasittumislämpötilaa (T_g). Lignoboostin T_g oli 178°C ja ESL T_g oli 138°C. EIL:llä ei havaittu selvää T_g:tä. Zeta potentiaali oli negatiivinen CLP-fraktioille ja positiivinen kationisille komponenteille. Partikkelikoot vaihtelivat eri fraktioilla, gelatiinilla päällystetyllä ligniinillä ja kationisella ligniinillä. Vetolujuuskokeessa kuumapuristetut näytteet antoivat parempia tuloksia kuin kylmäpuristetut näytteet ja tämä johtui ligniinin pehmenemisestä korkeassa lämpötilassa. Paras liimasauman vahvuus oli kuumapuristetulla gelatiinilla 6.4 MPa, sitten gelatiini+EIL CLP:llä, gelatiini+CLP:llä and gelatiini+ESL CLP:llä. Kationisella ligniinillä liimasauma oli heikoin. PVA-liiman vahvuutta 7.7 MPa ei saavutettu. ABES-testauksessa FF:n arvo ylitettiin koivuvanereilla mutta ei kuusivanereilla. Kuusivanereilla liimasauman vahvuus pieneni lämpötilan kasvaessa. Liimasidoksen kosteudenkestävyys CLP+gelatiinille oli stabiili, joten tällä voisi olla potentiaalia vaneriapplikaatioissa. Tässä diplomityössä käytetyt ligniiniliimat osoittivat hyvää sitoutumista, mutta eivät saavuttaneet kaupallisen liiman ja FF:n suorituskykyä.

Avainsanat Ligniini, liimat, ligniinifraktiot, kolloidiset ligniinipartikkelit, vetolujuus, gelatiini, DSC

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List of abbreviations

ABES	Automated Bonding Evaluation System
AQ	anthraquinone
CLPs	colloidal lignin particles
CP	cold-pressed
DI	deionized water
DSC	differential scanning calorimetry
EIL	ethanol insoluble lignin fraction
ESL	ethanol soluble lignin fraction
EIL CLP	ethanol insoluble lignin colloidal lignin particles
ESL CLP	ethanol soluble lignin colloidal lignin particles
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared Spectroscopy
HP	hot-pressed
KL	Kraft lignin
LVL	laminated veneer lumber
MUF	melamine-urea-formaldehyde resin
M_n	number average molecular weight
M_w	weight average molecular weight
OSL	Organosolv lignin
PCL	polycaprolactone
PF	phenol-formaldehyde resin
pMDI	polymeric isocyanate
PU	polyurethane
PVA	polyvinylacetate
T_g	glass transition temperature
THF	tetrahydrofuran

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1. Introduction

Industrially used adhesives for bonding applications can be divided into thermoplastics, thermosetting materials and elastomers. (Habenicht, 2009) In thermoplastic material, polymer chains are linear or branched and in thermosets polymers are cross-linked. Linear polymer chains can slide when heated giving thermoplastic materials their liquid-like structure and melting and softening properties. Cross-linked structures are hard and will not melt or soften when heated. This results in cross-linked structures being very long-lasting. (Hon 2003)

Currently used thermosetting wood adhesives in plywood manufacturing are mainly based on formaldehyde resins (Vick, 1999) However, formaldehyde is toxic and oncogenic and there is a need for its replacement (Pizzi, 2016) and the interest has increased towards natural or bio-based adhesives. Bio-based adhesives mean adhesives that are produced from a natural source, but they behave like the synthetic adhesives. These include adhesives based on natural materials, such as tannin, lignin, carbohydrates, unsaturated oils, as well as wood welding without adhesive and possibly in the near future protein, collagen and blood. (Pizzi, 2006)

Natural adhesives are known since the Egyptian times. However, the petrochemical boom after world war II, resulting from the need to create products for the idle capacity, generated synthetic resins on the market. Synthetic resins replaced glues based on natural raw materials, such as casein, starch glue and blood. Synthetic resins still strongly dominate the adhesives market, despite the increasing interest in natural adhesives, especially during increasing oil prices, as during the oil crisis in 1970's. (Lambuth, 1989) After the oil crisis the demand for the natural adhesives subsided. Since the 21st century, the interest in the natural adhesives has increased again and this is because of the public interest in protecting the environment and the government regulations that aim for the same thing. (Pizzi, 2006)

The natural adhesives of today do not mean producing the same resins as before the synthetic adhesives were invented. The new natural/bio-based adhesives would use innovative technology, combinations and methods. (Pizzi, 2006) The low production cost as well as the excellent properties of synthetic adhesives, such as exterior durability of phenol-formaldehyde resin has kept their popularity over natural adhesives so strong (Lambuth, 1989). Natural materials, such as lignin and lignosulfonates have been used in small proportions in the adhesives to decrease the cost of synthetic resins, but the cost advantage of the raw material is lost in the longer pressing times (Pizzi, 2006). Lignin could be used as a phenol replacement due to its similar phenolic structure but the problem with lignin is its low reactivity. Lignin has been purified and modified with several methods to increase its reactivity, however, only around 30% of lignin has been successfully used for the adhesives without lowering the adhesive strength (Gosselink et al. 2004).

There are other attempts to use more environmental-friendly wood bonding methods, such as wood welding that uses no adhesive, but this is not suitable for exterior applications as wood welding is not water-resistant. (Pizzi, 2006) There are also plywood applications that are prepared without any adhesive by thermal modification (Ruponen et al. 2014) but despite the efforts, there are still no adhesives that use 100% natural materials.

The aim of this thesis was to produce a lignin-based adhesive for plywood applications without any petrochemical/fossil-based additives. The hypothesis was that different lignin fractions and colloidal lignin particles (CLPs) of lignin fractions would produce a strong adhesive in combination with cationic polymers that expectedly improve adhesion. Lignoboost lignin was fractionated to ethanol soluble lignin (ESL) and ethanol insoluble lignin (EIL) fractions and CLPs were produced from these fractions. Cationic lignin and gelatin were used as natural based polycations for glue formulations.

2. Wood properties

Wood is a porous material that contains 40-50% cellulose, 20-40% hemicellulose, 20-30% lignin (Figure 1) and 2-7% extractives, such as resin and fatty acids, monoterpenes and phenolics. Wood is a complex material and its physical properties are anisotropic. (Brockmann et al. 2005)

2.1. Cellulose and hemicellulose

Both cellulose and hemicellulose are polysaccharides. Cellulose is a linear homopolysaccharide, which consists of cellobiose units and each of the cellobiose unit contains two glucose units. Cellulose molecules form fibrils, which are aligned parallel forming cell walls and giving strength to the structure. (Brockmann et al. 2005) Cellulose contains high amount of hydroxyl groups which form intra- and intermolecular hydrogen bonds and covalent bonds with adhesives. The polydispersity (M_w/M_n) of cellulose in the plant cell wall is <2 and therefore quite low and the degree of crystallinity 60-75% indicating that cellulose is quite vastly ordered structure. (Alén, 2000)

Whereas cellulose consist of hexoses, hemicellulose is consisted of both hexoses and pentoses. Therefore, hemicellulose is a heteropolysaccharide and its chains are shorter than cellulose chains and contain branches. (Alén, 2000) It also decomposes more easily than cellulose and its main functions are to support the cell wall and to act as a water reserve. (Brockmann et al. 2005) Hemicelluloses have a lower level of crystallinity and are therefore more amorphous and degrade more easily than cellulose. (Alén, 2000)

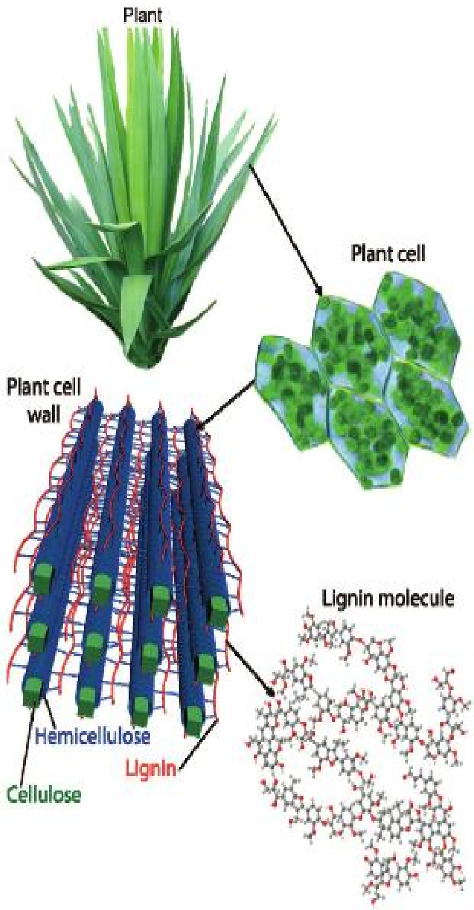


Figure 1- *Main components of lignocellulosic material. (Zakzeski et al. 2010)*

2.2 Lignin

Lignin can be found in the cell wall of plants and it acts as a glue, binding wood cells together in the wood matrix. (Alén, 2000) Lignin is more hydrophobic than cellulose and hemicellulose, however its hydroxyl groups are in contact with water (Hatakeyama, 2010). Lignin structure and its properties are described below.

2.2.1 Lignin structure

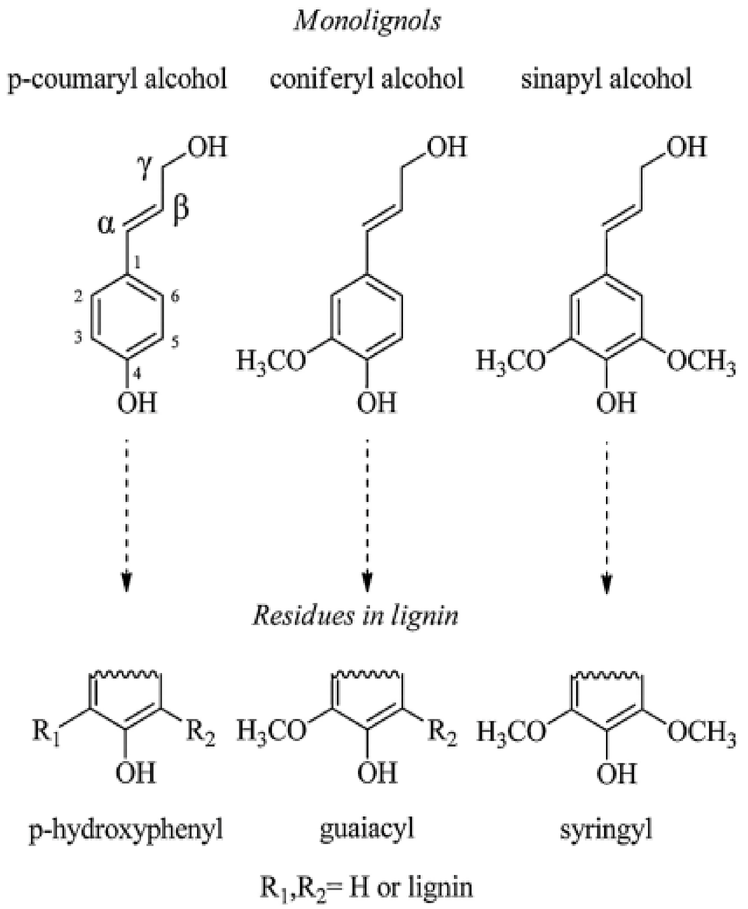


Figure 2 - Monolignols and their structure in lignin polymers. (Laurichesse et al. 2014)

Lignin is a cross-linked high molecular mass polyphenol that consists of phenylpropane units that are irregularly linked to each other. Lignin is a challenging polymer as its complete structure and molecular mass of native lignin is still unknown since when lignin is separated from wood it undergoes degradation depending on the extraction method, changing both its structure and molecular weight. Lignin is biosynthesized by the polymerization of three p-hydroxycinnamyl alcohols: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 2). (Hatakeyama, 2010)

Lignin monomer unit structure can be divided in to two parts, one being the aromatic ring and the other the C3 chain. The reactive sites in lignin are the OH-groups which are either in the aromatic ring (phenolic hydroxyl groups) or in the carbon chain (aliphatic hydroxyl groups). (Hatakeyama, 2010) Polyurethane, polycaprolactone (PCL) and epoxy resins are some of the products that are obtainable from lignin utilizing the hydroxyl groups as reaction sites. (Hatakeyama, 2010)

Lignin contains several linkages that link phenylpropane units together. These linkages are mainly ether linkages, especially β-O-4 linkages, and carbon-carbon bonds. (Figure 3) (Stenius, 2000) It is because of these ether linkages that lignin reactivity is low as most of the reactive sites are unavailable. Reactivity is also decreased by the presence of methoxyl groups, which hinder the reactivity of the available phenolic hydroxyl groups. (Hu et al. 2011)

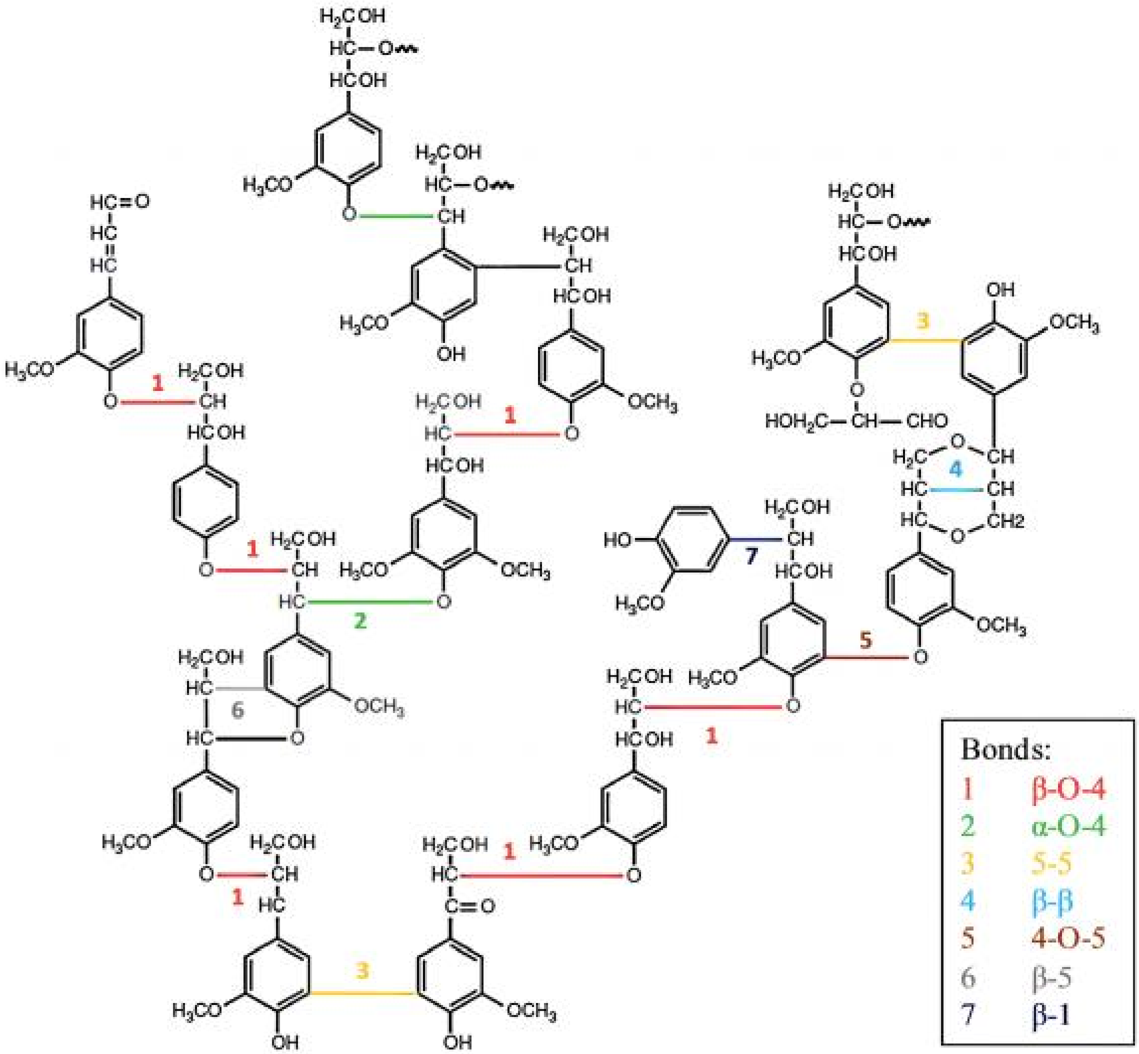


Figure 3 - Linkages in softwood lignin. (Laurichesse et al. 2014)

The complex structure of the lignin polymer differs by its origin. The native lignins can be classified into softwood, hardwood and grass lignins. Softwood lignin contains mainly trans-coniferyl alcohol, over 90%, and trans-p-coumaryl alcohol (Figure 4). Hardwood lignin contains around 50% trans-coniferyl and 50% trans-sinapyl alcohols (Figure 5), whereas grass lignin contains 40% trans-coniferyl, 40% trans-sinapyl alcohol and 20% other residues. Industrially extracted lignin differs from the native lignin and this poses some challenges for lignin utilisation. Lignin in wood is also bonded to hemicellulose via lignin-carbohydrate complexes (LCC). (Stenius, 2000)

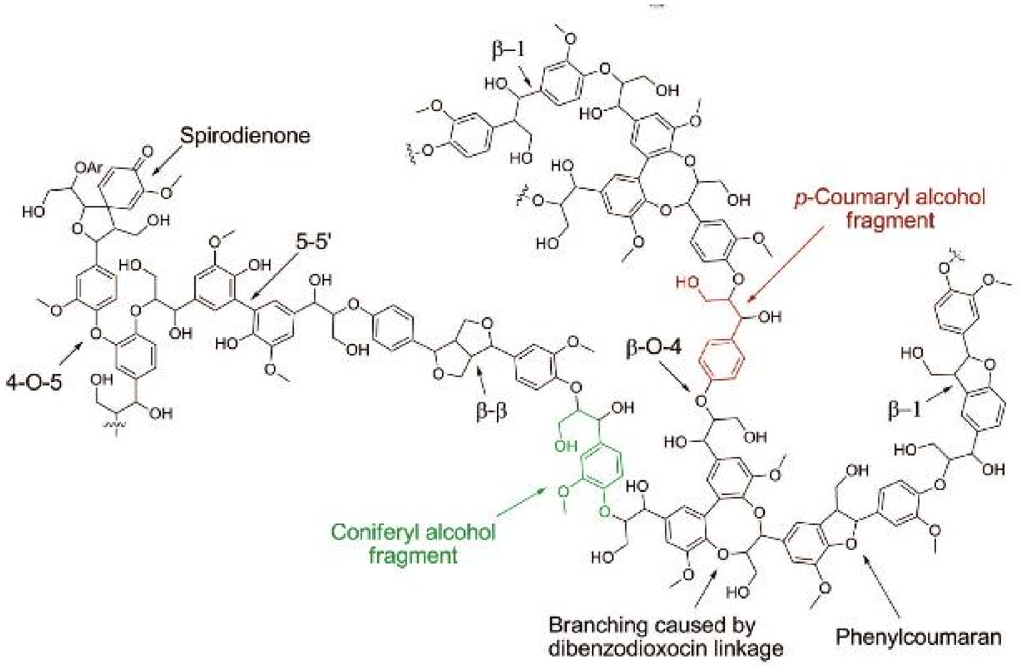


Figure 4 - Softwood lignin structure. (Zakzeski et al. 2010)

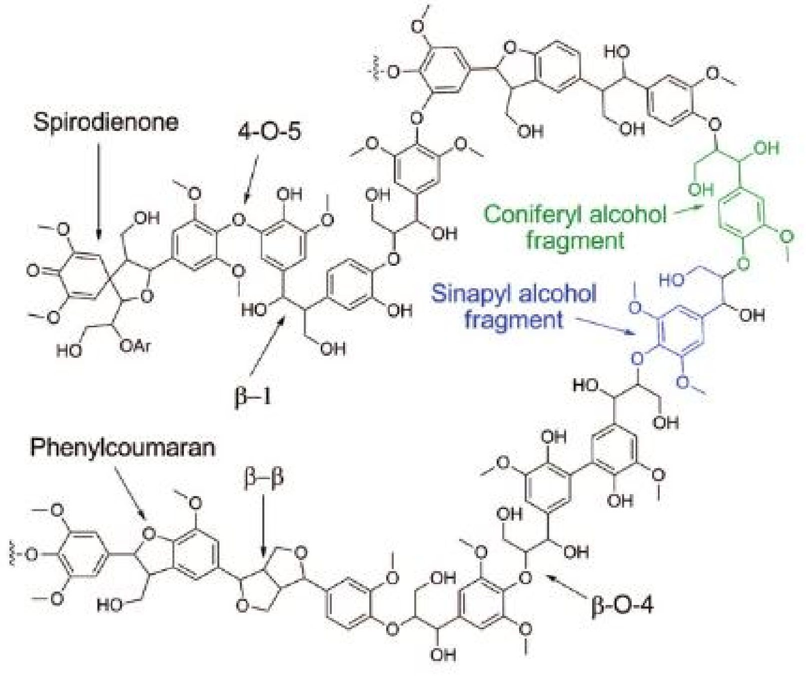


Figure 5 - Hardwood lignin structure. (Zakzeski et al. 2010)

2.2.2 Sources and extraction methods of lignin and its effect on certain properties

Lignin extraction methods can be divided into sulfur and sulfur-free processes. Sulfur processes include sulfite and Kraft (alkaline) pulping and their products are lignosulfonates and Kraft lignin, respectively. Sulfur-free processes include solvent pulping and soda pulping and their products are Organosolv lignin (OSL) and soda lignin, respectively. (Figure 6) (Laurichesse et al. 2014) Of these the first three lignins are produced industrially, and there has been also small-scale lignin production of OSL as well as acid hydrolysis lignins from bio-ethanol production. (Stenius, 2000) Of these lignins lignosulfonates are produced the most, one of the world leading companies being Norwegian Borregaard Lignotech (Hatakeyama, 2010).

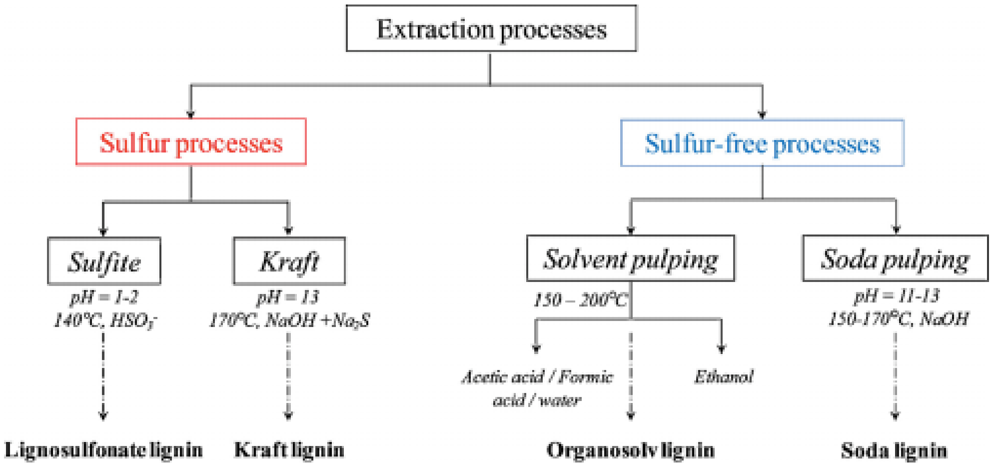
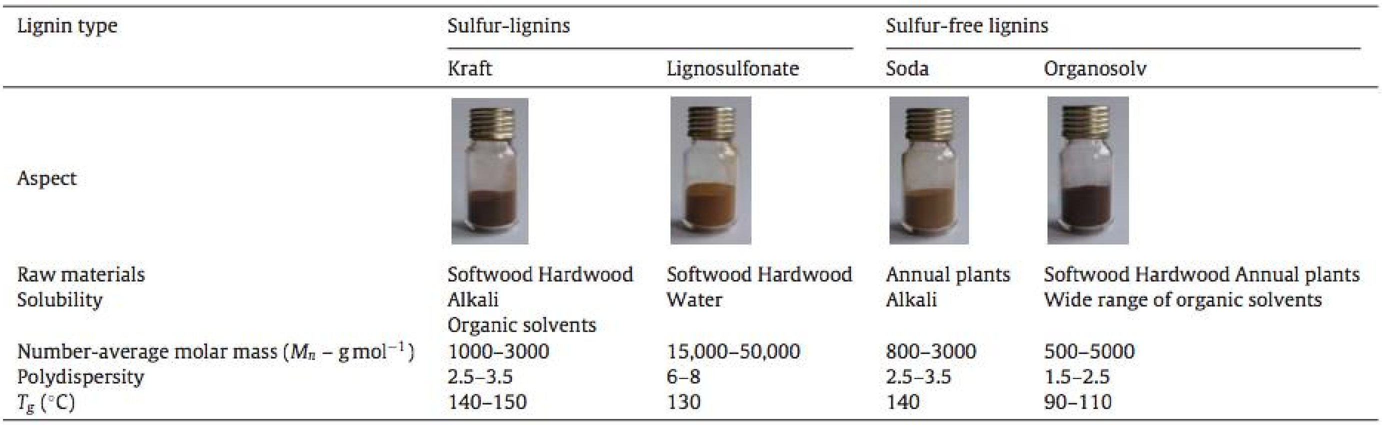


Figure 6 - The most common lignins and their production methods. (Laurichesse et al. 2014)

Lignins have different properties (Figure 7) and reactivity depending on the pulping method. According to Pizzi et al. (1989), soda bagasse lignin shows higher reactivity than for example Kraft pine or soda/AQ lignin. This is because the pulping process of soda bagasse is done at mild conditions (170°C) and for short periods of time (15mins). Bagasse lignin also naturally contains more unsubstituted C5-positions in the aromatic ring and therefore it is more reactive towards formaldehyde. According to Pizzi's work (1989) bagasse lignin had 0.7 reactive points per nine-carbon unit of lignin, whereas Kraft pine lignin had 0.3 reactive points and Soda/AQ lignin 0.1.

Native lignin can be also extracted in a laboratory scale as milled wood lignin (MWL), dioxane lignin and enzymically liberated lignin. Milled wood lignins have a low amount of sugars and they lack minor acyl moieties, therefore making it easy to analyse the structure. (Balaskin et al. 2016) Even though the structure of lignin is altered in the industrial extraction methods, these are the most effective and cheapest sources of lignin (Hatakeyama, 2010).



Lignin type	Sulfur-lignins		Sulfur-free lignins	
	Kraft	Lignosulfonate	Soda	Organosolv
Aspect				
Raw materials	Softwood Hardwood	Softwood Hardwood	Annual plants	Softwood Hardwood Annual plants
Solubility	Alkali Organic solvents	Water	Alkali	Wide range of organic solvents
Number-average molar mass (M_n – g mol^{-1})	1000–3000	15,000–50,000	800–3000	500–5000
Polydispersity	2.5–3.5	6–8	2.5–3.5	1.5–2.5
T_g (°C)	140–150	130	140	90–110

Figure 7 - Properties of different lignins. (Laurichesse et al. 2014)

2.2.3 Kraft pulping and Lignoboost lignin

In Kraft pulping wood chips are cooked with white liquor (NaOH and Na_2S) and the aim is to decrease the lignin content as much as possible, indicated by the kappa number, because lignin is unwanted in other pulping stages, such as in bleaching of pulp. During the cooking, 90% of lignin dissolves in the black liquor, which contains lignin and cooking chemicals. Black liquor is separated in pulp washing and concentrated. The concentrated solid fraction, which contains lignin and aliphatic carboxyl acids, is majorly combusted for energy in the recovery boiler. There is an energy surplus as not all lignin is needed to fulfill the mill electricity need (Stenius, 2000), which allows also production of lignin as a by-product of the process. There is a growing interest in converting Kraft mills into biorefineries, which utilize wood as well as possible. The conversion shows *e.g.* water and energy savings and no need for fossil-fuel. (Mateos-Espejel et al. 2010)

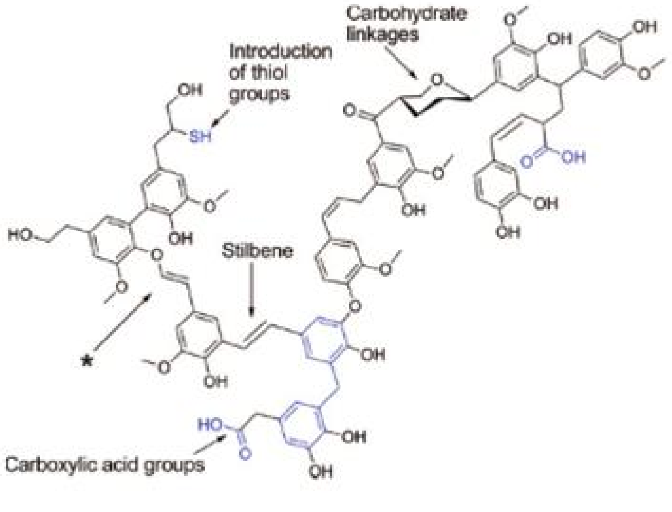


Figure 8 - Structure of Kraft pine lignin. (Zakzeski et al. 2010)

Lignin removal, delignification, occurs mainly via strong nucleophile HS^- as this reacts with lignin. As lignin degrades, the phenolic hydroxyl groups are formed, and lignin hydrophilicity is increased, molecular weight decreased, resulting in water- and alkali-soluble lignin that dissolves in the cooking liquor as sodium phenolates. Aryl-ether linkages (such as β-O-4 and α-0-4) are cleaved easily. Also, some demethylation, as well as some condensation reactions, in the form of new C-C bonds, occur increasing the molecular mass and reducing solubility. Enol ethers, stilbenes and quinone methide intermediates are also formed (Figure 8). Quinone methide intermediates can create C-C linkages. (Gierer & Petterson, 1976) As a result, Kraft lignin has a wide molecular weight distribution. High molecular weight lignin is considered to be >500Da and low molecular weight lignin <500Da. (Stenius, 2000) Kraft lignin and soda-AQ lignins have a lower weight average molecular weight compared to other lignins, due to the cleavage of α-O-4 and β-O-4 in the pulping process and therefore resulting in a high content of phenolic hydroxyl groups. According to Laszlo (1999), Kraft lignins have small anionic charge and their molecular weight is low.

Lignin precipitates with acid (Stenius, 2000). According to Öhman, Wallmo & Theliander (2007), if the recovery boiler is the bottleneck of the pulp production and lignin is removed from the recovery boiler feed, the pulp production can be increased. Lignin commercialization also brings new revenues and increases pulp production. According to their work, the plugging problems of lignin separation can be overcome with low pH values. Lignoboost process is an example of commercialization of lignin and it uses CO_2 and H_2SO_4 to precipitate lignin from black liquor (Tomani, 2010).

2.2.4 Sulfite pulping

In sulfite pulping, the delignification occurs with sulfonation and hydrolysis. In sulfonation hydrophilic sulfonic acid groups are formed and the hydrolysis breaks aryl-ether linkages which creates free phenolic hydroxyl groups (Figure 9). Lignin becomes a water and acid-soluble lignosulphonates. Lignosulfonates have an anionic charge and a high molecular weight. Some examples of lignosulfonates products are dispersants and complexing agents. (Laszlo, 1999) One example of commercial products produced from lignosulfonates is a low molecular weight vanillin. (Tejado et al. 2007)

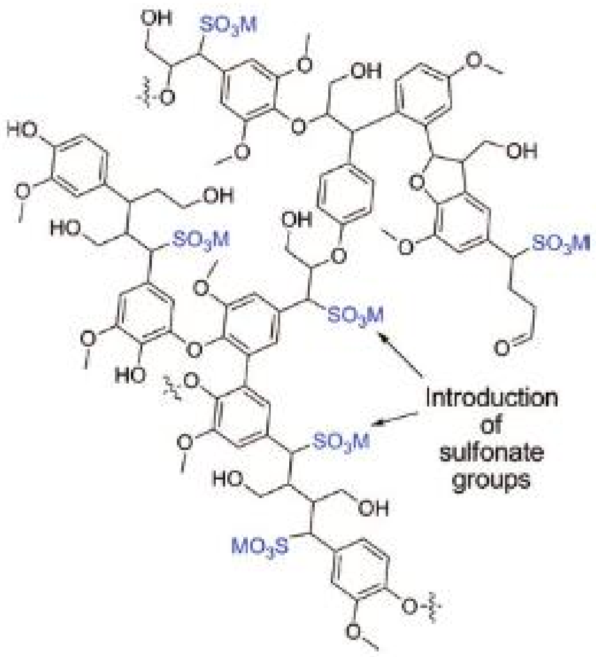


Figure 9 - Structure of lignosulfonate lignin. (Zakzeski et al. 2010)

2.2.5 Solubility of lignin

Native lignin is insoluble in water and many solvents, whereas extracted lignin is highly soluble in dioxane, acetone, methyl cellosolve, tetrahydrofuran (THF), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (Stenius, 2000). According to Campbell & Walsh (1985), Kraft lignin does not easily dissolve in water but will dissolve in alkaline mixtures. Solubility of lignin varies even within lignins from a same tree species. According to Lievonen et al. (2016), one sample of softwood lignin from Kraft process dissolved in THF and not in ethylene glycol, whereas other sample of softwood lignin from Kraft process did not dissolve in THF but dissolved in ethylene glycol. This difference in solubility was attributed to be due to the hydroxyl groups, especially the phenolic hydroxyl groups. This is also in accordance with Evstigneev (2011) as increased phenolic hydroxyl groups increased the lignin solubility in aqueous alkali. According to Hatakeyama (2010), the presence of acetyl and hydroxypropyl groups make the solubility in THF and other organic solvents possible.

2.2.6 Heterogeneity and polydispersity of lignin

The problem with Kraft lignin is that it is very heterogeneous and therefore varying e.g. in reactivity and functionality. Heterogeneity of lignin is caused by the varying combinations of side chains and building units of lignin. (Hatakeyama, 2010) According to Cui et al. (2004), the heterogeneity can be decreased by fractionation, *e.g.* with acetone and hexane. Lignin can be fractionated into homogeneous fractions and well-defined molecular weights with fractional precipitation. Aliphatic hydroxyl groups decrease with the isolation process, whereas the phenolic hydroxyl content increases with the isolation process. The heterogeneity of lignin is reduced with the polydispersity index (PDI) between 1.5-1.1. (Cui et al. 2014). Leskinen et al. (2015) have fractionated hydrolysis lignins and according to their study the weaker solvation capacity of ethanol compared to the alkali resulted in lower molecular weight fractions and narrower polydispersity of the isolated lignin fraction. Lignin that is dissolved in organic solvents contains low molecular weight fractions and the residue contains high molecular weight fractions. (Ropponen et al. 2011). According to Shao et al (2009) in steam explosion lignin pretreatment low molecular weight components are achieved due to the inter-monomer breakage of β-aryl-ether linkages.

2.2.7 Lignin nanoparticles

In lignin adhesives, the size and shape of the Kraft lignin particles reduce the reactivity of lignin due to the limited accessibility of the functional groups (Campbell & Walsh, 1985). The usage of lignin particles in several other applications, such as fillers is reduced by the large particle size and the propensity to agglomerate due to the intermolecular hydrogen bonding. One solution is to reduce the lignin particle size (Frigerio, 2014), which is within the range of 10-100µm for non-refined technical lignins (Bahl et al. 2014).

Nanoparticles are used in numerous chemical products of today, as they can offer additional properties that are otherwise difficult to obtain for example for traditional petrochemical polymers. Nanoparticles can improve properties such as the polymer durability in terms of strength as well as thermal and light stability and therefore increase the value of the product. In a similar way, as small hard particles can improve hardness of the polymer, the nanoparticles can improve properties such as colour and UV absorption (TiO_2 and ZnO). Nano-sized pigments can increase refractive index and therefore affect the visible colour and they can also increase UV absorption (<50nm) and hence protect the skin from UV rays, and affect antimicrobial properties i.e. activity towards micro-organisms. (Stark et al. 2015) It is especially important to produce nanoparticles from biomaterials, such as lignin, as these are more likely to be less harmful for humans and the environment than the nanomaterials from metals and inorganic compounds (Frangville et al. 2012). Lignin nanoparticles have different properties compared to the macro sized lignin particles (Zhao et al. 2016) as lignin nanoparticles increase e.g. mechanical properties and lignin miscibility with other polymers, such as polyvinyl alcohol (PVA) (Kubo & Kadla, 2003). Small particles have large surface area and therefore better performance per mass or volume (Stark et al. 2015) and the physical properties change drastically when moving from microparticles to nanoparticles (Hussain et al. 2006).

Lignin nanoparticles with various sizes are mainly produced with solution-based processing and precipitation of the particles (Zhao et al. 2016) Lignin is usually precipitated with water with an electrolyte as a stabilizer (Nair et al. 2014). Nanosized particles have been produced through dialysis by using ethylene glycol (Frangville et al. 2012) or by using THF as a solvent (Lievonen et al. 2016). According to Hatakeyama (2010), isolated lignin particles are almost spherical. Lignin nanoparticles are produced in various shapes and sizes, and therefore the size distribution is an important parameter affecting the quality for industrial uses. (Stark et al. 2015) The size of nanoparticles is dependent on the initial lignin concentration, the solvent and pH. (Frangville et al. 2012) Several authors have investigated the production of lignin nanoparticles. Qian et al. (2014) produced spherical colloidal lignin particles from acetylated lignin by dissolution in tetrahydrofuran (THF) and precipitation with water. The precipitation with water is based on the hydrophobic interactions of the lignin polymers, which drives them to aggregate, and this can be detected with scattered light intensity. THF was removed with rotary evaporation and the colloids were stable below pH 12. (Qian et al. 2014) Lievonen et al. (2016) were able to produce spherical particles that were stable between pH 4-12 with the same ingredients but from unmodified lignin and in the process the THF was removed with dialysis. Frangville et al. (2012) produced lignin nanoparticles with ethylene glycol and precipitated them with HCl, however, not obtaining spherical particles. The size of nanoparticles is dependent on the initial lignin concentration and the rate of HCl addition. With slow HCl addition, the smaller the particles are formed. The stability of the particles improved when ethylene glycol was replaced with water i.e. at the dialysis stage. (Frangville et al. 2012). According to Lievonen et al. (2016) particle size and structure is dependent on the solvent that is used before dialysis. They found that with THF the size is more symmetric and round shape compared to ethylene glycol, and this might be because THF is less polar than ethylene glycol. Also, there is weak effect of lignin concentration on the particle size.

2.2.8 Lignin cationisation

Lignin can be cationised with amination that also increases charge density and solubility of lignin. The net charge of the polymer is changed from anionic to cationic after the derivatization. According to Kong et al. (2015), one method for lignin cationisation is to use glycidyl trimethylammonium chloride (GTMAC). The charge density increased with increasing pH during the reaction, reaching the maximum charge density and solubility at pH 12.5. NaOH catalyses lignin nucleophilic intermediate, which reacts with the epoxy group of GTMAC (oxirane ring opening reaction) and produces GTMAC grafted cationic lignin. (Kong et al. 2015)

2.2.9 Thermal properties and reactivity of lignin

Thermal softening of a polymer can be measured with glass transition temperature (T_g) and it is important for thermosetting polymers (Anonymous, 2017a). For example, the fractionation of lignin has effect on the T_g. According to Leskinen et al. (2015), lignins extracted with ethanol showed 30^o C lower T_g compared to the alkali extracted lignins. This was attributed to the fact that ethanol extracted lignins have a higher amount of aliphatic CH-groups, higher amount of phenolic OH-groups and lower amount of carboxylic acids than alkali extracted lignins. Therefore, the higher the number of aliphatic CH-groups and phenolic OH-groups the lower the T_g. Huijgen et al. (2014) found that OSL that was fractionated with ethanol, showed decreased cross-linking and there was a correlation between molecular weight and T_g. The lower the average molecular weight, the lower the T_g. Helander et al. (2013) fractionated Kraft lignin with ultra-filtration and found that the lower the molecular weight of lignin, the higher the sulfur content and the amount of phenolic hydroxyl groups and therefore less condensed structures.

Lignin is relatively stable at elevated temperatures because of its aromatic structure. (Sen et al. 2015) Upon heating its structure breaks rather than softens (Kadla, 2001). Lignin behaves somewhat like a thermoplastic and sometimes as a thermoset material. It is also tough with a high T_g. Lignin has been combined with soft materials to form thermoplastic elastomers that could be used e.g. as adhesives. (Sen et al. 2015) The complex structure and high amount of various functional groups expands the lignin T_g range compared to the synthetic amorphous polymers, such as polystyrene, which has similar sized repeating unit than lignin. The intermolecular hydrogen bonds result in decreased molecular movement and hence increasing glass transition temperature (T_g), whereas methoxyl groups increase molecular movement. (Hatakeyama, 2010) According to Yoshida et al. (1987), lignin becomes thermally more stable with increasing molecular weight and this might be because of increased branched structures and condensation reactions. According to Sarkat & Adhikari (2000), ether linkages increase the thermal stability of lignin.

2.3 Charge of wood

Wood contains several acidic functional groups, such as carboxylic, phenolic, hydroxyl and hemiacetal groups that result in the net negative charge on wood fibers (Sjöström, 1989). The negative charge is mainly caused by the carboxylic acids present in hemicellulose, which dissociate into carboxylate salts in aqueous environment (Biermann, 1996). The carboxylic acids dissociate in neutral or slightly acidic conditions, whereas the phenolic and alcoholic hydroxyl groups dissociate in highly alkaline conditions. Also, lignin contains some carboxyl groups. In the pulping process, the carboxylic content decreases compared to the native wood as most of the hemicelluloses are dissolved in cooking. Also, some carboxyl groups are introduced in the lignin structure and the carboxyl group content of lignin is on average higher after pulping than in native lignin. (Sjöström, 1989)

The surface charge is especially important in colloids as it increases stability in aqueous media. The repulsive forces between particles need to be larger than the attractive forces to prevent coagulation. The contact of the counter-ions with the charged surface forms a charge layer, which is called an electric double layer (Figure 10). It consists of the surface, Stern and diffuse sub-layers. The dissociation of functional groups affects the charge density and therefore the surface layer. Charge density is affected by the degree of substitution and by pH, which affects the level of dissociation. The Stern layer contains the opposite charged adsorbed ions and the interactions are formed with van der Waals and acid-base interactions. In the diffuse double layer the electrostatic interactions are present and ions move more freely. The electrical double layer increases stability of the charged components. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, which explains the stability of colloids, the interactions between charged particles/surfaces can be described as the sum of the electrostatic double layer interaction and the van der Waals forces. The van der Waals forces are not affected by the electrolyte concentration or particle charge. (Stenius, 2000) The charge of wood is interesting as especially cationic components, such as cationic lignin and gelatin could adsorb on the anionic wood. High surface charge (positive or negative) indicates colloidal stability of the adhesives and it can be measured with zeta potential (Biermann, 1996).

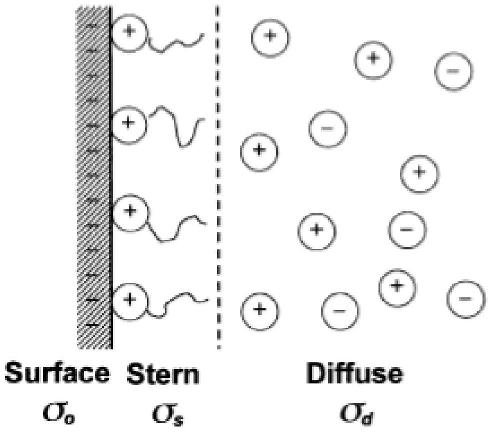


Figure 10 – The electrical double layer and its sub-layers. (Stenius, 2000)

2.4 Hygroscopicity and effect of moisture

Wood is affected by the temperature and moisture content of air. Moisture affects properties, such as the weight, strength and shrinkage of wood. Moisture content in wood can vary between 30%-200%. (Simpson & TenWolde, 1999) Hydroxyl groups of wood form strong hydrogen bonding with water and this results in cell walls being saturated with water, also known as fiber saturation point (FSP), which is around 30% moisture content, depending on the wood species. Above the FSP wood will shrink and below FSP it will swell. Shrinkage and swelling will differ in tangential, longitudinal and radial directions. This difference in dimensional stability cause varying stresses for adhesives and can break the adhesive bond. High moisture content in wood prevents water and adhesive absorption. Moisture content is especially critical in hot pressing, where pressure is applied and if the moisture content of wood is too high, the adhesive will only stay on the surface and will squeeze-out. (Vick, 1999) Wood moisture content should not be over 8-10% in adhesive applications (Habenicht, 2009).

2.5 Adhesion to wood

Adhesion occurs when two different surfaces are attached to each other by interfacial forces. These forces can be valence forces or mechanical interlocking. Valence forces is attraction that is caused by atoms, ions and molecules. In mechanical interlocking, e.g. liquid is attached into a porous structure, such as wood. Generally, both of the adhesion mechanisms are essential for effective bonding. Adhesion is therefore dependent on both the wood and adhesive properties. Properties affecting wood behavior are its density, porosity, moisture content and dimensional stability. (Vick, 1999)

The purpose of an adhesive is to give strength and stiffness and therefore transfer and spread stress in the composite. An adhesive must wet and spread over the surface, and have viscosity high enough that it solidifies. Wetting is high if the contact angle between the adhesive and the surface is low. The adhesive also needs to have affinity for the surface. Thermosetting adhesives transform from liquid to solid by irreversible chemical polymerization and form cross-linked arrangement. They are very resistant to heat, moisture and ensure static loading. Thermoplastic adhesives change physically to solid, which occurs when the adhesive cools down or solvent is lost via evaporation. They re-soften with heat. (Vick, 1999)

In order to the adhesive application to be successful, the adhesive should easily run on the adherend, e.g. wood, surface and penetrate the adherend. (Hon, 2003). But it should not be too runny as for porous materials, such as wood, high adhesive viscosity is desired to avoid adhesive from penetrating inside the pores. (Habenicht, 2009) The end product is typically a solid and high-molecular weight polymer. There are three ways to prepare adhesives: 1) An adhesive can be prepared by producing a dispersion where the solvent evaporates after application of the adhesive and a high-molecular weight polymer is then attached on the adherend surface. Natural adhesives are mainly produced with this method. 2) Thermoplastic adhesives can be heated and then applied, and the adhesive attaches to the adherend surface when cooled. 3) By chemical reaction where a low molecular weight monomer is converted into high-molecular weight polymer and this is the main method for synthetic adhesives. (Hon, 2003)

Molecular weight affects many properties of polymers, and applies to resin adhesives as well. The properties change up to a certain molecular weight after which the increase in molecular weight doesn't affect the properties. For example, tensile strength, glass transition temperature and elasticity increase with increasing molecular weight, whereas e.g. solubility and brittleness decrease with increasing molecular weight. (Saunders, 1960) Also, adsorption increases with increasing molecular weight. This is because of the entropy increase due to the solvent and polymer molecule release at the surface. Adsorption is also increased between cations and anions, or strong Lewis acid-based contact. Also, if the polymer is close to its solubility limit in the solvent, the adsorption is increased.

3. Plywood applications and processing methods

Plywood is a composite wood material (Pizzi& Ibeh, 2014). It has several advantages, such as the cross-ply orientation of the veneers results in stable material independent on the orientation and therefore anisotropy effect of wood is minimized. Plywood also has other advantages, such as good insulation, compared to solid wood and it can be used between -200ºC-120ºC. (Hughes, 2014)

The importance of plywood as a construction material was due to two innovations: rotary peeling of veneers, which enabled the production at an industrial scale, and the waterproof adhesives, such as phenol-formaldehyde, which enabled the plywood usage in long-lasting exterior applications. The structure of plywood is made of thin veneers. After veneers are peeled from wood logs and dried, they are coated with a glue and pressed together to form a plywood structure. (Hughes, 2014) Laminated veneer lumber (LVL) is also made of veneers but it differs from plywood in the grain direction, as in LVL the veneer grains face the same direction, making it very strong in that direction. The advantage of plywood compared to sawn wood is the high yield as the veneers are sliced. (Hughes, 2014)

3.1 Plywood manufacturing process

The felling season and the preparation method of the veneer have an effect on the success of the gluing and therefore affect the adhesive development (Rohumaa et al. 2014). The main steps affecting the gluing process in the plywood production are soaking i.e. log conditioning, veneer peeling, drying, gluing and pressing. It is important to have knowledge of these steps as they affect adequate wetting, spreading and penetration of the adhesive. (Vick, 1999)

The plywood production process is shown in Figure 11. When the log arrives at the mill, the wood is debarked (Hughes, 2014). To ease debarking and soften the wood, the logs are heated. This also improves the end-product qualities. (Salmen, 1982) During heating i.e. log conditioning, the logs are heated at 30-40ºC for 24hrs. If the wood is for decorative purposes, the heating temperature can be 70°C as the temperature makes the colour lighter. (Hughes, 2014) The conditioning temperature influences wettability of the surface and bond strength, as soaking in 70ºC gives better bond strength than soaking in 20°C. Therefore, the conditioning temperature affects the application of some resins such as the phenol-formaldehydes. (Rohumaa et al. 2014). Drying is important as uneven moisture content can affect the gluing during hot press. After drying of the veneers, they are cooled and then strength properties (specific gravity) and moisture content are tested non-destructively. When glue is added on the veneer, an uneven number of veneers (3,5,7 etc.) are laid-up on top of each other. As a comparison to laminated veneer lumber (LVL), in LVL all the grain directions are the same and due its high strength in axial direction, LVL is used e.g. as beams. After the glue addition, it is let to stay and to penetrate the wood surface to increase the bond strength. The veneers are then pre-pressed and hot-pressed where the resin curing occurs. In curing a chemical reaction takes place and the adhesive is transformed from liquid form to a solid form. For PF resin the pressing temperature is commonly 130ºC and for UF resins even higher. Also, pressure and thickness are controlled. The thicker the panel, the longer the press time. (Hughes, 2014)

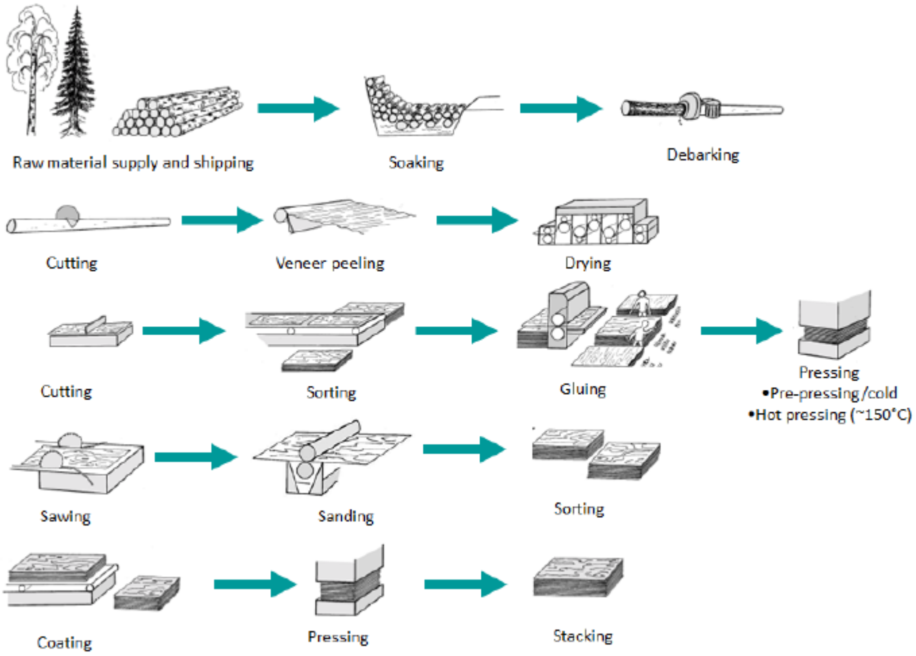


Figure 11 - The plywood production process. (Hughes, 2014)

3.2 Adhesives

There are many wood adhesives, such as dispersion adhesives, hot-melt adhesives and condensation adhesives. Condensation adhesives i.e. various formaldehyde resins, are usually used for the industrial applications and for plywood production. (Habenicht, 2009) More than half of the adhesives used today (by volume) are based on formaldehyde resins and it was the first fully synthetic commercial resin. Its popularity is based on many advantages, such as ease of manufacture and high reactivity. (Pizzi & Ibeh, 2014) Phenolic resins generally are popular as they are for example easy to mold in different shapes and have good heat resistance. In the cured state wood adhesives do not emit toxic formaldehyde emissions as formaldehyde is reacted efficiently in the production stage. Only exception is urea-formaldehyde resin, which emit formaldehyde in the cured state under certain conditions. (Vick, 1999)

Phenolic resins in the adhesives are produced from synthetic materials, but there is interest in natural polyphenols, such as lignin and condensed tannin resins. (Pizzi & Ibeh, 2014) Adhesives used in wood products account for the largest part of the adhesive market, more than 65%. (Pizzi, 2016) For example, urea-formaldehyde consumption is 11 million tons (resin solids) per year (2016). (Pizzi, 2016; Pizzi & Ibeh, 2014). Whereas for PF resins solids it is 2.5-4 million tons. (Pizzi & Ibeh, 2014). Mainly thermosetting resins are used for veneer bonding. Functionality of plywood can, however, be improved and thermoplastic adhesive can be used as in UPM Grada. (Hughes, 2014)

Currently the most widely used components for wood adhesives are formaldehyde resins, in which formaldehyde has reacted with chemicals such as urea, melamine, phenol, resorcinol and isocyanate. The bonding quality and therefore the performance of the final product is dependent on the wood surface, the adhesive and the manufacturing process, of which the adhesive accounts 50% of the performance. Formation of the bond is a condensation reaction in which at delivery the resin is in liquid form after which it goes through hardening and gelling in which a three-dimensional cross-linked form is created. Molar mass, molecular structure of the resin and additives, among other things affect the hardening. When the adhesive is cross-linked, it becomes insoluble, non-melting and non-thermoformable. For phenolic resins the hardening occurs in alkaline conditions. In the industry, to reduce the production costs, increased production rate and therefore shorter press times are desired. This can be achieved with fast gelling and hardening of adhesives, which increase the bond strength, with adhesive mixtures that are highly reactive in terms of cross-linking or hardeners or optimizing the processing conditions of the final product. (Dunky, 2003) There has been research in self-bonding or autoadhesion of plywood. The adhesion is based on moisture and specific parameters, such as 9% moisture content and parallel grain direction for beech veneer. (Cristescu, 2008)

3.2.1 Phenol-formaldehyde resins

Phenol-formaldehyde (PF) resins are known since 1930s (Lambuth, 1989). Phenol-formaldehyde resins are used for water resistant gluing and therefore for exterior products. According to Dunky (2003), PF resins have very low formaldehyde emissions and it is considered one of the advantages of phenolic resins compared to the UF resins. These lower emissions of PF resins than UF resins are due to the fact that PF resins are resistant to hydrolysis and therefore have stable C-C bonds between aromatic ring and methylene bridges. The downsize is that they have long press times and the colour of glue is dark compared to UF resins. (Dunky, 2003) Even though the formaldehyde emissions are low, according to Hughes (2014) formaldehyde is a human carsinogen and there is a need for alternative solutions. In addition to the oligomeric and polymer chains, the PF resins contain methylphenol and free formaldehyde (<0.3 mass%), as well as unreacted phenols (<0.1 mass%) of which the two latter ones need to be minimized. Phenolic resins have a high alkalinity (pH 10-13) as in alkaline conditions phenolate ions are formed that keeps resin water soluble, but the alkaline content also lowers the viscosity and storage stability. High F/P indicates high reactivity and increase in bond strength. (Dunky, 2003) The PF resins produced in alkaline conditions are called resol resins, whereas the resins produced in acidic conditions are called novolac resins. (Pena et al. 2006)

In phenol-formaldehyde adhesive formation formaldehyde reacts with phenol (Figure 12) and water is cleaved via thermal condensation reaction. Because of water-vapour originating from the condensation reaction, the adhesives need high temperature and high pressure for curing in order to avoid volume increase caused by water. (Habenicht, 2009)

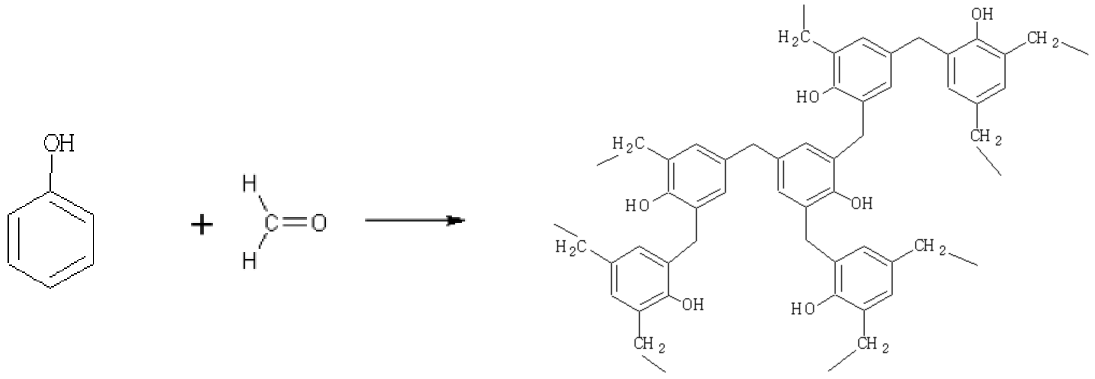


Figure 12- The reaction between phenol and formaldehyde forming PF resin (e.g. Bakelite).

3.2.2 Urea-formaldehyde resins

Urea-formaldehyde (UF) resins are aminoplastic and thermosetting resins that are used mainly for interior products and in dry conditions, such as in indoor furniture. The glue is white and therefore it is almost invisible. (Hughes, 2014) UF resins have higher reactivity and shorter press times than other formaldehyde resins. UF resins contain free formaldehyde, monomeric and oligomeric methylol groups and high molecular mass polymers. Free formaldehyde has positive and negative effects. The higher the F/U molar ratio, the more there is free formaldehyde formed and the more time the post-added urea has time to react as free formaldehyde is needed for the hardening reaction. The reduction of formaldehyde content is not possible without affecting the performance of the resin. This is because formaldehyde is the reactive component in the condensation reaction, as well as in curing and therefore, the lower the formaldehyde content, the lower the reactivity. Formaldehyde also causes odors. (Dunky, 2003) Urea addition (usually in the final state) in the adhesive decreases the free-formaldehyde content, decreases the adhesive viscosity, quickens hardening, reduces cost and has a dilution effect. (Pizzi & Ibeh, 2014) The cost of UF resin is cheaper than PF resins, but the strength properties are worse, and it hydrolyses more easily. (Hughes, 2014)

3.2.3 Natural adhesives

There have been many attempts during the last decades to use natural products as the raw materials for adhesives. The emission of formaldehyde and possible emissions of free phenols are of concern in the current formaldehyde adhesives. (Dunky, 2003) There is interest in natural adhesives due to their low level of toxicity, biodegradability, wide availability, but they need to be more efficient and cost less than the current products based on synthetic raw materials. (Pizzi & Ibeh, 2014). As lignins and tannins both have a phenolic structure, they could replace phenol in phenol-formaldehyde (PF) resins (Pizzi, 2006). Despite the efforts, there are still no adhesives that use 100% natural materials.

3.2.4 Lignin adhesives and other applications

There are no clear statistics on how much lignin is produced annually, but several estimates exist. Hatakeyama (2010) estimated the lignin production to be over 30 million tons a year, whereas Laurichesse et al. (2014) estimated it to be 50 million tons in 2010. Only 2% of lignin is used commercially in adhesives, dispersants, surfactants or antioxidants (Laurichesse et al. 2014). Lignin has been also used for binders, for electrical uses (Glasser & Sarkanen, 1989) and for molding stabilisers and concrete additives (Pizzi, 2003b). Lignin could also be used in UV stabilisers and anti-oxidant with other polymers (Gosselink et al. 2004) and there is a lot of potential for other applications. Lignin can absorb UV radiation because of its aromatic structure, which has a radical scavenging ability. (Gosselink et al. 2004)

Problems with lignin in certain commercial applications, such as adhesives, is that lignin is brittle and has a low chemical reactivity (Aracri et al. 2014) This is due to the complex and heterogeneous lignin structure and the lack of available reaction sites. The current success with lignin adhesives has been to substitute some of the phenol-formaldehyde or urea-formaldehyde with lignin (Pizzi, 2006). The structure of lignin affects is suitability as a phenol replacement. According to Tejado et al. (2007), Kraft pine lignin is more suitable phenol substitute in lignin-phenol-formaldehyde (LPF) resins than for example soda-anthraquinone (AQ) flax lignin or ethanol-water wild tamarind lignin, as Kraft lignin has higher molecular weight and more free positions for reaction. According to Cook & Sellers (1989), OSL is purer and more reactive than Kraft lignin as it has less sulfur and ash, and more carbohydrates. Also, molecular weight and polydispersity are smaller.

Problems with lignin is that it needs longer press time and higher press temperature than phenol-formaldehyde resins. According to Pizzi (2003a), main problems with the commercial use of lignin adhesives have been that it is either not suitable for the equipment e.g. in terms of corrosive effect or it is not economical due to too long press times, whereas Mansouri et al. (2007) states that the pressing rate at plywood production is not the main parameter to determine if the production is economically viable or not. According to Pizzi (2016), in plywood applications, the process is less dependent on the pressing time than for other wood products.

Lignin-phenol-formaldehyde (LPF) adhesives have been prepared with two methods. In the first method, unmodified lignin is mixed with formaldehyde and in the second method lignin is first modified and after this mixed with formaldehyde. (Laurichesse et al. 2014) Unmodified lignin has low reactivity and results in long press times and therefore is uneconomical, whereas modified lignin increases the reactivity towards formaldehyde and is therefore more interesting commercially. When aiming to increase lignin reactivity, the main lignin modification methods are demethylation, methylolation (aka hydroxymethylation) and phenolation. They introduce reactive functional groups to lignin structure. Also, other methods, such as oxidation, reduction and hydrolysis exist. (Hu et al. 2011)

As the reactivity of phenolic hydroxyl groups of lignin are reduced by the methyl groups, demethoxylation (i.e. removal of methyl groups) is one way of increasing reactivity as the reactivity of more than 50% of the aromatic hydroxyl groups are hindered by methyl groups (Hu et al. 2011). Liu & Li (2006) produced an adhesive without formaldehyde by mixing demethoxylated Kraft lignin with polyethylenimine (PEI). Hydroxyl groups were first oxidised to form quinones which further reacted with PEI. The best shear strength of demethoxylated Kraft lignin with PEI was 6.5MPa and optimum curing conditions 120ºC and 5 mins for lap-shear specimens. (Liu & Li, 2006)

Methylolation introduces hydroxymethyl groups ($-CH_2OH$) in to the lignin structure and in phenolation lignin is introduced with a phenol (Hu et al. 2011). Vazquez et al. (1997) made lignin adhesives with methylolation and phenolation. The methylolated lignin-phenol-formaldehyde (MLPF) plywood panels met the water resistance standard, whereas phenolated lignin-phenol-formaldehyde panels (PLPF) did not, however, the PLPF plywood panel with 50:50 or 75:50 PLPF/commercial PF resin showed better knife test performance than pure PLPF or commercial PF resin. This was due to the better spreading and higher solids content on wood compared to the pure resins. Phenolation is the most commonly used method for modification lignosulfonates in the adhesive applications, as it increases the amount of phenolic hydroxyl groups making the lignosulfonate structure simpler (Hu et al. 2011).

It seems that moderate replacement of phenols with lignin does not lower the adhesive strength too much, while at high proportions of lignin the adhesive strength is reduced. Cook & Sellers (1989), replaced 35-40% phenol with purified OSL in laminate maple wood and bond southern pine flake boards. This did not harmfully affect the bond properties and gave better results than unpurified or purified Kraft lignin. With Kraft lignin replacement of 40%, the shear strength was 4.14 MPa, whereas OSL-PF gave shear strength of over 5 MPa. According to Danielson & Simonson (1998a), phenol could be partly replaced with non-pretreated Kraft lignin in PF resins. From 20% to-60% replacement the shear strength remained same or higher, but with lignin replacement higher than 80% the strength reduced drastically. With 100% lignin replacement the adhesive was very low in strength and brittle. The shear strengths were as follows with phenol replacement with lignin: 20% addition, shear strength 1.5 MPa, 40%:1.7MPa, 60%: 2MPa, 80%: 0.5MPa. Even though OSL and purified Kraft lignin gave better results than unmodified Kraft lignin, the usage of these is not economically feasible. According to Zhang et al. (2013), the lignin reactivity as well as the cost increase with modification and according to Jin et al. (2010), the phenol could be replaced with enzymatic hydrolysis lignin only up to 20% if the cost and other properties were taken into account.

According to Gosselink et al. (2004), lignins such as Kraft lignin and sulphur-free lignin from alkaline pulping process, called NovaFiber, can replace phenol in formaldehyde resins up to 31% without too low perfomance in the adhesive strength. Lignins were modified with sodium dithionite (reduction reaction). The Kraft lignin values increased with increasing temperature (up to 140ºC) (but high std) and decreased when the temperature was further increased. NovaFiber seemed to give better results than unmodified NovaFiber. Kalami et al. (2017) were able to replace all the phenol with corn stover lignin in an adhesive with a shear strength value of 3.4 MPa. This value was only slightly less than the reference value for phenol resorcinol formaldehyde (3.6 MPa). This is a good step towards replacing petroleum-based phenol in the adhesives, however, the formaldehyde is still present. Also, UPM's WISA BioBond (UPM, 2017) and VTT's reactive lignin, called CatLignin, aim at replacing phenols with lignin. UPM will use BioBond in its WISA plywood products and VTT is aiming to have reactive lignin commercial by 2020. As a conclusion, none of the adhesives containing pure lignin resin without formaldehyde present have made success commercially for the time being.

3.2.5 Other glue options

Aldehydes, such as glyoxal, furfural and glutaldehyde are possible alternatives in replacing formaldehyde. According to the literature, *e.g.* glyoxal has been used but for particleboard applications. The molecular weight of lignin affects its suitability in the adhesives according to Mansouri et al. (2007), as low molecular weight lignin gives better results than high molecular weight lignin and this is because low molecular weight lignin has more reactive sites. Mansouri et al. (2007) used glyoxal which is non-toxic but less reactive than formaldehyde. They first hydroxymethylated calcium lignosulfonate lignin with formaldehyde and then glyoxal was added as a formaldehyde replacement into the adhesive and then mixed with polymeric isocyanate (pDMI). The results gave bond strength that reached the standard values of EN 312 for exterior wood particleboard. It should be noted that the standard EN 312 measures the internal bond (I.B.) strength which differs from the shear strength testing and therefore the values cannot be directly compared. Lei et al. (2007), used two low-molecular weight lignins and tannin with lignin glyoxalation. Low molecular weight lignin gives better internal bond results with MDI-based formulations for particleboard and 80% in the adhesive was made of natural materials. Mansouri et al. (2011), mixed glyoxalated low molecular weight organosolv lignin with tannin (using hexamine as a hardener) in order to prepare an interior wood panel adhesive. The 50/50 mixture of tannin/hexamine + glyoxalated non-purified lignin gave the best results in terms of dry internal bond (I.B.) strength. Lower amount of tannin decreased the I.B. strength and this was due to the lower number of reactive sites which the glyoxalated lignin can react with when hot-pressed. Only 0.5% of synthetic materials (glyoxal and hexamine) were used.

Dongre et al. (2015) used furfural as a cross-linking agent with lignin, however the highest tensile strength was for the glue that had no furfural present. Their experiment showed that low molecular weight lignin showed better mechanical properties than high molecular weight glues. This was believed to be because in high molecular weight widespread cross-linking reduces the mobility therefore resulting in weaker glues. Da Silva et al. (2013), prepared glutardehyde-organosolv lignin for composite reinforcement aiming at replacing formaldehyde with success.

3.2.6 Proteins in adhesives

Proteins are also an interesting source for adhesives, and suit well for lignin based formulations. For example, Luo et al. (2015), improved the water resistance of soy protein-based adhesive with corncob lignin. Commercial adhesive Ashland's Soyad is formaldehyde free and based on soy protein, but it is only suitable for indoor applications (Hughes, 2014). Another protein, gelatin, has been used as an adhesive for centuries. Gelatin is a degradation product of collagen and it is extracted from animals. (Fakirov & Bhattacharya, 2007) Gelatin has a molecular weight between 65000 and 300000 Da. (Pena et al. 2010) The structure of gelatin is firmly bound with hydrogen bonds and therefore gelatin is brittle. Gelatin is also polar and therefore it absorbs moisture. (Karnnet et al. 2005)

The low water resistance of protein adhesives can be improved by phenolic compounds. For this purpose, other natural polymers, such as tannins, could be used together with proteins. Tannins can coagulate alkaloids and proteins, such as gelatin, and their usage as converting animal skin to leather i.e. tanning, is based on this coagulating ability (Bisanda et al. 2003). Tannins are low-molecular weight and water-soluble and they have a polyphenolic structure. Industrially tannins are mainly used in leather manufacture, but also in phenol-formaldehyde resins. (Holmblom, 2011). Condensed tannins are specific with the protein interactions and they have varying affinity for different proteins. For example, the affinity for gelatin is higher than for BSA, and for BSA higher than for ovalbumin. (Asquith & Butler, 1985). Especially proline-rich proteins have high affinities for tannin. The affinity is related to strength of interaction with tannin rather than the rate of reaction. The reaction rate with ovalbum is twice as fast as with BSA, but the affinity is lower. (Hagerman & Butler, 1981). Polyphenol-protein complexation occurs when hydrophilic polyphenol acts as a ligand and coats the protein, which act as an acceptor. (Spencer et al. 1988) Tannin reacts with gelatins peptide, carbonyl and guanidine groups which are polar. According to some views, the reaction between gelatin and tannin is based on hydrophobic reaction. (Yi et al. 2005) Due to the structural similarities of different polyphenols, protein interactions with other polyphenols, such as lignin, are expectedly similar with tannin.

4. Summary of the literature part

Phenol-formaldehyde resins that are currently used in the plywood production pose environmental and health concerns. Phenol is derived from fossil resources and formaldehyde is toxic to humans. There have been several attempts of replacing phenol with more environmental-friendly options, such as lignin, however, only around 50% of phenol is possible to replace without lowering the performance of the adhesive. This is because of the complex and heterogenous lignin structure which makes its reactivity challenging. There are also attempts to replace formaldehyde with other aldehydes, but the performance has not exceeded the formaldehyde performance.

Therefore, as currently used methods for lignin adhesives haven't been successful commercially at replacing both phenol and formaldehyde, there is a need for alternative effective lignin based products with a low cost. As lignin heterogeneity can be reduced with fractionation and nanoparticles can improve the properties of lignin fractions, this work is aiming to produce a new type of lignin adhesive for plywood applications. As with decreasing molecular weight also the glass transition temperature decreases, the different lignin fractions can have varying molecular weights and therefore the adhesive curing and cross-linking can occur already at a lower temperature, therefore forming a stronger glue bond. Cationic lignin and gelatin mixed with lignin fractions could form a strong bond with anionic wood.

5. Materials and methods

5.1. Materials

UPM BioPiva 100 Kraft lignin powder (23.01.2017, Lignoboost lignin, dry matter content 64.1%), dried Lignoboost lignin (74.7%), ethanol (EtOH), tetrahydrofuran (100%, VWR Chemicals, density 0.888g/ml), NaOH (0.2M), H_2SO_4 (0.05M), Glycidyltrimethylammoniumchloride(GTMAC) (density 1.13g/ml)

5.2 Dry matter content determination

The dry matter content was aimed to be ~30%. The dry matter content was determined by the gravimetric method according to the standard *ISO 638:2008 Paper, board and pulps — Determination of dry matter content — Oven-drying method*. Two vials were dried in the desiccator for 10 minutes. The weights of the empty vial (m_1) and the vial containing the sample (m_2) were recorded before and after inserting the samples in the oven (105°C) for overnight. After taking the samples from the oven, the vials were again placed in the desiccator for 10 minutes before weighing (m_3). The dry matter content was calculated for both samples as according to the equation (1) and the average value of the two samples was used.

$$\textbf{Dry matter content}\ (\%) = \frac{\mathbf{m_2 - m_1}}{\mathbf{m_3 - m_1}} * \mathbf{100}(\%) \qquad \textbf{(1)}$$

The dry matter content of an adhesive affects the performance in the hot pressing as in hot pressing water will be evaporated. With low dry matter content, high amount of water is evaporated, and this affects the adhesive distribution and therefore the bond strength of the adhesive. However, dry matter cannot also be too high as with according to Gao et al. (2011), with soybean meal adhesives the viscosity increased drastically when the dry matter content was over 30%. High viscosity causes difficulties, such as problems with the adhesive application on wood. According to Imam et al (2011), with starch adhesives the dry matter content below 27% gave best flow properties and according to Luo et al. (2015), adhesive with high viscosity also has difficulties in penetrating in the wood. According to Onusseit (1993), low solids content also results in low drying time, which is not viable in the industrial processes.

5.3 Lignin fractionation

Lignins with different molecular weights can be obtained with fractionation (Figure 13). Lignoboost lignin (dry matter content 64.1%) was dried with Buchner funnel until the colour changed from dark brown to light brown. After this, the lignin was dried in the Vacutherm vacuum oven (40°C) overnight. The dried Lignoboost lignin (dry matter content 74.7%) was fractionated by adding 3 g Lignoboost lignin (dry basis) into test tubes and then adding 40ml ethanol. Ethanol was used as, according to Leskinen et al. (2015), the mild ethanol media used with lignin extraction keeps the lignin structure unaltered. The samples were then inserted in the centrifuge (ThermoScientific SL 40 FR) for 15 minutes with speed 4000 RPM. Centrifuging was repeated by collecting the supernatant and adding ethanol in the test tubes. The supernatant contained the ethanol soluble lignin fraction (ESL) and the solid fraction contained ethanol insoluble lignin fraction (EIL). The supernatant fraction containing ethanol and lignin were separated with the Buchi R-210 rotavapor using 250 ml boiling flask, 175 mbar vacuum and 40°C water bath until dry and the solid fraction was evaporated dry with a Buchner funnel. The dry matter contents of the lignin fractions were considered as 100%.

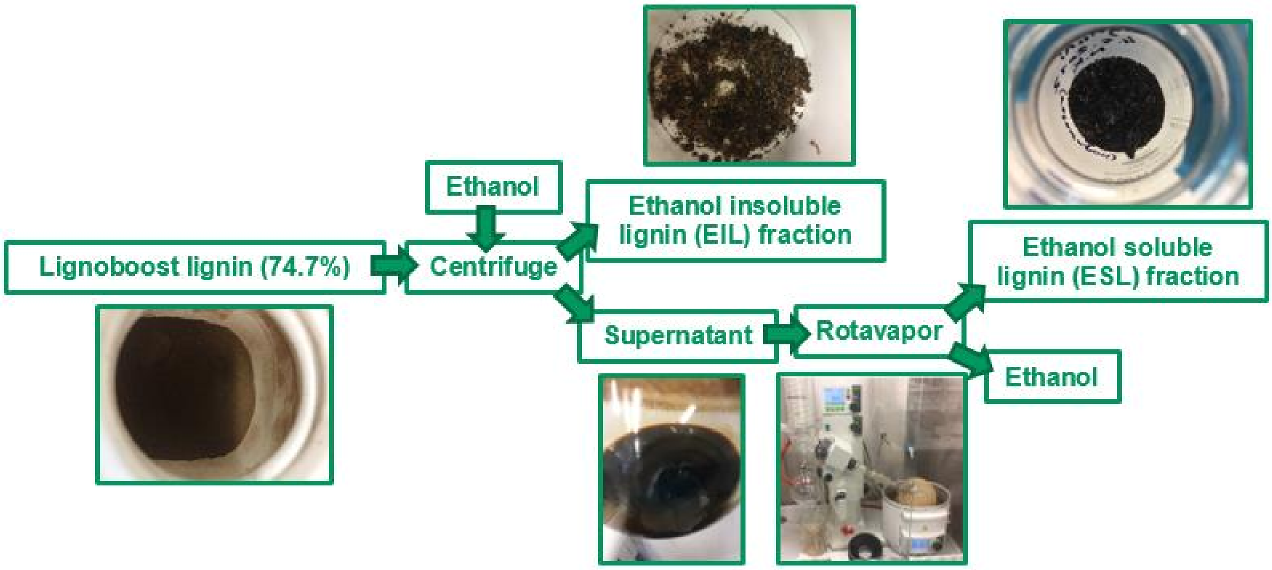


Figure 13- Lignin fractionation process.

5.4 Differential scanning calorimetry (DSC)

It is useful to be able to predict the adhesive behavior in different temperatures and thermal analysis, such as differential scanning calorimetry (DSC), is used for this (Hon, 2003). Thermal analysis measures the energy absorbed (endothermic) or the energy released (exothermic). Endothermic behavior is related to the softening and exothermic behavior to the curing (Danielson & Simonson, 1998a) and these are shown as phase transitions (Figure 14), such as the glass transition temperature

(T_g). At T_g the molecular mobility increases (Saunders, 1960) with increased cross-linking and molecular weight (to a certain value).

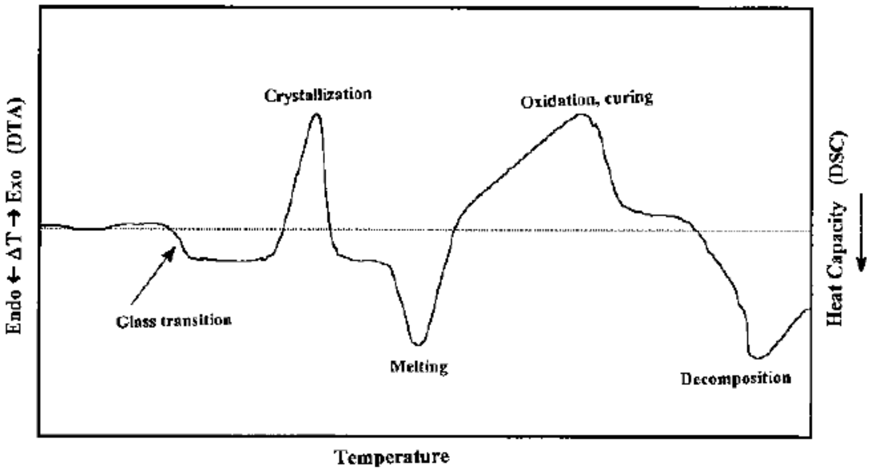


Figure 14 – The DSC curve. (Hon, 2003)

The DSC samples were prepared with freeze-drying. 20ml of each lignin sample (Lignoboost, ESL and EIL) was placed in a freezer for 6 hours. After the samples were frozen, they were placed in the freeze-drier (Labconco FreeZone 2.5) for overnight and after the freeze-drying, the samples were placed in the vacuum oven for an hour. The analysis was carried out using a TA Instruments Q2000 model. The temperature program was following: equilibration 40°C, heating 20°C/min to 220°C and cooling 20°C/min to 40°C. 5-10mg of sample was inserted into an aluminum pan and the pan with a lid was placed in the DSC for measurement.

The heating rate was first set to equilibration at 40°C, heating 10°C/min to 200°C and cooling 10°C/min to 40°C and 5mg sample was added as according to Leskinen et al. (2015). As there was no clear T_g for EIL fraction, the program was changed to equilibration at 40°C, heating 20°C/min to 200°C and cooling 20°C/min to 40°C and sample amount was increased to 5-10mg. The faster heating rate and higher amount of sample was believed to show a clearer T_g peak for EIL but this had no effect on the results.

5.5 Preparation of colloidal lignin particles (CLPs) by precipitation method

CLPs were prepared from Lignoboost lignin, ESL and EIL fractions. Lignoboost CLPs are referred from now on as CLP lignin. The steps included preparation of lignin solution, precipitation of CLPs and finally purification as according to Lievonen et al. 2016. Lignin solution was prepared by mixing 2.78g (dry basis) lignin, 38g deionized (DI) water and 101g tetrahydrofuran (THF). The solution was stirred at least 1 hour and then filtered through 0.7 μm Whatman GF/F filter. CLPs were precipitated by adding 350ml of DI water as quickly as possible with simultaneous stirring. The stirring was continued for 15 minutes. CLPs were purified (i.e. removal of THF) by adding the dispersion in 6-8 kDa Spectra/Por dialysis membranes and dialyzing in DI water under continuous flow so that the water was changed at least three times. After the dialysis, CLPs were filtered through 0.7 µm Whatman GF/F filter.

5.6 Particle size determination and zeta potential

Particle size and zeta potential was determined with Malvern Zetasizer. For the particle size measurements, the samples were diluted with DI water to 1:40 and for the zeta potential they were diluted to 1:20. For zeta potential measurement two last measurements (total of 3) were taken from the data and for the particle size the average of all (total of 2) measurements were taken into calculations.

5.7 FTIR

Infrared spectroscopy is used to identify polymers and the effect of chemical reactions. It can also give information about the curing and cross-linking of adhesives. (Hon, 2003) FTIR is a non-destructive and useful method for lignin analysis (Derkacheva &Sukhov, 2008).

The differences in chemical structures of Lignoboost lignin, lignin fractions and CLPs were analysed with Fourier transform infrared (FTIR) spectroscopy (Nicolet 380 FT-IR Spectrometer by Thermo Fisher Scientific). 30 scans with resolution of 4cm^{-1} and within the range of 400-4000cm^{-1} were recorded for each sample. Spectra were adjusted using automatic base line correction using built in OMNIC FTIR Software.

5.8 Cationic lignin preparation

Cationic lignin synthesis was adapted from Kong et al. 2015. 2.5g (dry basis) dried Lignoboost lignin was slowly added into 244.4ml 0.2M NaOH solution. pH was adjusted to 12.5 with NaOH. The mixture was heated to 70°C in oil bath (Figure 15) and 5g (4.42ml) glycidyltrimethylammonium chloride was added dropwise with a syringe (1 drop/s). The mixture was then heated with magnetic stirring at 70°C for 1hr. A beaker with 250ml 0.05M H_2SO_4 was inserted in an ice bath and the reaction mixture was added dropwise in it. The pH was adjusted to 3. The mixture was inserted in membranes (Pre-treated RC Tubing MWCO:1kD) and dialysed (Figure 16).

Figure 15 - The equipment for cationic lignin preparation.

Figure 16 - The dialysis.

5.9 Gelatin + ESL lignin preparation

Gelatin was mixed with ethanol soluble lignin (ESL) fraction to see how they behave together. Gelatin + ESL lignin was prepared by adding 75 mg gelatin (≥1000Da) in 10.2g 40°C water. 6.72 g EtOH was added slowly until the solution was clear. After this 222mg ESL was added slowly and the solution was precipitated by adding 60ml DI water. The mixture was filtrated with Whatman GF/A filter (diameter 110mm, cat MO1820110) and then ultrafiltrated (Micon 8200 and 150 kDA PES membrane) in order to remove excess of gelatin. 70ml of gelatin + ESL and 70ml of DI water was added in ultrafiltration, and it was filtrated until there was 70 ml left. This was repeated six times in order to decrease the theoretical concentration of free gelatin to ~1% from the initial amount.

5.10 Glue preparation for lap shear and ABES testing

Lignoboost lignin was dispersed with ultraturrax (IKA T18 basic) for 5-10 minutes to ~30% dry matter content (exact value depending on the CLP concentration). Each lignin fraction and cationic lignin was concentrated (Figure 17c) to ~30% dry matter content with a rotavapor (Figure 17a&17b) (40°C, 50mbar). Gelatin was dissolved in 50°C or warmer DI water to form ~30% dispersion. Formulations contained 2/3 (wt%) lignin (either CLPs, ESL CLPs or EIL CLPs) and 1/3 (wt%) other component (either gelatin or cationic lignin). Polyvinylalcohol (PVA) glue (brand name: Kiilto) was diluted to ~30% dry matter content from initial dry matter content of 49%.

The following glues were prepared for lap shear test (Table 1):

Glue	Lignin fraction wt%	Cationic lignin wt%	Gelatin wt%	Kiilto glue wt%
1. Lignoboost lignin	100 %	0 %	0 %	0 %
2. Colloidal lignin particles (CLPs)	100 %	0 %	0 %	0 %
3. Ethanol soluble lignin (ESL) CLPs	100 %	0 %	0 %	0 %
4. Ethanol insoluble lignin (EIL) CLPs	100 %	0 %	0 %	0 %
5. Cationic lignin	0 %	100 %	0 %	0 %
6. Cationic lignin + CLPs	~66 %	~34%	0 %	0 %
7. Cationic lignin + ESL CLPs	~66 %	~34%	0 %	0 %
8. Gelatin	0 %	0 %	100 %	0 %
9. Gelatin + CLPs	~66 %	0 %	~34%	0 %
10. Gelatin + ESL CLPs	~66 %	0 %	~34%	0 %
11. Gelatin + EIL CLPs	~66 %	0 %	~34%	0 %
12. PVA glue	0 %	0 %	0 %	100 %

Table 1. Different glues used for lap-shear testing

Figure 17a-c - CLP concentration with rotavapor.

Same glue concentrations were used for the ABES testing as in the lap shear testing. The following glues were tested with ABES (Table 2):

Glue	Lignin fraction wt%	Gelatin wt%	PF wt%
1. Colloidal lignin particles (CLPs)	100 %	0 %	0 %
2. Gelatin + CLPs	~66 %	~34%	0 %
3. Gelatin + ESL CLPs	~66 %	~34%	0 %
4. Gelatin + EIL CLPs	~66 %	~34%	0 %
5. Phenol-formaldehyde (PF) (birch:14J025 & spruce:14J553)	0 %	0 %	100 %

Table 2. Different glues for ABES testing

5.11 Test piece preparation and glue application for lap-shear testing

Commercial ice cream sticks (114x10x2mm) were used for the gluing experiments (Figure 19). The sticks were cut in half in longitudinal direction (57x10x2mm) with an upright drill (Figure 20). The glue application followed the standard ASTM D-1002 (Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)) and the test length in grips and the overlap length was set equal (10mm) as in Sarkar & Adhikari (2000). The glue was applied in the 90mm^2 area (10mmx9mm) on a stick and other stick was applied on top as in single-lap joint (Figure 21&22a-c). In the used single-lap joint the adherends are joined with an adhesive.

Adhesives can be tested with several methods and the main tests include tensile, shear, cleavage and peel testing (Figure 18). Stress values are affected e.g. by the overlap and thickness of the adhesive and adherend. The maximum stress occurs at the end of the bonds. Adhesives are typically more prone to cleavage than shear failure and cleavage usually dominates the lap joint fracture. (DeVries & Borgmeier, 2003)

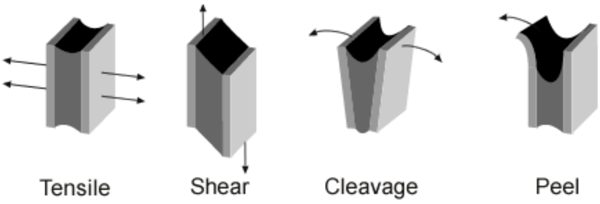


Figure 18 - Different stresses. (Adhesives toolkit, 2017)

In shear testing the forces are parallel to the adhesive plane, in tensile testing the forces are perpendicular to the bond and in peel testing forces separate the flexible part from the stiff part in the bond. (Vick,1999) The single-lap joint is a simple, cheap to manufacture and it is one of the most frequently used method in measuring shear strength of adhesives. (Tsai & Morton, 1993; Goudarzi & Khedmati, 2015). Shear strength or adhesive strength can be defined as the maximum force (N) at the break divided by the adherend surface area (mm^2). (Habenicht, 2009) Surface roughness of the adherend, thickness of the adhesive, pressure and hold time as well as cure time all affect the joint strength (Raos et al. 2007).

Figure 19 - Test piece preparation.

Figure 20 - Upright drill.

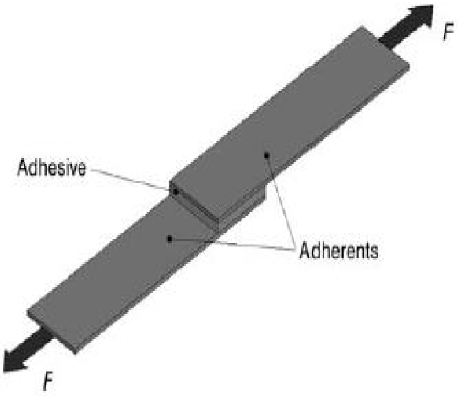


Figure 21 – Single-lap joint.

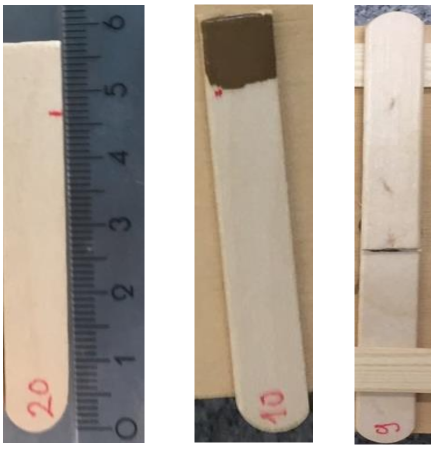


Figure 22a-c - Scheme of glue application.

Figure 23 - Cold press set up.

Figure 24 - Cold pressing using screw clamps.

5.12 Pressing & conditioning for lap shear testing

5.12.1 Cold pressing

Cold pressing was done in room temperature. In cold pressing two flat wood pieces, two support pieces and three screw clamps were used, and the samples were kept drying overnight (Figure 23&24). After drying the samples were conditioned (50% humidity and 23°C) for 24 hours before lap-shear testing.

5.12.2. Hot press gluing

For the hot press gluing two metal sheets were used (one underneath and one on top) (Figure 25a). The hot press (Carver laboratory press) (Figure 25b) was used for 10 minutes with temperature of 120°C and pressure of 20kg/cm^2. After hot pressing the samples were conditioned as mentioned above. According to Stephanou & Pizzi's work (1993), in the particleboard testing the maximum pressure was 23 kg/cm^2.

Figure 25a-b – Hot press set up.

Figure 26a-b – Lap-shear equipment

5.13 Lap-shear test

Lap-shear testing was done with Instron R-33 (4204 Universal tensile tester) (Figure 26a-b) and 1kN load cell. The parameters were chosen as according to the standard ASTM D-1002. The rate was 1.3 mm/min, thickness (considered here as the length of the glue area):10mm: width (of the glue area): 9mm. Gauge/span length was set as 84mm. The load at break (N) and strain at break (%) were recorded and the adhesive strength was calculated according to equation (2).

Adhesive strength (τB) is defined as

$$\tau\mathrm{B} = \frac{\text{Max force at break}}{\text{Adherend surface area}} = \frac{Fmax}{A} = \frac{N}{\mathrm{mm2}} = MPa \tag{2}$$

5.14 Test piece preparation and glue application for ABES testing

Birch (Betula Pendula) and spruce (Picea Abies) veneer pieces (Figure 27) (117mmx20mm0.8mm) were used for testing. Veneer pieces were conditioned in 35% relative humidity and 26°C. 8.6µl phenol-formaldehyde glue was applied with automatic pipette. Lignoboost lignin and CLPs were applied manual pipette with setting 9µl (some lignin remained in the tip). Lignoboost lignin, CLPs and gelatin formulations were applied so that the whole application area was covered. The glue was applied in 60mm^2 area (20mmx3mm) on a veneer piece and other veneer piece was applied on top as in single-lap joint.

5.15 ABES testing

ABES (Adhesive Bonding Evaluation System) (Figure 28) was used for measuring simultaneously the effect of hot press and lap shear. Testing was done in 64% humidity and at 20°C. As lignin decreases the curing rate compared to the phenol-formaldehyde resin, the curing time was set to be ~30% higher than for phenol-formaldehyde and hence 150°C as according to Danielson & Simonson (1998b). Two different curing temperature and times were used. First the temperature and time was set to be 130°C with cure time 60s and then 150°C with cure time of 300s. Load at break (N) was recorded and adhesive strength (N/mm^2=MPa) was calculated.

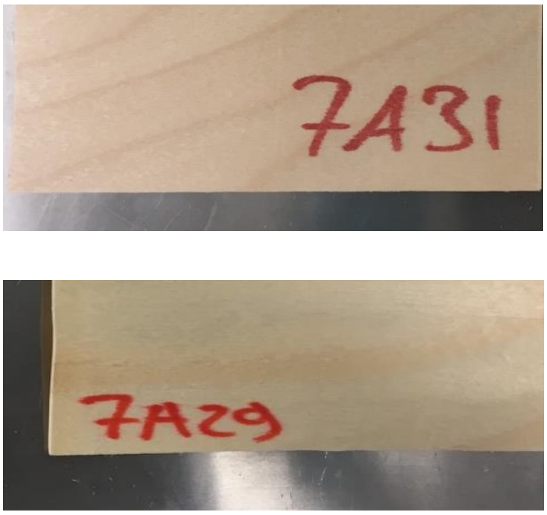


Figure 27 – Birch and spruce veneers.

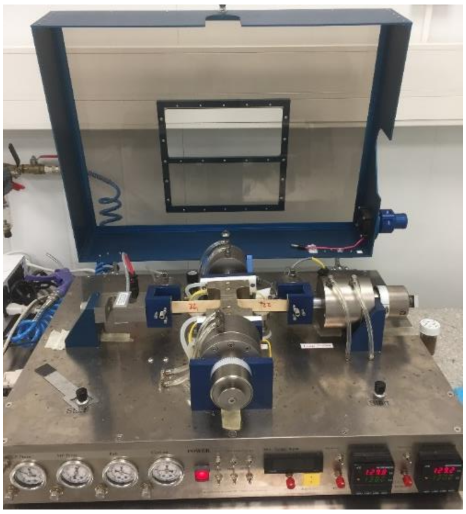


Figure 28 - ABES testing equipment.

5.16 Moisture resistance test

Moisture resistance was tested with phenol-formaldehyde, CLPs and CLP + gelatin. Ice cream sticks were glued and hot-pressed as in shear testing and samples were put in a beaker which contained tab water. Cold water resistance (24h in 20°C) and hot water resistance after 6hrs was visually observed.

5.17 FESEM

FESEM (Field Emission Scanning Electron Microscope) was used to study the surface of the broken glue bond. Samples were gold coated (Figure 29) and FESEM JSM-7500F was used (voltage 1.50 kV, sample holder 12,5mm) and the images we taken at three different magnifications (x25, x50, x100). FESEM images were taken for the following hot-pressed samples after shear strength testing: cationic lignin, gelatin, EIL CLPs and EIL CLPs+gelatin.

Figure 29 - Gold coated FESEM samples.

6. Results and discussion

6.1 DSC

Glass transition temperature was measured to find out the softening temperature of the adhesive. Lignoboost lignin showed T_g in 178° C with standard deviation of 0.1. Ethanol soluble lignin (ESL) showed T_g in 136°C with standard deviation 3.0. There was no clear T_g for ethanol insoluble lignin (EIL). The DSC graphs can be found in appendix (6.2). Starting material and insoluble fraction showed higher T_g and this was probably because of the condensed structures.

According to Ropponen et al. (2011), T_g of acetone soluble fractions had lower T_g than starting lignin and this might be because of the high amount of depolymerized structures material in these fractions. According to Cui et al. (2014) the T_g for Kraft lignin (KL) is 148° C, for acetone insoluble Kraft lignin (AIKL) 180° C and for acetone soluble lignin (ASL) 110° C. According to Yoshida et al. (1987), different lignin fractions showed T_g from 32° C to 173° C, and Kraft lignins are thermally unstable above 200° C. Ropponen et al. (2011), also found that softwood KL shows higher T_g than hardwood KL and in hardwood KL there is more syringyl (S) lignin in the acetone soluble fraction and hydroxyphenyl (H) lignin in the insoluble fraction. According to Brebu & Vasile (2010), thermal analysis of different lignins using differential thermal analysis (DTA) reveals an endothermic peak at 100-180ºC, associated to the evaporation of water molecules. Exothermic peaks are shown in 280-390 ºC and at 420 ºC. Lignin degrades slowly and in 700ºC the mass loss is only 40wt%.

These literature findings are in accordance with the experimental results. The T_g for the ethanol insoluble lignin might be higher than for starting lignin and therefore out of the DSC measurement range. This is likely because of the molecular weight of ethanol insoluble lignin is expectedly higher than the molecular weight of ethanol soluble lignin and therefore also the T_g is higher.

6.2 FTIR

The spectrum for Lignoboost lignin and different lignin fractions (Figure 20 shows the characteristic peaks for lignin. We can see that there are no new peaks arising and therefore the fractionation has not affected the lignin structure, although small differences in relative contents of functional groups can be observed between fractions.

According to Derkacheva & Sukhov (2008), a complete lignin spectrum can be seen in 740-1849cm^{-1}. The band in 1705-1517 cm^{-1} is non-conjugated carbonyl group and the bands seen in 1600, 1515 and 1425cm^{-1} are C-C stretching vibrations caused by the aromatic ring. These values were similar with the obtained spectrum. The carbonyl groups can be seen in 1702-1706 cm^{-1} , the vibration caused by the aromatic ring can be seen within the range 1592-1596 cm^{-1} and 1511-1593 cm^{-1} . The band in 1460 cm^{-1} is C-H vibration from CH$_2$ and CH$_3$. This can be seen in 1461 cm^{-1}. According to Faix (1999), the band seen in 1423 cm^{-1} is aromatic vibrations together with C-H group. This was seen within range 1423-1427 cm^{-1}. The non-etherified phenolic OH groups, which are the result of the cleavage of β-O-4 and α-O-4 bonds in Kraft pulping, can be seen in 1365 cm^{-1} (Tejado et al. 2007). This can be seen within range 1365-1367 cm^{-1}. Also, the differences between hardwood and softwood can be seen in IR spectrum. G bands (typical for softwoods) of Kraft pine lignin can be seen in 1270, 1125, 855 and 810cm^{-1}. (Tejado et al. 2007). These can be seen within range 1265 cm^{-1}, 1122-1126 cm^{-1}, 811-813 cm^{-1}.

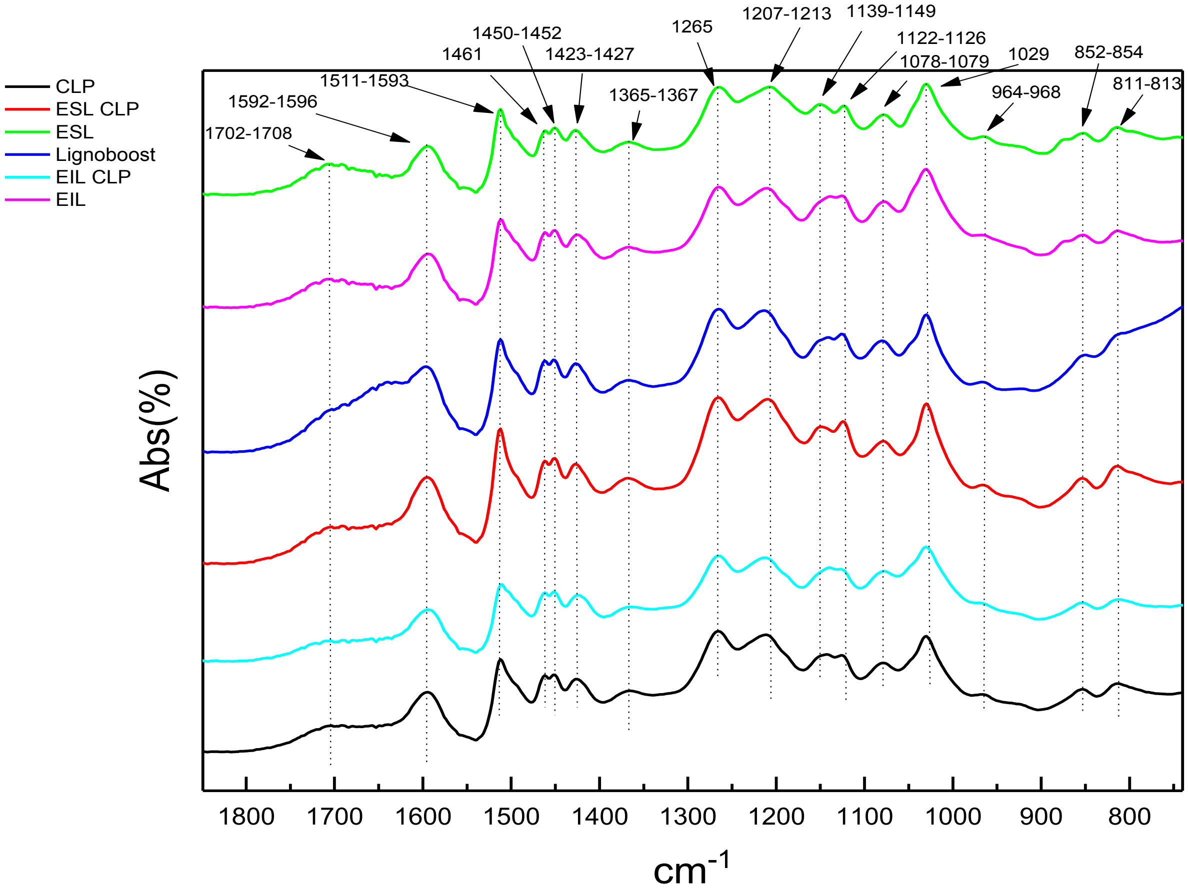


Figure 30- FTIR-spectra of lignin fractions, and corresponding CLPs.

6.3 Particle size and zeta potential

In order to see how the fractionation affects the formation of CLPs, the particle sizes and zeta potentials were measured for CLPs, EIL CLPs, ESL CLPs and gelatin+ ESL. (Figures 31 & 32).

Cationic lignin as itself was also detected to consist small particle size (100nm) which is likely to be caused by aggregation.

The particle size was the smallest for CLPs, then EIL CLPs and ESL CLPs. Gelatin + ESL showed positive zeta potential and therefore it can be assumed that gelatin formed a thin coating on ESL as in Leskinen et al. (2017) and this coating was due to the gelatin adsorption on the oppositely charged lignin particle. According to Leskinen et al. (2017) proteins have an affinity towards hydrophobic polymers, such as lignin. Other CLPs showed negative zeta potential. This is as expected as according to Lievonen et al. (2016), lignin nanoparticles have negative zeta potential.

According to Lievonen et al. (2016) the stable lignin nanoparticle sizes varied between 320-360nm with zeta potential -60mV. The stability was caused by the high zeta potential as electrical double layer repulsion prevents aggregation of the particles. The particle sizes were not dependent on pH between pH 4-12. Wei et al. (2012) found that the zeta potential was -91.5 mV at pH 11 and the average particle size was 182nm. Aggregation occurred at high lignin concentrations. Various factors, such as concentration of lignin and pH affect the particle size distribution of formed CLPs (Frangville et al. 2012).

The pH of the lignin fractions varied between 4-6. After the CLP preparation and dialysis, the CLPs were filtered. ESL CLP fraction took a longer time to go through the filter paper than EIL CLP particles, and therefore filter paper grade 5 was used. ESL CLPs also showed higher particle size than EIL CLPs so it might be because ESL CLPs were aggregated.

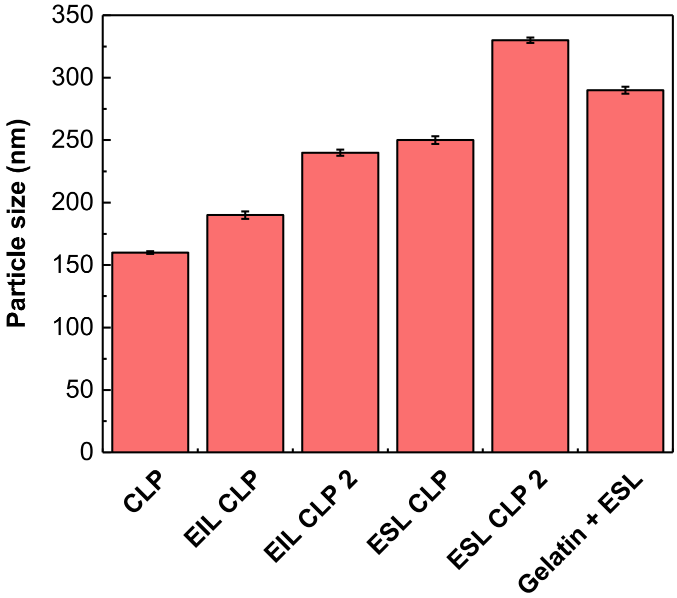


Figure 31 - Particle sizes of different fractions.

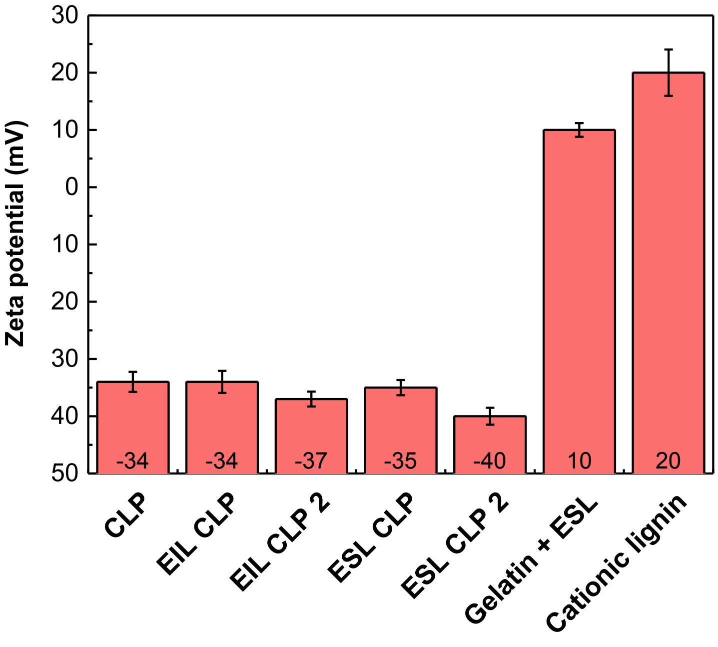


Figure 32 - Zeta potential of different fractions.

6.4 Lap-shear test

The lap-shear test was done for the cold-pressed and hot-pressed samples to measure the adhesive strength (N/mm^2) and to see how different adhesives compare with the commercial PVA based glue.

6.4.1 Cold-pressed samples

Cold-pressed Lignoboost samples (Figure 33a-b) were mud-like and breaking almost immediately when touched. Cold-pressed CLPs provided more uniform spreading and were not breaking immediately; however, they broke when inserted in the tensile tester clamps, which indicates poor adhesion of lignin alone to the wood. Cationic component in the adhesive improved adhesion, and gelatin and gelatin + CLPs did not break when inserted in the clamps.

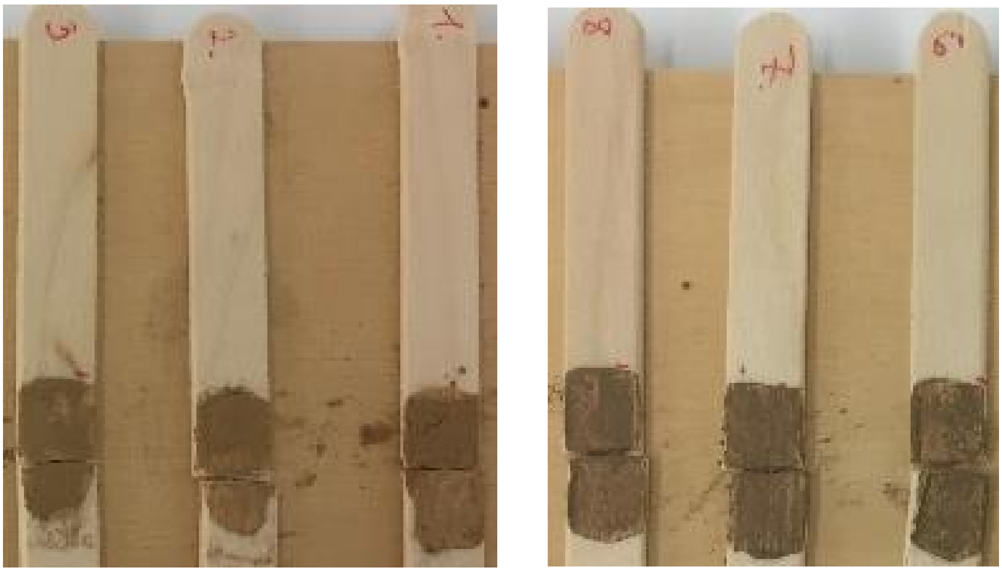


Figure 33 a-b - Broken bonds of cold-pressed Lignoboost (1-3) & CLPs (6-8).

6.4.2 Hot-pressed samples

All the hot-pressed samples, such as Lignoboost and CLPs (Figure 34a-b) gave some shear strength values. With the gelatin and PVA glue there were problems with the slippage in the clamps, resulting high deviation to the strength data.

According to Goudarzi & Khedmati (2015), failure occurs due to the energy release in the adhesive and the failure can occur in several ways, such as adhesive failure or cohesive failure. Cohesive failure in the adhesives is the most common failure and it is due to the failure at the bond-line. In adhesive failure, the failure occurs in the adhesive-adherend bond, whereas in the cohesive failure the failure occurs in the adhesive. In the cold-pressed samples, it can be seen that the glue was less evenly spread and especially with the gelatin + ESL (CP) (Figure 35) the glue was not penetrated on the other side of the stick. In the hot-pressed samples the glue spread quite evenly on both sides of the stick. Therefore, the cold-pressed samples seemed to show adhesive failure, as the breakage occurred in the glue line, whereas the hot-pressed samples showed cohesive failure, as the breakage occurred mostly in the adhesive-adherend bond.

Figure 34 a-b – Broken bonds of hot-pressed Lignoboost (11-13) & CLPs (18-20).

Figure 35- Types of bond failure occurring in different samples.
From left to right: Gelatin + CLP (HP), gelatin + CLP (CP), gelatin + ESL (HP) & gelatin + ESL (CP)

6.4.3 Load at break, adhesive strength and strain at break

The highest load at break was found for hot-pressed samples and for commercial PVA glue (700N), then for gelatin (580N), ethanol insoluble lignin (EIL) CLPs + gelatin (490N), CLPs + gelatin (420N), ethanol soluble lignin (ESL) CLPs + gelatin (390N). Cationic lignin showed lowest load at break (120N) (Figure 36). Cold-pressed load at break for commercial PVA glue was 660N, for gelatin 220N and for gelatin + CLPs 120N (Figure 37).

The highest adhesives strength was found for commercial PVA glue (7.7 MPa), then for gelatin (6.4 MPa), ethanol insoluble lignin (EIL) CLPs + gelatin (5.4 MPa), CLPs + gelatin (4.5 MPa), ethanol soluble lignin (ESL) CLPs + gelatin (4.13 MPa). Cationic lignin showed lowest adhesive strength (1.3 MPa) (Figure 38). Cold-pressed adhesive strength for commercial Kiilto glue was 7.3 MPa, for gelatin 2.7 MPa and for CLPs + gelatin 1.3 MPa (Figure 39).

According to Hon (2003), at low molecular weights the tensile strength or bonding power is close to zero and increasing molecular weight also increases tensile strength up to a certain level and then levels off. If EIL lignin is assumed to have a higher molecular weight, then it should also show better adhesive strength. ESL CLP and EIL CLP values are quite similar, ESL CLP showing slightly better results, but taking into account the standard deviation, the order could be also different. With gelatin + EIL CLP the results were better than for gelatin + ESL. The difference could be because it was difficult mix gelatin and lignin in exactly same proportions.

The highest strain at break was for commercial PVA glue (0.89%), then for gelatin (0.72%), ethanol insoluble lignin (EIL) CLPs + gelatin (0.53%), ethanol soluble lignin (ESL) CLPs + gelatin (0.37%) and CLPs + gelatin (0.3%). Cationic lignin showed lowest load at break (0.1%) (Figure 40).

Cold-pressed strain at break for commercial PVA glue was 0.61%, for gelatin 0.7% and for gelatin + CLPs 0.1 % (Figure 41).

As a conclusion, gelatin and lignin fractions did not the reach the PVA glue adhesive strength values. Gelatin is important for a good adhesion whereas cationic lignin does not increase adhesion much. The cold-pressed lignin samples performed poorly and only gelatin seemed to give some adhesion. In terms of strain the gelatin and lignin fractions did not reach the PVA glue values in toughness. Gelatin improved toughness, but the effect was relatively smaller than in increasing strength. The high standard deviation with pure gelatin (both hot-pressed and cold-pressed) does not give a clear indication of the actual gelatin strain. Cationic lignin was brittle and showed low toughness.

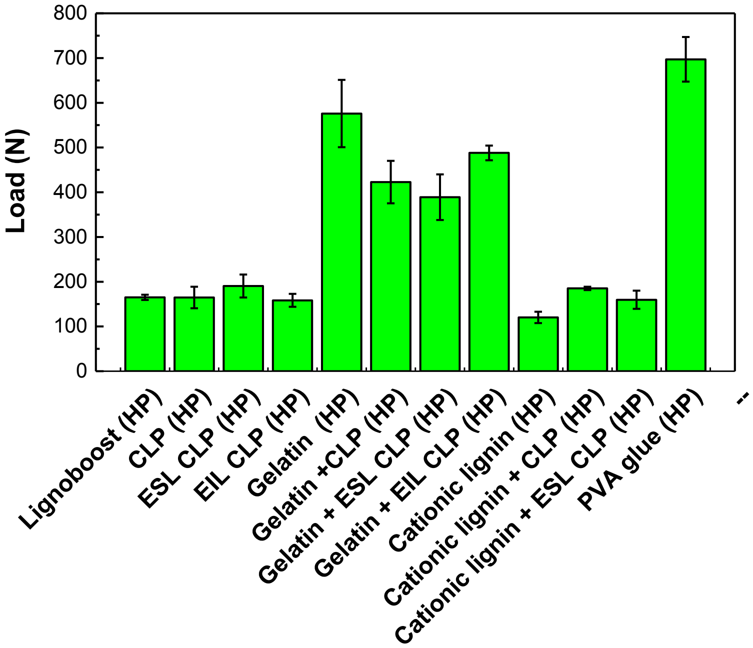


Figure 36 - Load at break of hot-pressed samples.

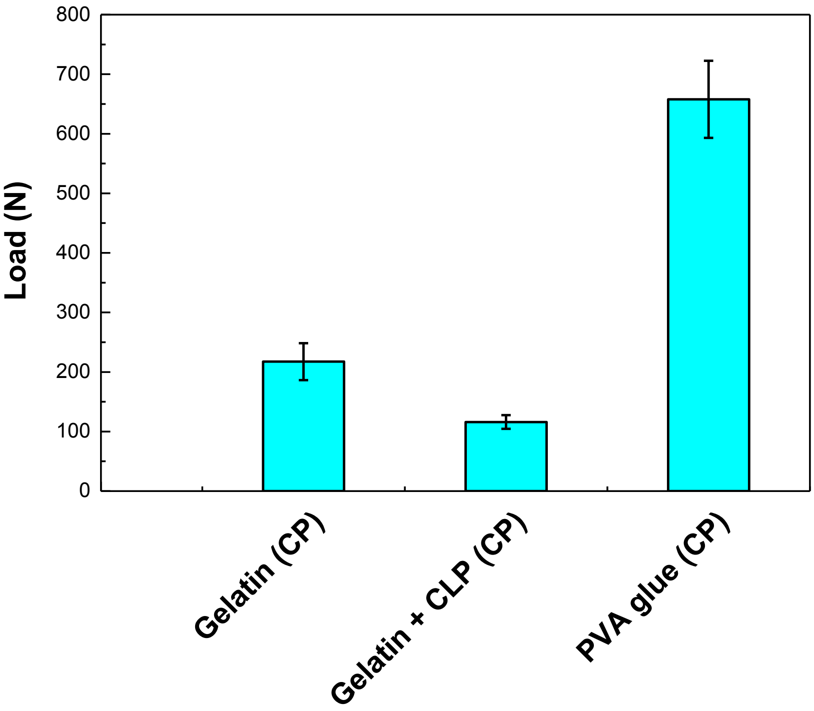


Figure 37 - Load at break of cold-pressed samples.

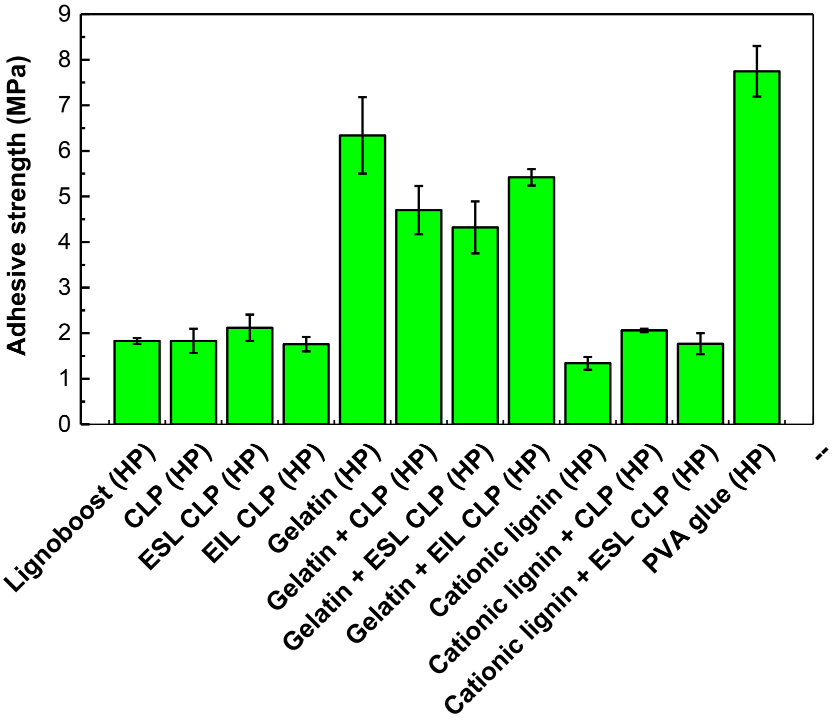


Figure 38 - Adhesive strength of hot-pressed samples.

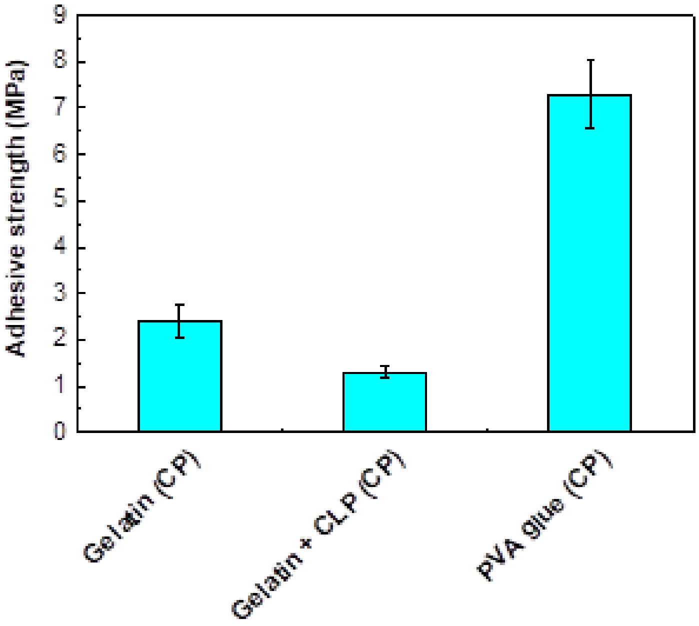


Figure 39 – Adhesive strength of cold-pressed samples.

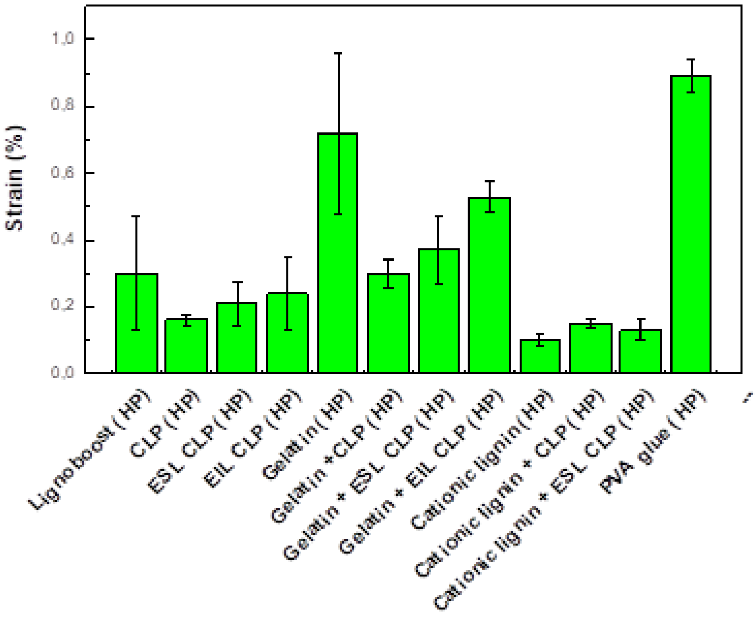


Figure 40 - Strain at break of hot-pressed samples.

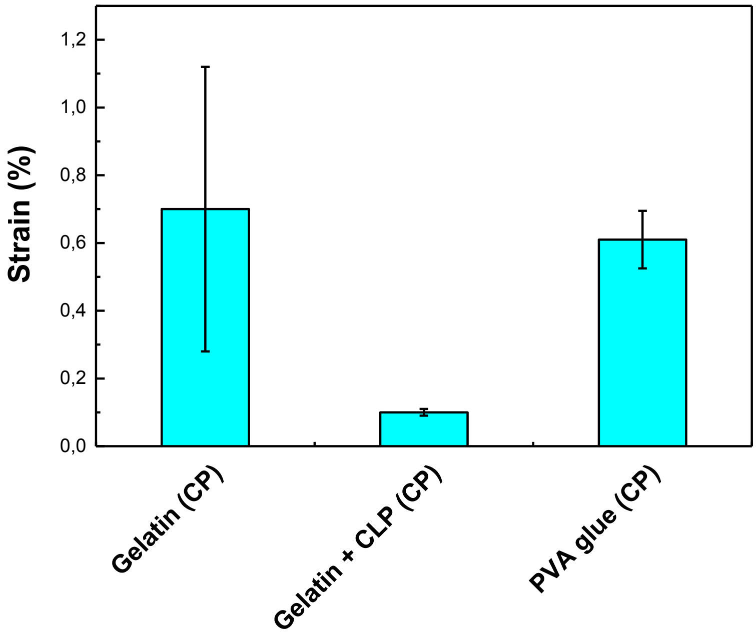


Figure 41- Strain at break of cold-pressed samples.

6.5 ABES testing

ABES testing was done to see how the increase of the pressing temperature affects the adhesive performance and how the CLPs and CLP + gelatin compare to the phenol-formaldehyde adhesives in the intended plywood pressing process.

6.5.1 Spruce veneers

Spruce veneers were glued and pressed at 130° C for 1 minute and at 150° C for 5 minutes. The adhesive strength decreased with increasing temperature (Figure 42 & 43), only exception being ESL CLP + gelatin, which showed a slight increase in the results with increasing temperature. With ESL the softening (*Tg* 138 °C) occurred at a higher (150° C) temperature therefore resulting in better results than in 130° C. This was also the only adhesive where the *Tg* was exceeded at 150° C. The best adhesive strength was for phenol-formaldehyde (6.8 MPa in 130° C and 6.6 MPa in 150° C) and of the lignin samples for CLP + gelatin (5.9MPa in 130° C and 5 MPa in 150° C). For CLPs the softening (*Tg* 178 °C) is expected to occur at a higher temperature and therefore the good results of CLPs might be because of the improved properties of colloidal particles, such as enhanced particle interaction. With CLPs the adhesive strength was higher in 150° C than for Gosselink's (2004) value for Kraft lignin in 180° C. According to his work, for Kraft lignin in 140° C, adhesive strength was 1.5 MPa and in 180° C it was 2.2 MPa. Also, wood failure increased with increasing temperature therefore indicating a stronger glue bond. (Gosselink et al. 2014)

The trend of decreasing adhesive strength (Figure 43) with increasing temperature is contradictory to the literature as according to Gosselink et al. (2014) lignin is activated at a higher temperature. According to his work, from 140° C to 180° C the adhesive strength has been reported to increase. Therefore, the load at break and adhesive strength of the lignin samples should have increased with increasing temperature. One reason that the values decreased could be that gelatin performs poorly in the increased temperature. There also other reasons which might have affected the results. One of the reasons might be the uneven quality of spruce veneers and the spruce veneers broke sometimes even at low forces (Figure 47). ABES gluing and pressing was first done in 130° C and after that in 150° C. This might also affect the results and high standard deviation especially with gelatin samples. Gelatin samples had to be mixed very well and heated at the same time as gelatin became solid-like very quickly (Figure 46), and also the mixture needed to be heated up each time before application, making the glue drier and more difficult to apply on the veneer.

6.5.2 Birch veneers

Birch veneers were also tested with the same parameters (Figure 44 & 45). Also with birch veneers, the results decreased with increasing temperature. CLP + gelatin showed the best adhesive strength (9.4 MPa in 130° C, 12.2 MPa in 150° C,), even better than PF. The good adhesive strength values might be due to the higher quality and strength of birch veneers compared to the spruce veneers. CLP adhesives might also show better potential with specific veneers, such as birch veneers. The phenol-formaldehyde values did not reach the literature values as according to Habenicht (2009), for heat or hot cured epoxy and phenol resin adhesives the bond strength is 25-30 MPa and for room temperature epoxy adhesives it is 20-30 MPa. Therefore, more testing should be done with PF resins and other glues. According to Danielson & Simonson (1998b), the Kraft lignin phenol-formaldehyde resin (KLPF) with 40% phenol replacement with lignin showed shear strength of ~1.7 MPa, with 60% replacement ~2 MPa and with 80% replacement ~0.5 MPa (non-pretreated and unmodified Kraft lignin used). Therefore, the CLPs and CLPs+ gelatin performed better in increased temperature than KLPF.

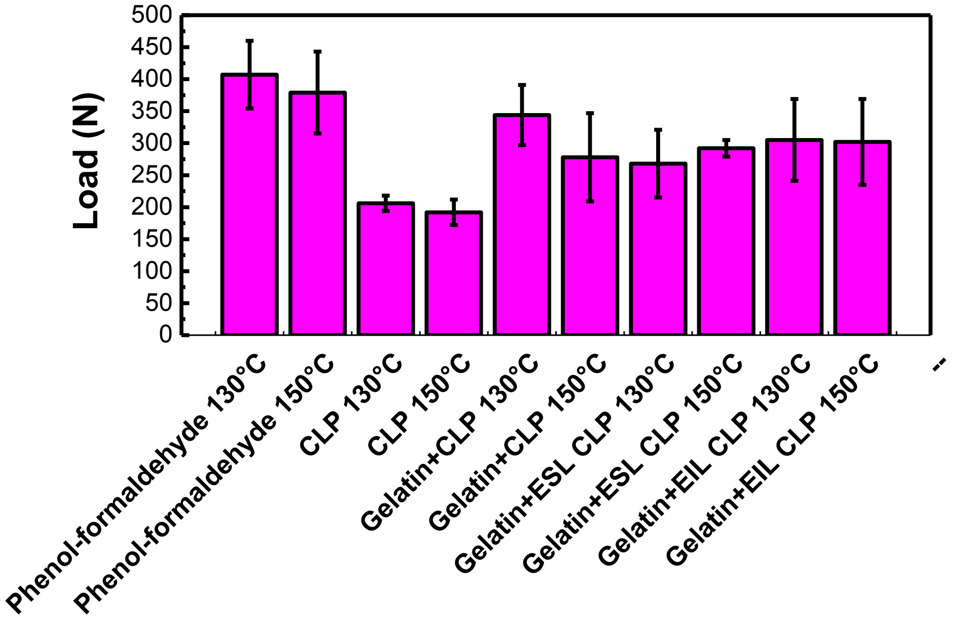


Figure 42 – ABES Load at break for spruce veneers.

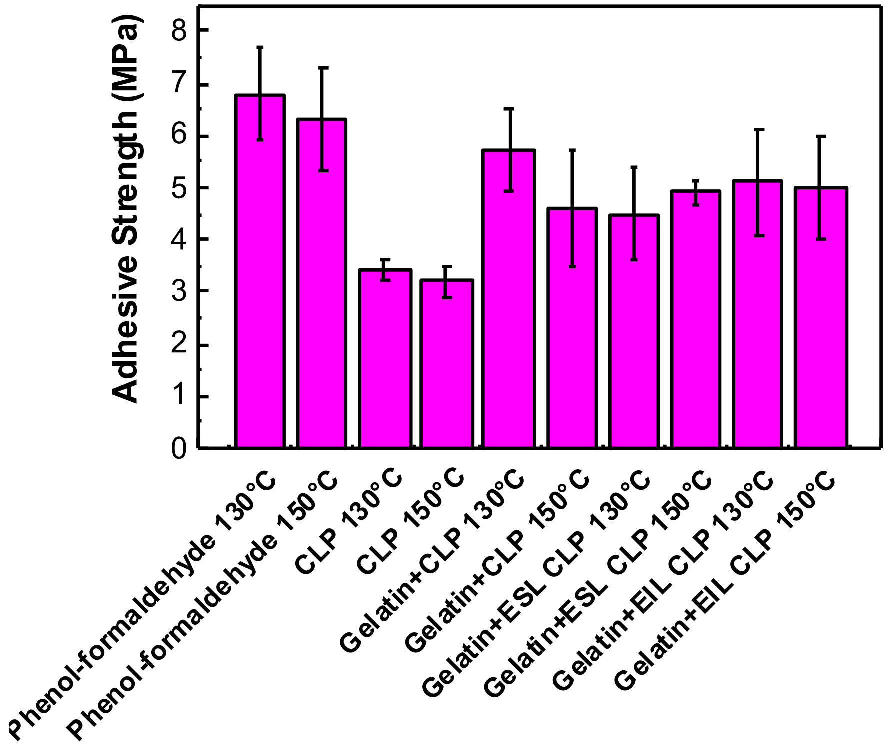


Figure 43 – ABES Adhesive strength for spruce veneers.

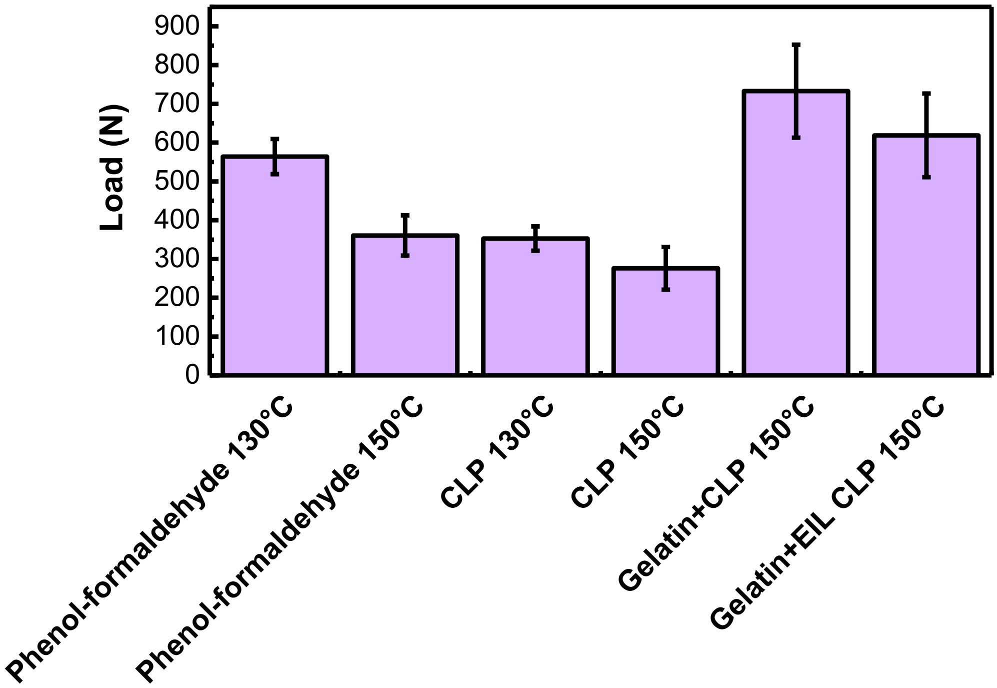


Figure 44 – ABES Load at break for birch veneers.

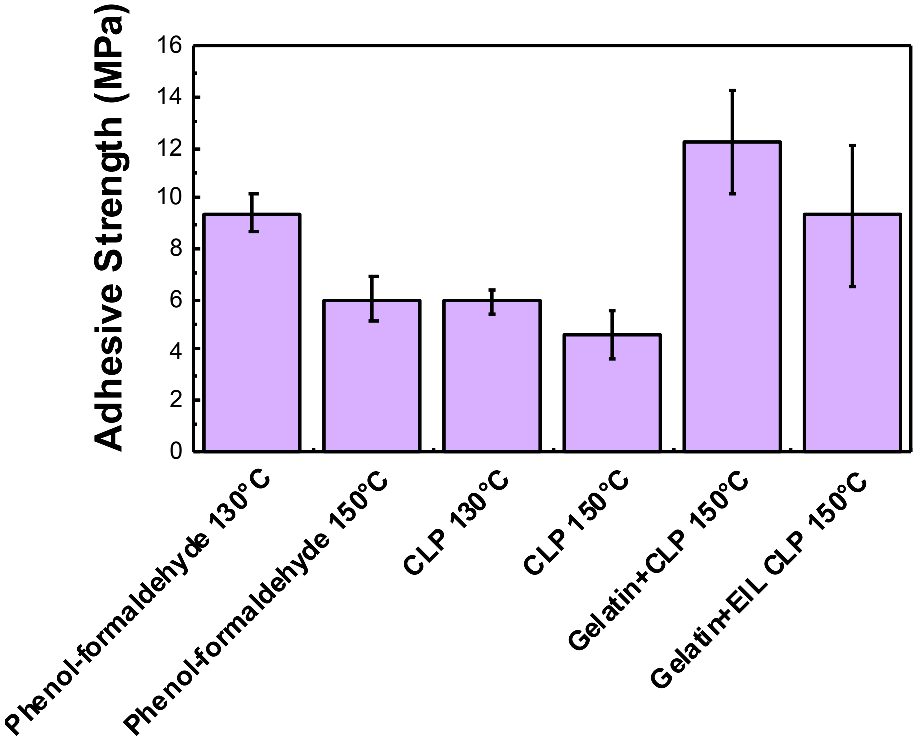


Figure 45 – ABES Adhesive strength for birch veneers.

Picture 46-CLP + gelatin mixture before mixing.

Picture 47-Broken spruce veneers.

6.6 Moisture resistance test

According to Luo et al. (2015), the cross-linking between denaturized protein and lignin improved water resistance. The cross-linking occurred due to the reaction with phenolic hydroxyl methyl groups with amino and hydroxyl groups of soy protein, resulting in rigid structure.

Moisture resistance was tested with PF, CLPs and gelatin + CLPs. With cold water resistance, CLPs broke immediately after adding them into the beaker, whereas PF and gelatin + CLPs remained intact. CLP + gelatin and phenol-formaldehyde lasted for 24hrs with cold and hot water. This indicates that gelatin improves moisture resistance and could potentially be used in the plywood applications.

6.7 FESEM

FESEM images were taken from the broken hot-pressed samples after shear strength testing. FESEM images show cationic lignin, gelatin, EIL CLPs and EIL CLPs + gelatin on the wooden ice-cream sticks. The images of cationic lignin on the wooden ice-cream sticks (Pictures 48, 49 & 50) show some cracks (top circle in picture 50) and the surface of the wooden ice cream stick is slightly exposed (bottom circle in picture 50). Cationic lignin seems to be mainly on the outer surface and not penetrated in the wood. This might be the reason why cationic lignin showed low adhesive strength. Gelatin showed some wood failure (Pictures 52 & 53). Wood failure means that the bond is broken on the wood and not in the glue line therefore indicating a strong adhesion of the bond (Gosselink et al. 2004). Also, the glue seemed to be a lot smoother and more penetrated than in the case of cationic lignin (Picture 51). EIL CLP also showed some cracks (Pictures 55 & 58) in glue similar to cationic lignin but not as much. The glue also seems to be more inside the wood compared to the cationic lignin and the wood surface is not exposed (Pictures 54, 56 & 57). EIL CLP + gelatin showed a smoother surface (Pictures 59, 60 & 61) compared to pure EIL CLP. The surface is slightly uneven but the there are no similar cracks as with cationic lignin or with EIL CLP. The surface is slightly more uneven than with gelatin and there is no wood failure present. It seems that an even surface with wood failure results in a strong adhesive strength. Also, cracks reduce the adhesive strength, but the more cracks are penetrated in the wood the less this affects.

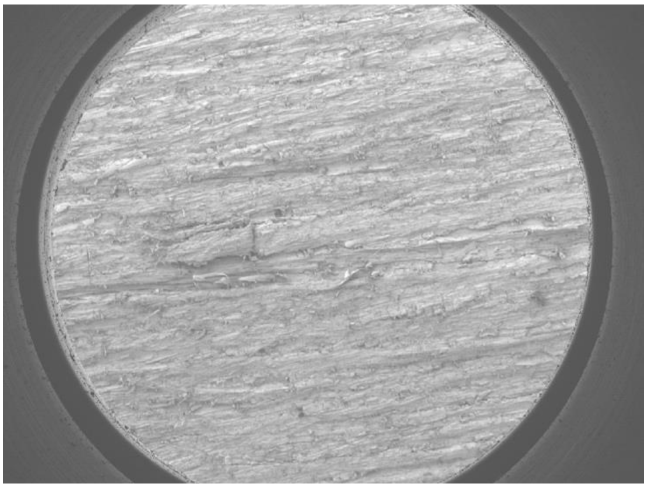


Figure 48- Cationic lignin, magnification x25

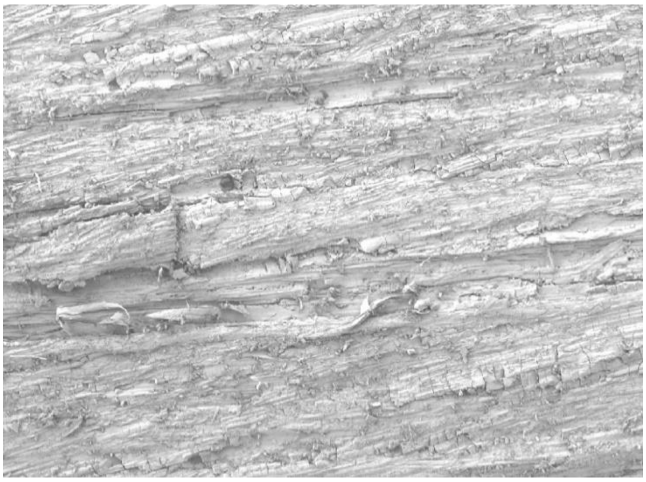


Figure 49 - Cationic lignin, magnification x50

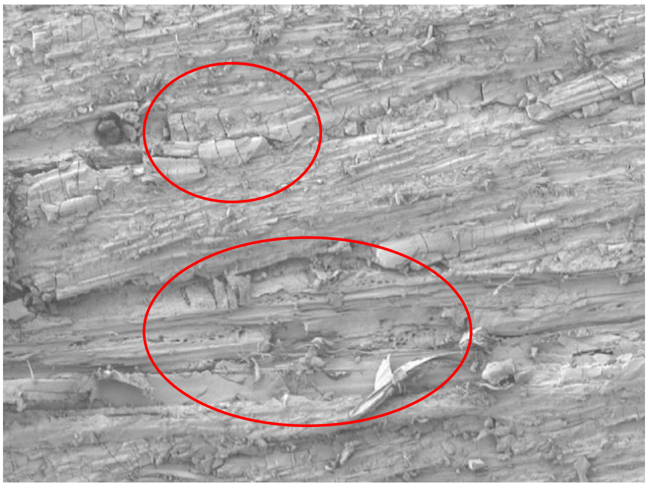


Figure 50 - Cationic lignin, magnification x100

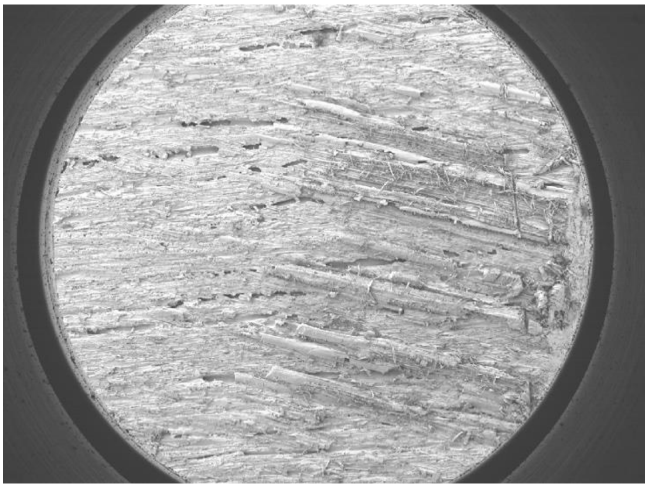


Figure 51 – Gelatin, magnification x25

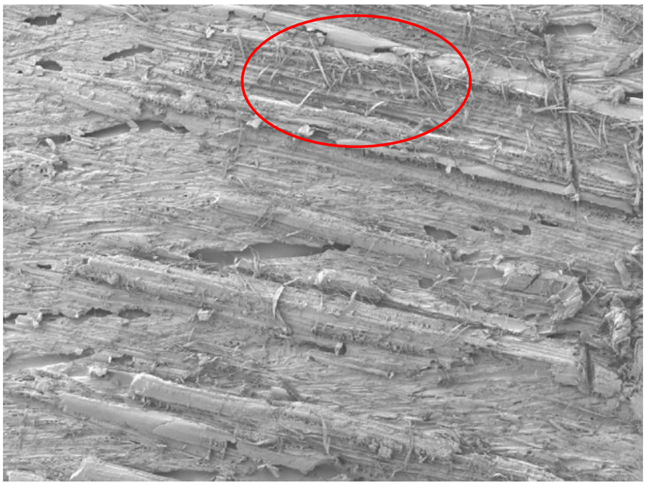


Figure 52 – Gelatin, magnification x50

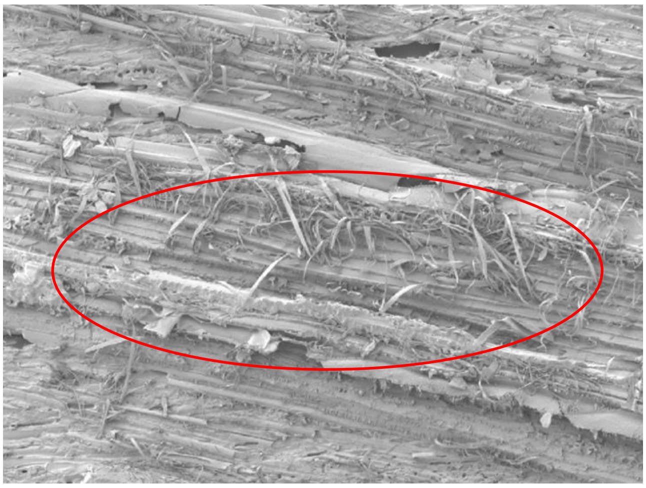


Figure 53 – Gelatin, magnification x100

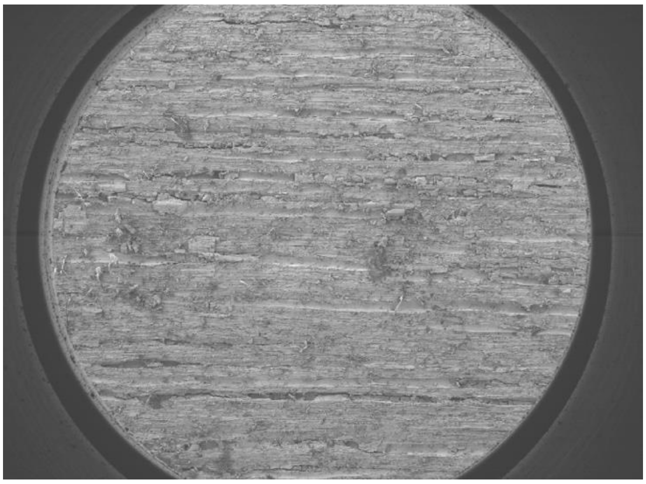


Figure 54 – EIL CLP, magnification x25

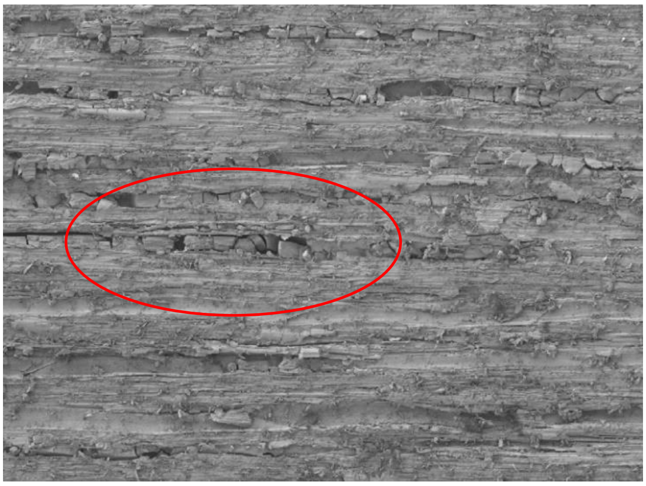


Figure 55 – EIL CLP, magnification x50

Figure 56 – EIL CLP, magnification x100

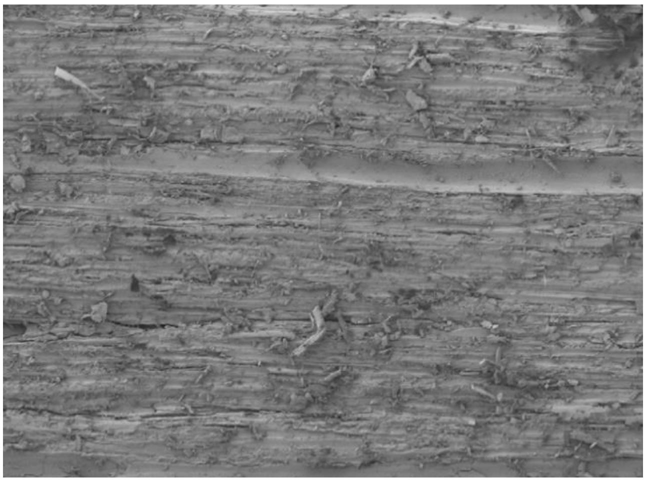


Figure 57 – EIL CLP, magnification x100

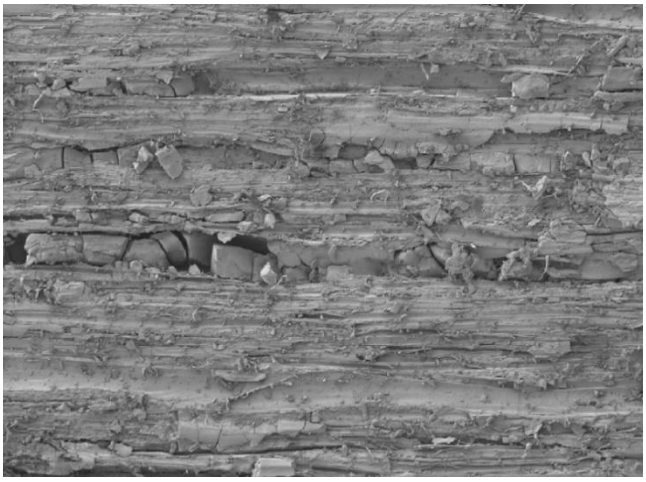


Figure 58 – EIL CLP, magnification x100

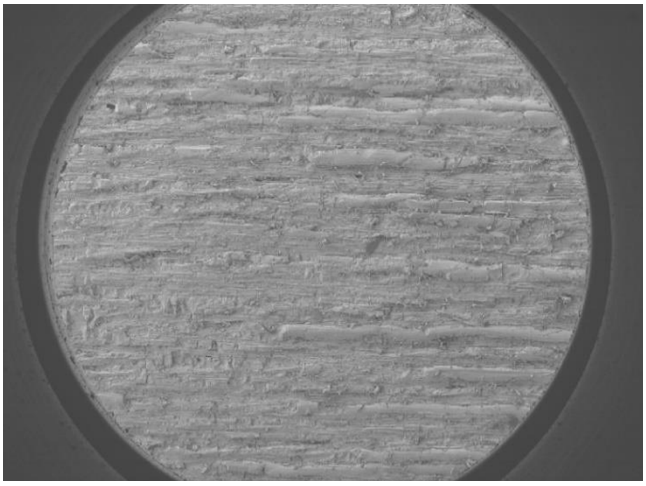


Figure 59 – EIL CLP+gelatin, magnification x25

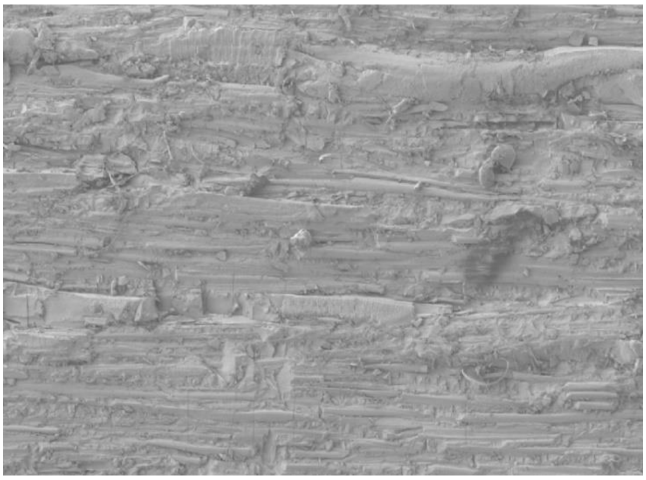


Figure 60 – EIL CLP+gelatin, magnification x100

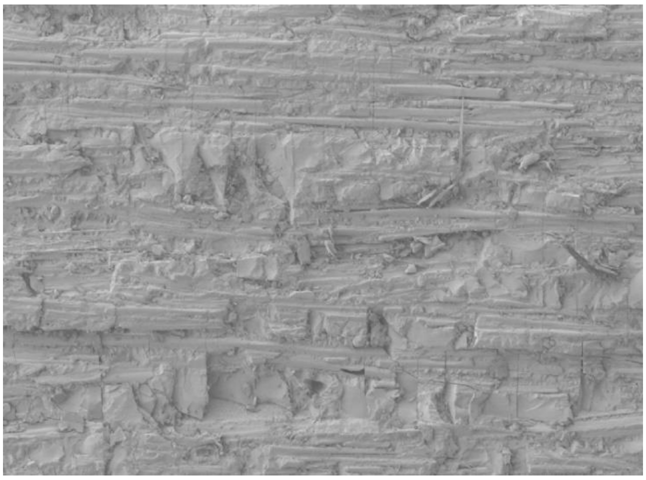


Figure 61 – EIL CLP+gelatin, magnification x100

7. Conclusions

The lignin fractionation was successful as lignins with different thermal properties were obtained and no new peaks arose in the FTIR spectra. Minor differences were observed in relative contents of functional groups between fractions. In thermal analysis, the T_g for EIL was not clear, and therefore further experiments should be done with different settings such as higher heating range. Particle sizes of formed CLPs varied with different lignin fractions, indicating that they might have different properties. Cationic lignin showed small particle size, even though it is mostly soluble in water solubility. Lignin fractions showed negative zeta potential, but not as high as according to the literature and therefore the particles might not be as stable. Cationic lignin and gelatin + ESL CLP showed positive zeta potential which indicated successful cationisation reaction and formation of a gelatin coating on ESL CLP.

In the shear strength testing, gelatin and lignin fractions did not reach the PVA glue in the adhesive strength values. Gelatin as a component in the adhesive can provide a good adhesion on wood whereas cationic lignin does not increase adhesion much. The cold-pressed lignin samples performed poorly and only gelatin seemed to give some adhesion. In terms of strain at break, the gelatin and lignin fractions did not reach the PVA glue values in toughness. The high standard deviation with pure gelatin (both hot-pressed and cold-pressed) does not give a clear indication of the actual gelatin strain. As hot-pressed and cold-pressed gelatin slipped in the shear testing clamps, more tests should be done in order to get accurate data with low standard deviation. Cationic lignin was brittle and showed low strength and toughness and therefore is not optimal for gluing. In the ABES testing the phenol-formaldehyde values were not reached with spruce veneers, indicating that spruce veneers might not be optimal. Birch veneers showed good bonding, but these were not researched extensively. Moisture resistance for CLPs + gelatin showed stabile bonding in room temperature water and boiling water and therefore indicating that there might be potential for plywood applications. According to the FESEM images, it seems that an even surface with wood failure results in a strong adhesive strength. Also cracks reduce the adhesive strength, but the more cracks are penetrated in the wood the less this affects.

Further research could include wet shear strength testing of the moisture resistance samples. Also, more research should be done with birch veneers. Some stages in the experimental parts should be improved such as the concentration of CLPs as CLPs produced foam in the rotavapor. This was a challenge especially with cationic lignin and this might be because of its surfactant properties. The foam could be possibly prevented by giving them anti-surfactant properties by adding some solvents, such as ethanol, in the mixture. Several factors also affected the reliability of the results, the most important being the glue quality and its application on wood. There should be a more efficient way of heating and mixing gelatin and lignin to get a homogeneous mixture with accurate amounts of both. Also, the amount of lignin that is applied on wood should be the same every time. This was challenging as lignin dried quickly and was quite sticky.

In conclusion, the lignin-gelatin adhesives show some potential as a replacement of PF-resins in plywood adhesives, and the best potential was shown for hot-pressed lignin mixed with gelatin. As lignin is more easily available than gelatin, the amount of lignin could be optimized to be as high as possible and therefore reducing the amount of gelatin. Also, the moisture resistance showed promising results for plywood applications. As gelatin is extracted from animals, it might in the long terms pose some ethical problems and therefore also other alternatives should be looked into. These could be *e.g.* tannins, hemicelluloses or some other proteins.

Appendix

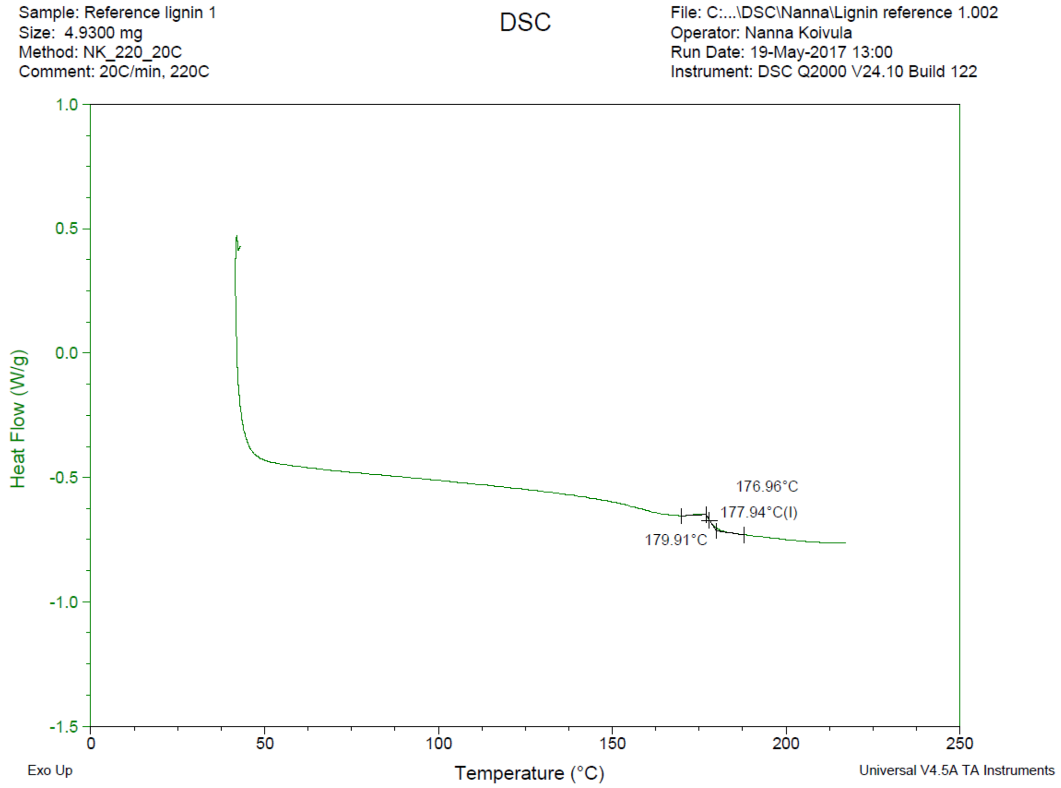
1. Dry matter content values for different adhesives

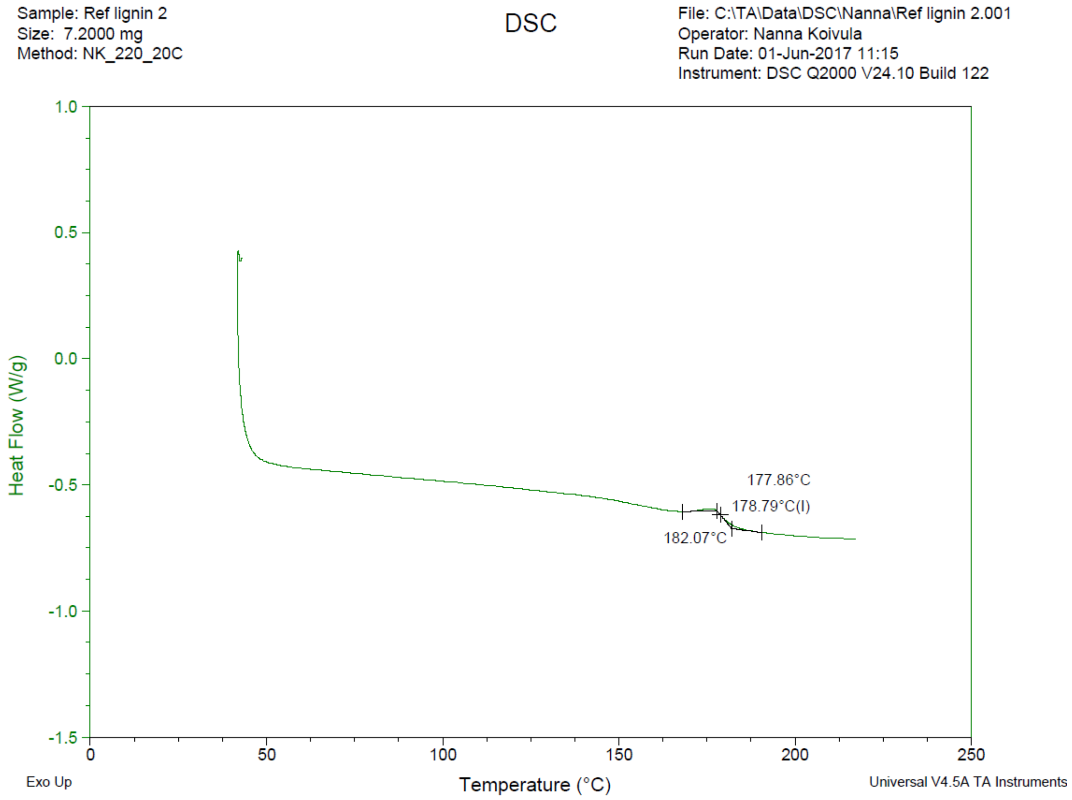
Lignoboost lignin	34.8 % (34.97 % and 34.63 %)
CLPs	34 % (34.13 % and 33.73 %)
Ethanol soluble lignin (ESL) CLPs	34.1 % (34.3 % and 33.9 %)
Ethanol insoluble lignin (EIL) CLPs	35.2 % (36.07 % and 34.33 %)
Cationic lignin	32.4 % (29.6 % and 35.1 %)
Gelatin	34 %
CLPs + cationic lignin	34 %*
ESL CLPs + cationic lignin	34 %*
CLPs + gelatin	34 %*
ESL CLPs + gelatin	34%*
EIL CLPs + gelatin	34 %*
PVA glue	34 %

*approximate dry matter content

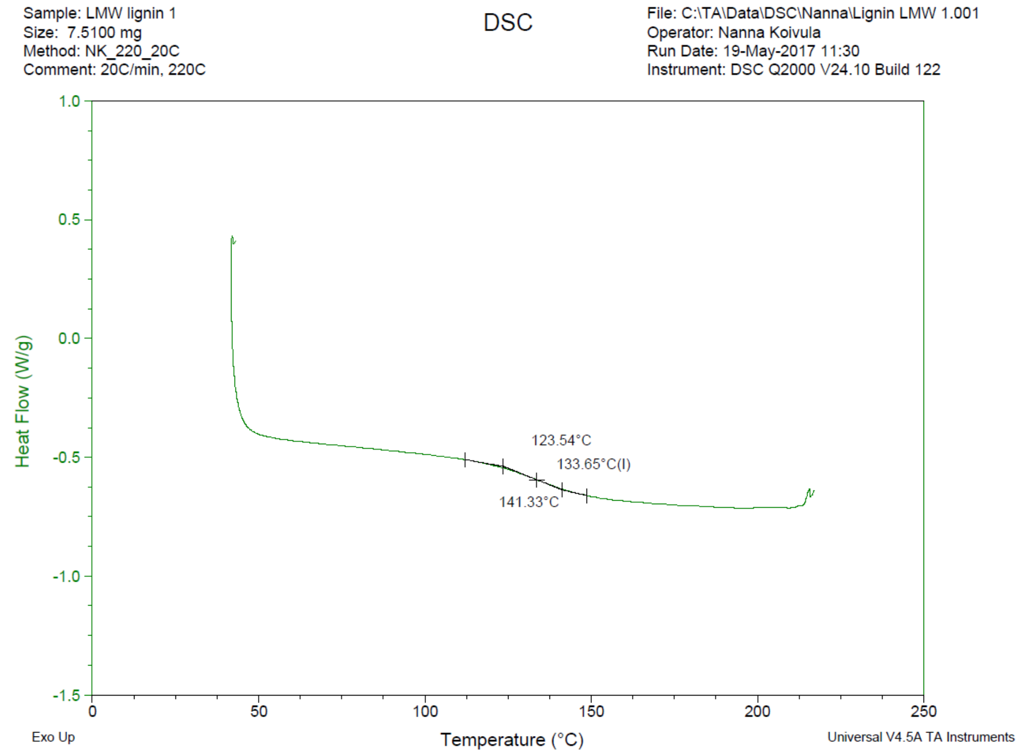
2. DSC results

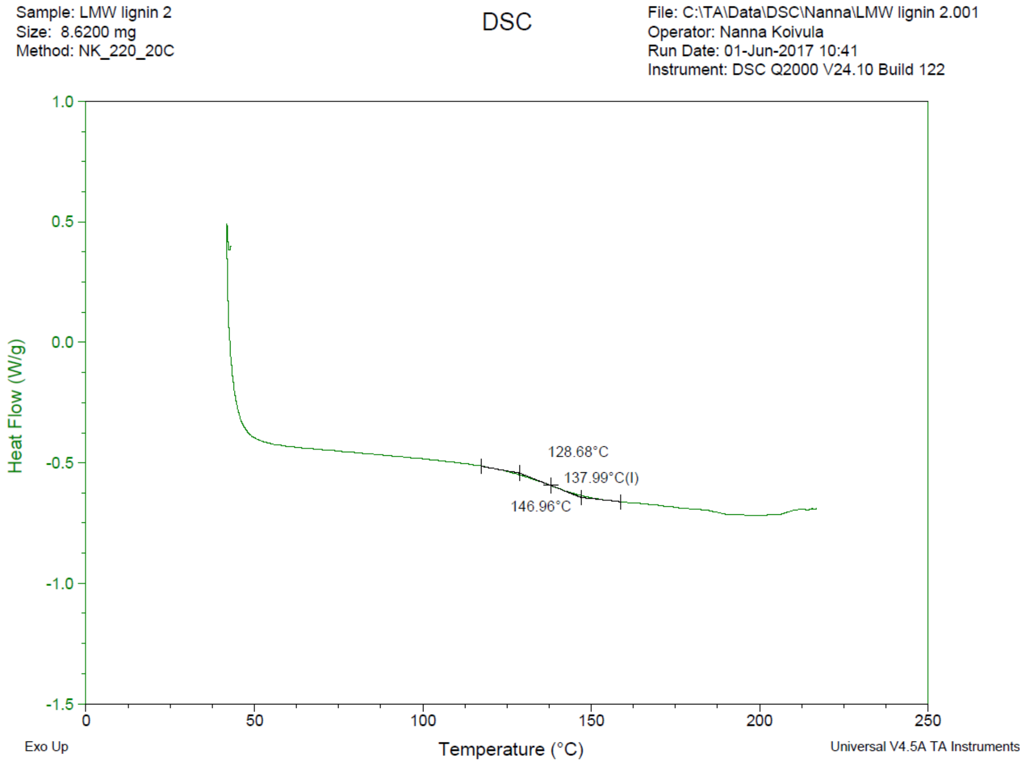
Lignoboost lignin



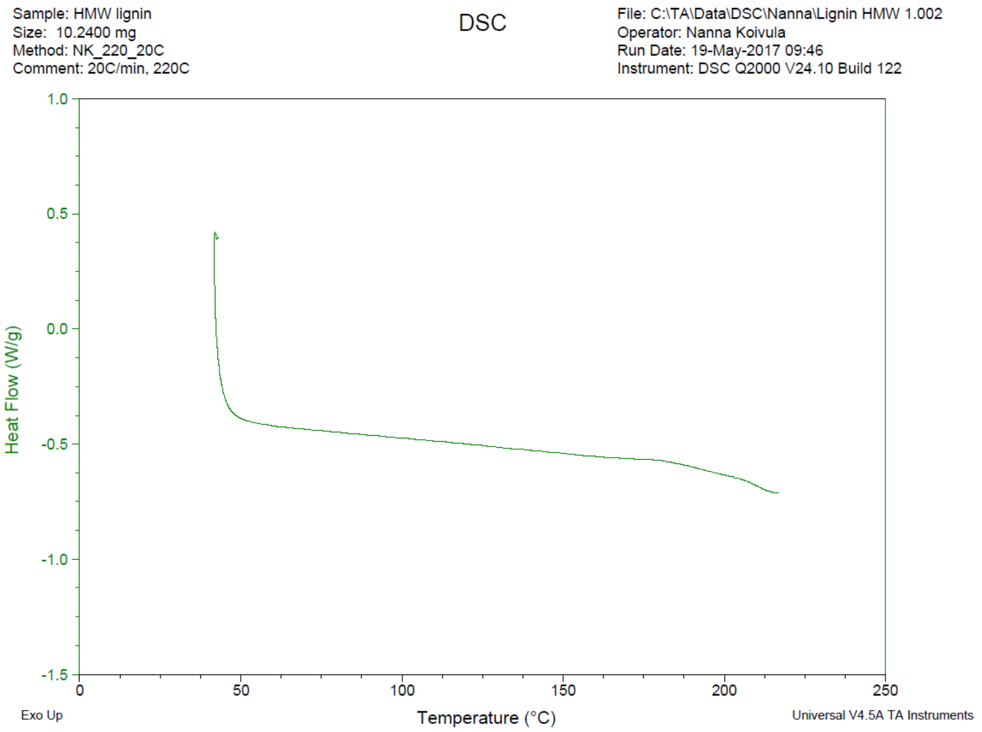


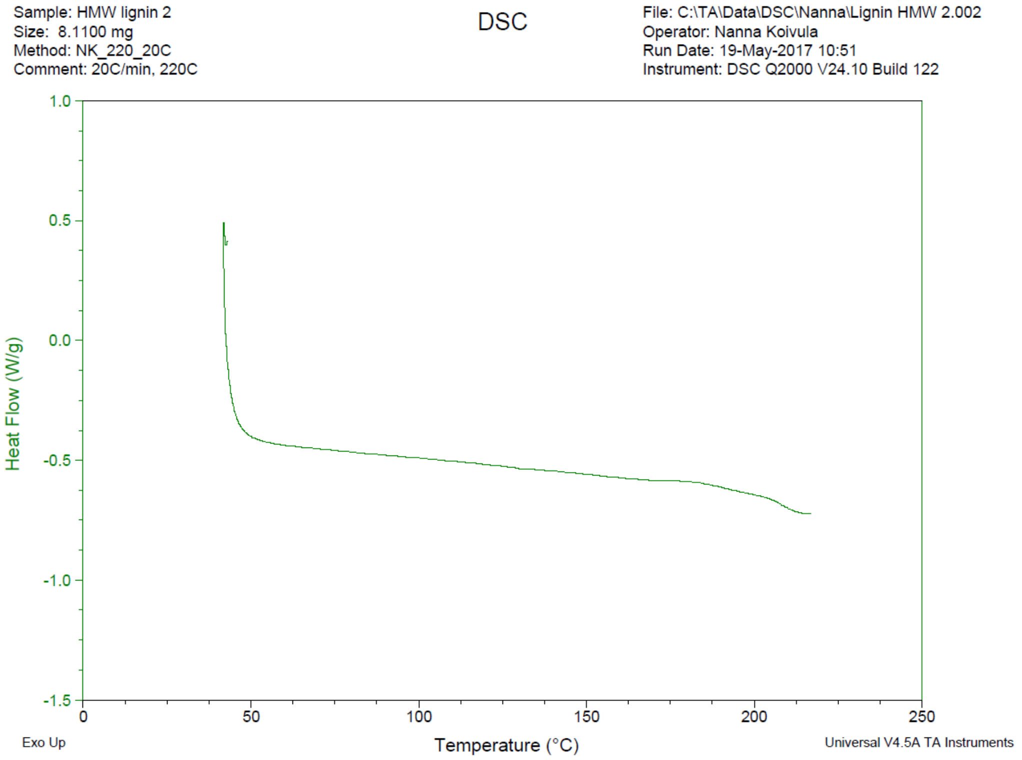
Ethanol soluble lignin (ESL) fraction





Ethanol insoluble lignin (EIL) fraction





3. Lap-shear testing data

	Lignoboost (HP)			CLP (HP)		
	STRAIN%	LOAD	Adh. Strength	STRAIN%	LOAD	Adh. Strength
	0,212	166,174	1,846377778	0,173	137,21573	1,524619222
	0,196	170,05	1,889444444	0,144	176,5878	1,962086667
	0,493	158,5668	1,761853333	0,152	180,6593	2,007325556
AVG	0,300333333	164,9302667	1,832558519	0,156333333	164,8209433	1,831343815
Sd	0,167045902	5,841757014	0,064908411	0,014977761	23,99333513	0,266592613

	ESL CLP (HP)			EIL CLP (HP)		
	STRAIN%	LOAD	Adh. Strength	STRAIN%	LOAD	Adh. Strength
	0,134	152,1439	1,690487778	0,142	158,22253	1,758028111
	0,274	200,3114	2,225682222	0,116	136,5997	1,517774444
	0,193	205,87	2,287444444	0,263	165,1786	1,835317778
	0,255	203,7275	2,263638889	0,382	175,80573	1,953397
				0,32	155,81407	1,731267444
AVG	0,214	190,5132	2,116813333	0,2446	158,324126	1,759156956
Sd	0,063566238	25,68175057	0,285352784	0,113981577	14,41224896	0,1601361

	Gelatin (HP)			Gelatin (CP)		
	STRAIN%	LOAD	Adh. Strength	STRAIN%	LOAD	Adh. Strength
	0,673	614,09062	6,823229111	0,776	274,66	3,051777778
	0,882	532,48781	5,916531222	0,521	241,63	2,684777778
	0,841	645,05428	7,167269778	0,436	227,07644	2,523071556
	0,58	493,55	5,483888889	0,5	242,20975	2,691219444
	0,908	622,28107	6,914234111	0,526	245,93183	2,732575889
AVG	0,7768	581,492756	6,461030622	0,5518	246,301604	2,736684489
Sd	0,14309682	65,00343778	0,72226042	0,130357969	17,41055312	0,19345059

	Gelatin + CLP (HP)			Gelatin + CLP (CP)		
	STRAIN%	LOAD	Adh. Strength	STRAIN%	LOAD	Adh. Strength
	0,291	368,55	4,095	0,08	101,77	1,130777778
	0,369	427,9	4,754444444	0,103	123,82	1,375777778
	0,317	455,09	5,056555556	0,103	125,21	1,391222222
	0,276	416,345	4,626055556	0,098	105,32	1,170222222
	0,26	398,33	4,425888889	0,103	123,96	1,377333333
AVG	0,3026	413,243	4,591588889	0,0974	116,016	1,289066667
Sd	0,042641529	32,38627518	0,359847502	0,009964939	11,46616893	0,127401877

Gelatin + ESL CLP (HP)				Gelatin + EIL CLP (HP)		
	STRAIN%	LOAD	Adh. Strength	STRAIN%	LOAD	Adh. Strength
	0,408	380,37369	4,226374333	0,573	495,25795	5,502866111
				0,496	511,34732	5,681636889
	0,289	329,16364	3,657373778	0,47	472,99343	5,255482556
	0,353	423,64272	4,707141333	0,562	472,4933	5,249925556
	0,286	356,2569	3,95841	0,565	487,53025	5,417002778
AVG	0,334	372,3592375	4,137324861	0,5332	487,92445	5,421382778
Sd	0,058212255	40,08063515	0,445340391	0,046911619	16,30661065	0,181184563

Cationic lignin (HP)				Cat lignin + CLP (HP)			
	STRAIN%	LOAD	Adh. Strength	#	STRAIN%	LOAD	Adh. Strength
	0,087	119,1656	1,324062222	177	0,144	186,4783	2,071981111
	0,083	108,2574	1,20286	182	0,155	188,3661	2,092956667
	0,116	129,7974	1,442193333	183	0,16	185,4117	2,06013
	0,088	108,0397	1,200441111	184	0,139	186,3799	2,070887778
	0,116	136,38781	1,515420111	185	0,129	178,7307	1,985896667
AVG	0,098	120,329582	1,336995356		0,1454	185,07334	2,056370444
Sd	0,016537835	12,70472251	0,141163583		0,012421755	3,703608028	0,0411512

Cationic lignin + LMW CLP (HP)				PVA glue (CP)		
	STRAIN%	LOAD	Adh. Strength	STRAIN%	LOAD	Adh. Strength
	0,152	173,5101	1,92789	0,671	680,90075	7,565563889
	0,137	168,3013	1,870014444	0,55	584,72389	6,496932111
	0,152	178,6279	1,984754444	0,0,663	707,72219	7,863579889
	0,116	147,4005	1,637783333			
	0,093	130,1601	1,446223333			
AVG	0,13	159,59998	1,773333111	0,6105	657,7822767	7,308691963
Sd	0,025406692	20,29039178	0,225448798	0,085559921	64,67606441	0,718622938

PVA glue (HP)			
#	STRAIN%	LOAD	Adh. Strength
204	0,929	732,42694	8,138077111
205	0,859	661,8863	7,354292222
	0,894	697,15662	7,746184667
	0,049497475	49,87976489	0,55421961

4. ABES testing data

Spruce veneers

	130C 1min					
	Lignoboost	**ad. Strength**	**CLP**	**ad. Str.**	**CLP+gelatin**	**ad. Str.**
			207,32	3,455333333		
			200,02	3,333666667	340,18	5,669666667
			212,43	3,5405	337,26	5,621
					377,41	6,290166667
average			206,59	3,443166667	351,6166667	5,860277778
st dev			6,237122734	0,103952046	22,38534416	0,373089069
			7A34		7A34	
	150C 5min					
	Lignoboost	**ad. Strength**	**CLP**	**ad. Str.**	**CLP+gelatin**	**ad. Str.**
					333,61	5,560166667
			197,1	3,285	340,18	5,669666667
			200,75	3,345833333	232,87	3,881166667
			208,05	3,4675		
average			201,9666667	3,366111111	302,22	5,037
st dev			5,575467096	0,092924452	60,1486334	1,002477223

130C 1min					
ESL CLP+gelatin	**ad. Str.**	**EIL CLP+gelatin**	**ad. Strength**	**PF**	ad. Strength
		345	5,75	371,57	6,192833333
303,68	5,061333333	284,7	4,745	467,93	7,798833333
		366,46	6,107666667	382,52	6,375333333
262,8	4,38				
237,25	3,954166667				
267,91	4,465166667	332,0533333	5,534222222	407,34	6,789
33,50851086	0,558475181	42,38969843	0,706494974	52,75733788	0,879288965
				7A34	
150C 5min					
ESL CLP+gelatin	**ad. Str.**	**EIL CLP+gelatin**	**ad. Strength**	**PF**	ad. Strength
276,67	4,611166667	316,09	5,268166667		
296,38	4,939666667			323,39	5,389833333
302,22	5,037	240,9	4,015	434,35	7,239166667
		336,53	5,608833333	432,89	7,214833333
291,7566667	4,862611111	297,84	4,964	396,8766667	6,614611111
13,38775684	0,223129281	50,35941918	0,839323653	63,64550678	1,060758446

Birch veneers

	150C, 5min				
	Lignoboost	**CLP**	**CLP+gelatin**	**EIL+gelatin**	**PF**
	251,12	303,68	776,72	544,58	355,51
	273,75	258,42	597,14	755,55	384,79
	233,6	298,6	824,17	653,35	290,54
	232,14	306,6		521,22	411,72
	249,66	322,66		303,68	
	200,02	251,85			
	284,7	200,02			
	177,39	189,8			
		353,32			
average	237,7975	276,1055556	732,6766667	555,676	360,64
st dev	35,73007247	55,29966029	119,7518962	169,0430029	52,06635446
adhesive strength (N/mm2)	3,963291667	4,601759259	12,21127778	9,261266667	6,010666667
60					
	130C, 1 min				
	Lignoboost	**CLP**	**PF**		
	252,58	376,68	567,21		
	308,79	313,9	622,69		
	364,27	381,06	624,15		
	314,63	332,15	507,35		
	303,68	329,23	560,64		
	237,25	395,66	542,39		
	319,01	338,72	523,41		
	216,81				
	227,03				
	199,29				
average	274,334	352,4857143	563,9771429		
st dev	51,75262393	29,02854253	42,10173282		
adhesive strength (N/mm2)	4,572233333	5,874761905	9,399619048		

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