

New approach on Phenol-Formaldehyde resins for Wood Composites

by

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A thesis submitted to the Graduate Faculty of
Auburn University in partial fulfillment of the
requirements for the Degree of Master of Science

Auburn, Alabama

August 8, 2020

Keywords: wood adhesive, lap shear, phenol-formaldehyde resins, particleboard,
mechanical properties.

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Abstract

Almost two-thirds of the state of Alabama is covered by forest. This generates a substantial market for wood products. Engineered wood products named particleboards (PB) are useful for low load bearing applications. Even though the market for PB has been growing for the past few years, there are concerns about the release of hazardous gases (e.g., formaldehyde emissions) from PB. These gases are generated when the adhesives do not cure entirely creating the tridimensional structures that allow for the bonding between the wood substrates. Instead, there are small unreacted quantities of chemicals that can generate these gases. The reaction of Phenol-formaldehyde (PF) resins, more precisely Novolac-type resins, represents a solution for this problem because they use small quantities of formaldehyde during their synthesis. Hence, the proposed systems have the advantage that most of the formaldehyde is consumed during the synthesis reaction, leaving few or no excess to be released after the pressing step. In this study, I will pursue a different approach to the conventional synthesis method. The monomers will be added separately during the blending step instead of using the commercially available pre-polymerized resins. The hypothesis was that the PF Novolac resins synthesized at room temperature and within the composite during pressing can develop the dimensional stability and mechanical properties that meet the industrial requirements to perform according to their applications. However, careful attention to formaldehyde emission was performed under a hood and monitored closely to see if complete polymerization in the board was possible and human safety could be preserved.

The experimental analysis was divided into two parts. In the first part, different ratios of phenol to formaldehyde chemical were used to synthesize different resins that had to be tested in order to determine which is the combination of reactants and also which is the optimum quantity of catalyst that provide the best adhesion. For that purpose, we tested the lap shear properties for different combinations according to the standard DIN EN 205 with the dimension 80mm long, 20mm wide, and 5mm thick¹. For this procedure, lap shear samples were pressed in 15.24 by 15.24 cm platens heated to 150°C and 1.38 MPa for 10 minutes. The same press was used to make small particleboards of 12.7cm long, 11.43cm wide and an average of 12mm thick. Similar panels were manufactured using urea-formaldehyde (UF) adhesive and used as the control. Due to the differences in densities that we encountered while making the PB, the variation in density values affected the mechanical properties. An Analysis of Covariance was run to eliminate the effect of this covariant in the final properties. The results showed that only for the Modulus of rupture, the control panels performed better than the suggested treatments. For all the other properties: thickness swelling, edge swelling, modulus of elasticity and internal bonding, there was not significant difference between the control and the treatments. The final analysis also demonstrated that for water absorption, the suggested treatments outperformed the results for the UF resins.

¹ European Committee for Standardization, "Wood adhesives for non-structural applications: Determination of tensile shear strength of lap joints," no. DIN EN 205. 2003.

Acknowledgments

Firstly, I would like to thank my family and friend that have been there throughout the whole process giving me their support from miles away. I would like to express my gratitude to my Major Advisor, Dr. Brian Via for his support, encouraging words and persistence to guide me through the process.

I would like to also thank Dr. Soledad Peresin, Dr. Maria Lujan Auad and Dr. Beatriz Vega for being part of the Forest Products Development Center team. These Drs. are really determined, hard-working and passionate women that helped me and gave me their support during my whole time as a student in Auburn University.

Lastly, I would like to express my gratitude to all the student member of the Center, MS. Maria Celeste Iglesias, MS. Diego Maldonado, MS. Osei Asafu-Adjaye, MS. Marina Hornus and to Alfredo Garcia. All the time and effort invested will always have the results we are wishing for.

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List of abbreviations

ES Edge swelling

HW Hardwood

HMTA Hexamethylenetetramine

IB Internal bonding

PB Particleboard

PF Phenol-Formaldehyde

MOE Modulus of Elasticity

MOR Modulus of Rupture

SW Softwood

TS Thickness Swelling

Chapter 1 Literature review

1.1 Introduction

Thermosetting adhesives such as Phenol Formaldehyde (PF) are used worldwide to manufacture wood products. Several studies have demonstrated that the properties of these type of resins improve the final quality of wood products due to the interactions with the wood substrates (He and Riedl 2004; Pizzi 2003). This is mainly because during the manufacturing process of these panels, veneers, or structures, it is possible to adequately distribute tensions and transfer stresses along them. This occurs because when PF resins are cured, they provide good adhesion to wood and excellent stability. These characteristics make the products suitable to withstand different loading conditions.

The wood products industry can be divided by the target properties requested for a particular application. In this aspect, particle size plays a really important role.

Reducing the particle size has the effect of increasing the surface area which could be beneficial for the bonding properties since we have more area available to react with the adhesives. Owing to the small particle size used for PB, these products are used for low load-bearing applications such as furniture and tables.

The present study focused on finding and optimizing the conditions that would improve the properties of particleboards made with resins that were synthesized during hot pressing. Due to the fact that these wood panels were manufactured using a small hot-press system, the most important variables to be studied were P/F ratios before synthesis, use of hardener and resin loadings.

1.2 International trends in phenolic resins

In 2015 the global phenolic resin market was valued at 9.30 billion dollars and the demand was expected to increase at a constant rate (Grand view research 2018). During

this year, Novolac-type resins were the most sold products, covering almost 50% of the market. Regarding their applications, the global market is led by wood adhesives, followed by molding, insulation, and laminated products.

Figure 1.1 shows the forecast for novolac and resol resins through 2025. We can see that both the demand for novolac and resol products has a constant growth throughout this period. On the other hand, products that are not categorized as one or the other present little or no growing. Some of the distinctive characteristics of these products are the fire and corrosion resistance. Meanwhile, resols have also been expanding their markets due to their applications in foamed plastics and abrasives.

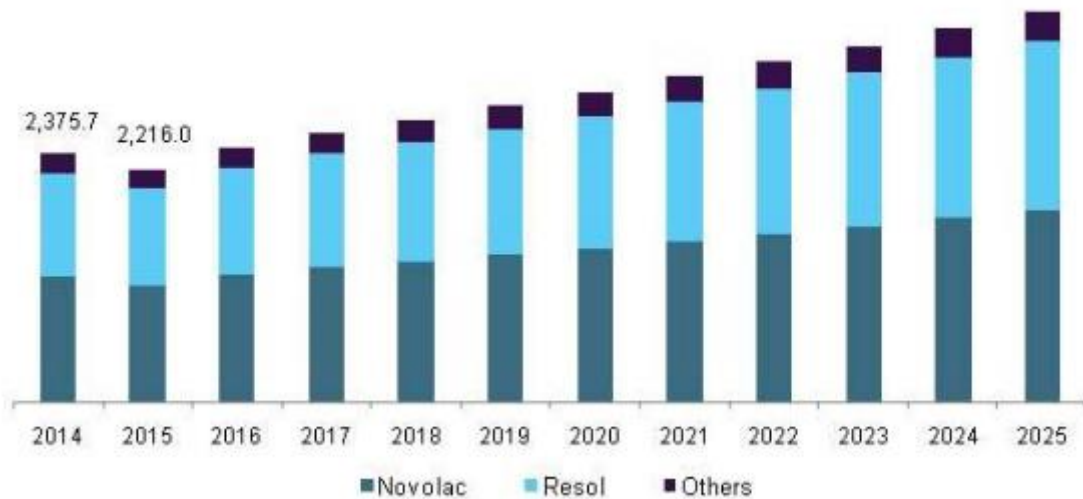


Figure 1-1 : U.S. phenolic resins market revenue by product, 2014-2025 (USD Million).

Grand view research, 2018.

North America is the largest consumer of wood adhesives worldwide (approximately 54% of the international market), mainly because of growth of the construction sector which is a function of urban growth (Kalami et al. 2017; Pilato 2010).

1.3 Particleboard market

The wood particleboard industry became significantly relevant due to the need of finding an application for sawdust and mill residues. These panels are manufactured

applying the adhesive to the particles and integrating them using a hot-press system that uses a combination of heat and pressure to make a robust product (Youngquist 1999). During the years 2000 to 2004, particleboards constituted the largest panel boards produced in Europe (Figure 1-6). In comparison, we can see that the production in North America has been moderately stable, with a mean of 11 million m³.

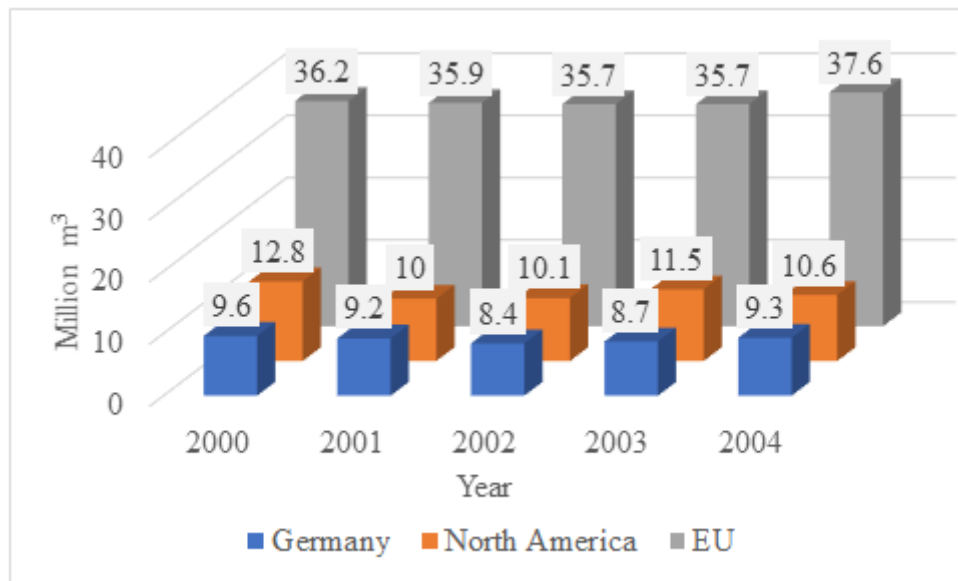


Figure 1-2: Particleboard production in Germany, Europe and North America from 2000 to 2004 (Kloeser et al. 2007).

The United States constitutes 64% of the total capacity in North America. The Composite Panel Association’s (CPA) reported in 2018 a total of 35 particleboard mills. Following the US, Canada and Mexico represent 25.7 and 10.3% respectively. CPA also claimed that particleboard shipments grew 1.7% (from 271 to 275 million square feet) in the period between April 2017 to April 2018. In recent news, the total investment of US\$463m that Kronospan made in their Oxford, Alabama expansion constitutes great news for the particleboard market in our region. This expansion also includes two laminate flooring and decorative paper impregnation lines (information from wood-based panels international).

1.4 Wood composition and its effect on bonding properties

Wood is a fibrous and renewable material that is composed by natural polymers namely cellulose, hemicellulose and lignin. All these chemicals compounds are bonded together by both chemical and physical forces in such a way that they define the sound, flexible and hygroscopic nature of wood. Concerning the percentages of each of these natural polymers, it varies depending on different species, soils, and weather conditions and even throughout the tree's extension. Wood is usually classified into two large groups: hardwood and softwood. Generally speaking, the dry weight of lignocellulosic biomass that constitute these two groups have approximately the same percentage of cellulose (between 37 - 45%), lignin (between 20 and 33) and extractives (2 - 5%)(Sjöström 1993). Some noticeable differences are the chemical structures that constitute the hemicelluloses which in the case of softwood contain galactoglucomanans (15 – 30%) and Xylan (5 – 10%). On the other hand, hardwoods do not contain the first group, contain a higher concentration of xylan (15 – 30%) and contain glucomannan (2 – 5%). Another important difference is the fiber length, where SW present longer dimension (2 – 6mm) than HW (0.8 – 1.6mm).

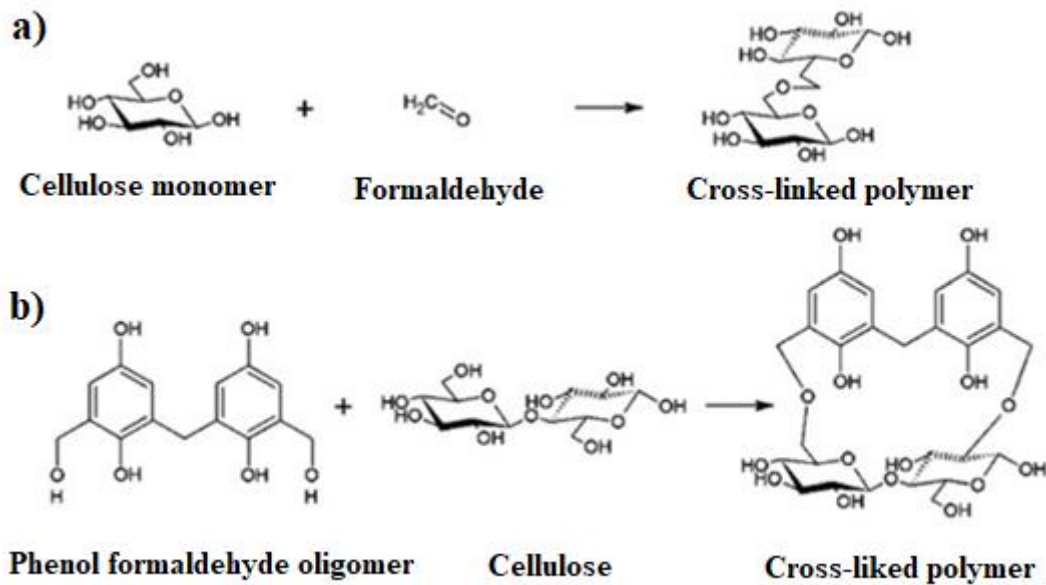


Figure 1-3: Modified from Schematic chemical reactions of cell-wall polymers and phenol formaldehyde resin: a) reaction of cellulose and residual formaldehyde; b) reaction of cellulose and resin oligomer. (Yang et al. 2014)

1.5 Adhesive theory and wood adhesive bonding strength evaluation

Marra used a chain analogy to describe the bond created between wood samples and the adhesives (Marra, 1992). Figure 1-3 shows the chain analogy. In this analogy, the author states that the bond is as strong as its weakest link. There are essentially three possible failure mechanisms in the system: structural, adhesive, and cohesive failures. The first type is when the failure occurs in the wood itself, the second when it happens in the adhesive itself and the third when the failure takes place in the interface between the adhesive and wood. In Figure 1-3, zones 8 and 9 represents untreated wood, while zones 6 and 7 represents wood cells that have been modified by the adhesion process. Modified wood cells refer to the diffusion process where the adhesive have penetrated the porous surface of wood and this process is known for having a strong influence on bond strength (Marra 1992; Voiustskii 1963; Xiao et al. 2007). Zones 4 and 5 represents

the outside layer of the interface between the substrate and the adhesive, while zones 2 and 3 symbolize the internal region of the interface of the system. Lastly, zone 1 represents the neat bulk adhesive.

Ideally, the adhesion should be strong enough for the failure to take place in the wood. If that were the case, the pieces of wood would have been created a bond that is stronger than the chemical and physical bonds within the wood. Voiutskii stated that in order to obtain good penetration of the adhesive into the wood surface, the diffusion requires similar solubility parameters and being amorphous. Therefore, the highly organized and structure of the crystalline portion of cellulose makes the adhesion more difficult. On the other hand, the amorphous portion of cellulose, plus the structure of hemicelluloses and lignin could help the adhesion if strong bonds are created with their complex structures. If the failure happens in the adhesive itself or in the interface, the adhesion was not acceptable.

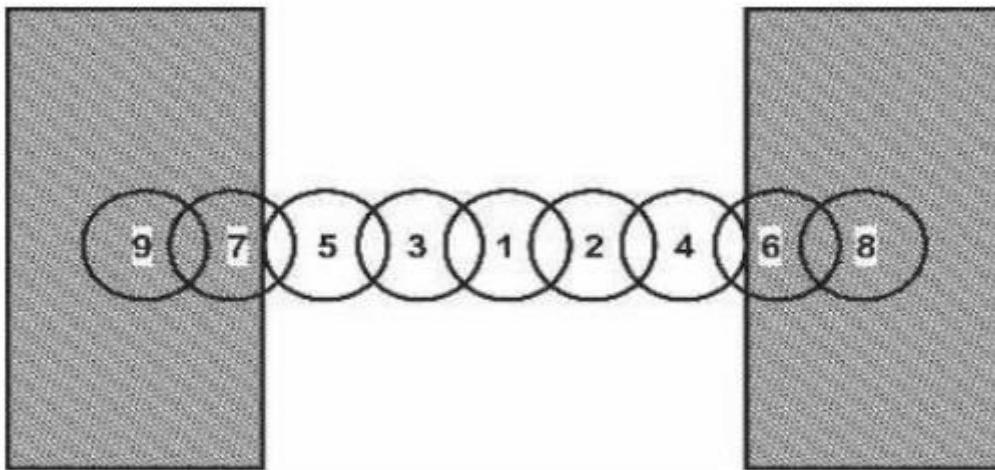


Figure 1-4: Chain link analogy for an adhesive bond in wood (Marra, 1992)

In order to determine the performance of synthesized resin regarding the bond strength, mechanical shear is evaluated. Lap shear test consists in applying an amount of resin in standardize wood samples and testing how much force has to be applied per area in

order to separate the bonded samples (Kalami et al. 2017; Lin et al. 2015; Xiao et al. 2007). Figure 1-4 shows the dimensions of the wood samples.

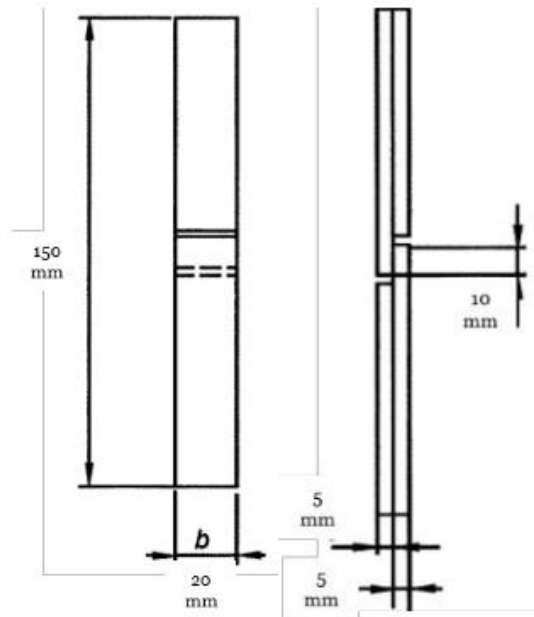


Figure 1-5: Lap shear sample

For the purpose of determining the strength of the bonding, the lap shear samples were pressed in a 23cm x 23 cm hot press. The platens were heated up to 150°C and a pressure of 1.38 MPa was applied for 10 minutes. Before pressing, all samples were wrapped in aluminum foil. (Figure 1.4). shows the disposition of the samples in the press.



Figure 1-6: Hot press used for the lap shear test

1.6 Particle size

Particle size plays a very important role when we think about wood composites. Since the properties of wood vary widely between species, one way to have uniform, consistent and in some grade homogeneous raw materials is to classify and separate them depending on their size into particles, flakes or fibers (Youngquist 1999). The classification of wood composites based on particle size, density and if they are made using a dry or wet process can be seen in figure 1.7 (Suchsland and Woodson 1986). Particleboards are manufactured using a dry process and the target density is between 600 to 800 kg/m³. Depending on the particle size, wood-based panels will require different process parameters and the final products will have different properties.

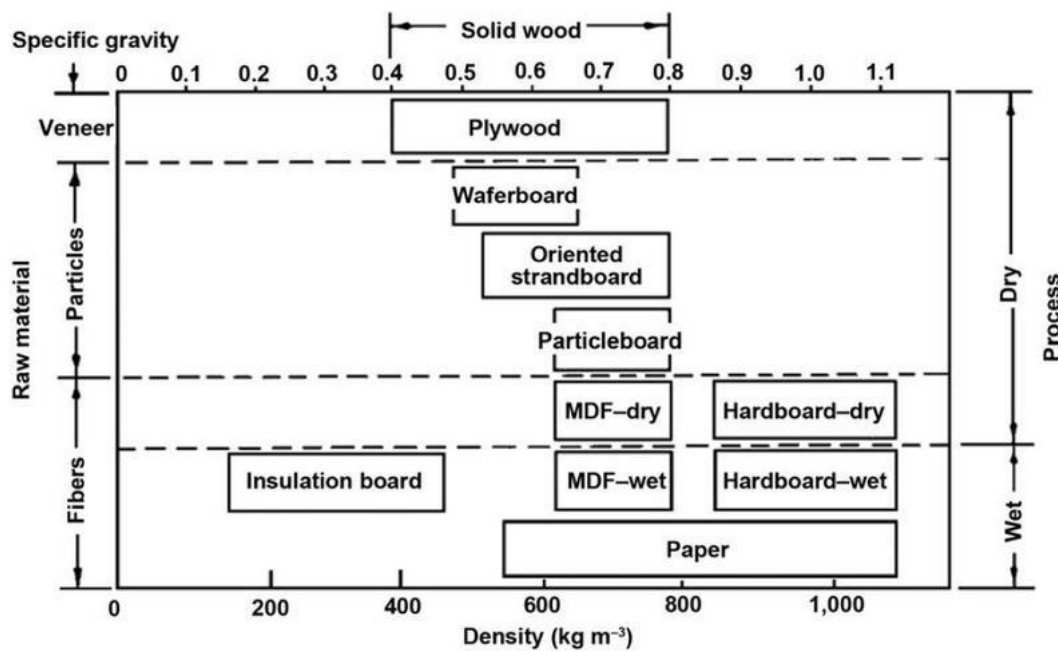


Figure 1-7: Classification of wood composite board materials by particle size, density and processing principle (Suchsland & Woodson 1986)

1.7 Pressing theory

Particleboards can be manufactured in single, three or five layers depending on their application. Usually, a smaller particle size is used in the surface and larger sizes in the

core layers. When the particles have the appropriate moisture content (about 2 to 7%), they are placed in an even mat to be pressed. This can be made using a batch or continuous process. Some systems utilize a cold press before the hot press, in order to reduce the mat thickness.

After pre-pressing, either a platen or a continuous system is used to obtain the final products. The temperature range used is from 140° C to 165°C and the pressure is usually between 1.37 to 3.43 MPa for medium-density boards (Youngquist 1999).

The pressing time varies according to the adhesive type, temperatures and pressure used and the moisture content of the particles. Hot pressing has the effect of bringing the particles together and creating the physical and chemical bonding between the wood substrate and the resin. It also provides the heat necessary for curing the adhesive.

1.8 Manufacturing process of PB

The manufacturing process for particleboards is described in Figure 1-7 (Çinar 2005).

Firstly, we need to make sure that the particles have the appropriate mesh and moisture content. Sometimes dust elimination or a drying process have to be performed. After that, the particles are transferred to a mat-forming step and the adhesives are added.

Different adhesive systems such as PF, UF, MUF or p-MDI are used to manufacture PB. The correct adhesive distribution and bond-line thickness are linked with the resin penetration and ultimately with the final strength of the composite (Gagliano and Frazier 2001).

The following process is the pressing step where temperatures of 130 to 180 °C are applied. After that, the panels can be either cut or let them sit to cool down before trimming the edges.

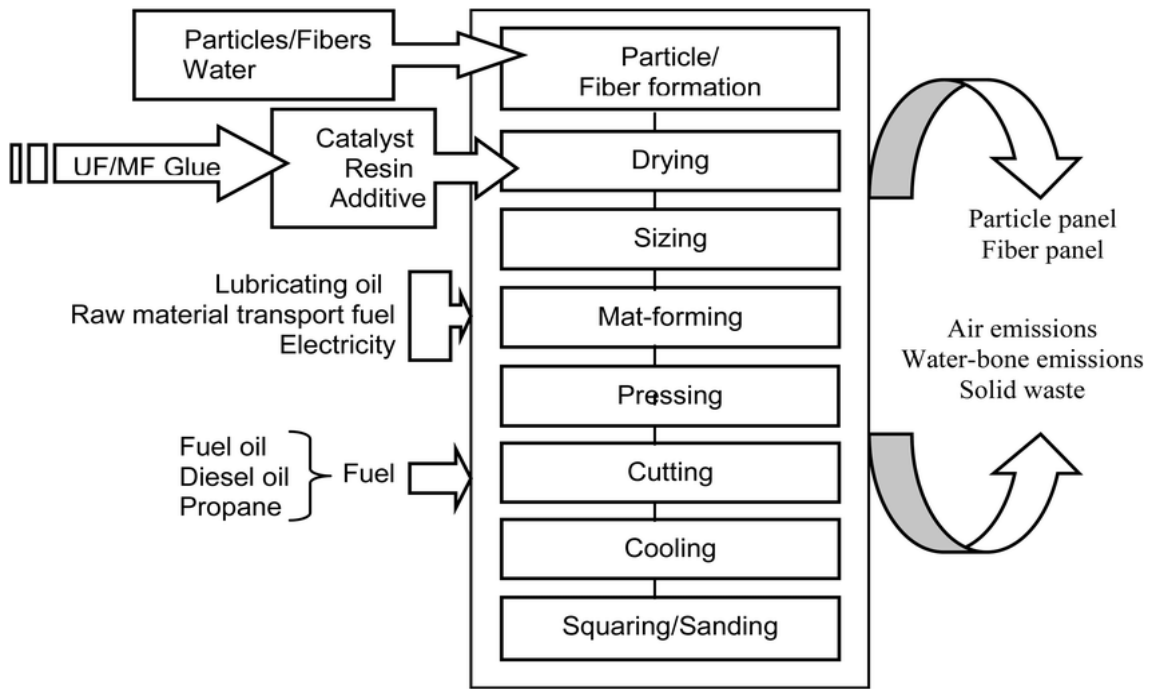


Figure 1-8: Particleboards manufacturing process

1.9 Physical and Mechanical Properties of PB

The most common properties usually tested for particleboards are: Internal bonding (IB), Thickness Swelling (TS), Edge Swelling (ES), Water Absorption (WA), Modulus of Rupture (MOR) and Modulus of Elasticity (MOE). U.S. industries follow the procedures of the American Society for Testing Materials ASTM D1037 (ASTM 2012). In order to determine MOE, MOR and IB a Static Material Testing Machine is used (MTS universal testing machine Zwick/Roell Z010).

Figure 1.9 shows an example of the sample disposition for measuring the MOE and MOR properties of a wood composite.

Modulus of rupture is calculated as follows:

$$R_b = \frac{3LP_{max}}{2bd^2}$$

Where P_{max} is the maximum load (N), b is the specimen's width (mm), d is the specimen's thickness (mm), L is the length of span (mm) (ASTM D1037)

MOE determines the stiffness of the sample. The higher the MOE values, the better.

The formula to determine MOE is:

$$E = \frac{L^3}{4bd^3} * \frac{\Delta P}{\Delta y}$$

Where $\Delta P/\Delta y$ is the slope of the straight-line portion of the load-deflection curve (N/mm) (ASTM D1037).

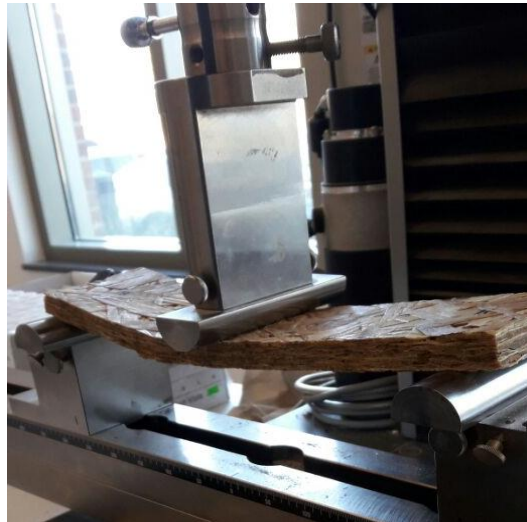


Figure 1-9: Bending test for wood composite

Internal bonding is the tension test perpendicular to the surface of the samples. The equation used to determine IB is:

$$IB = \frac{P_{max}}{ab}$$

Where P_{max} is the maximum load (N), a is the specimen's width (mm), and b is the specimen's length that is being tested (ASTM D1037). Figure 1-10 shows the disposition of the sample for IB measurement.

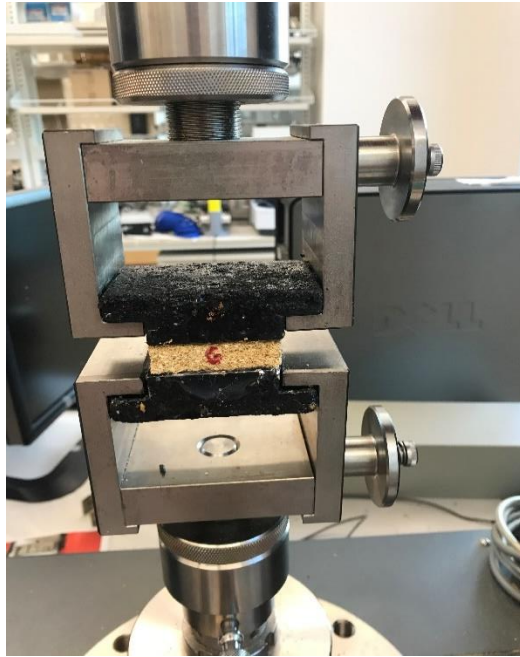


Figure 1-10: IB measurement

The last three properties TS, ES and WA are calculated after soaking the wood samples in tap water for 24hours (ASTM D1037). Since the samples have to be fully submerged in water, a wire netting and weights are used in order to assure the samples do not float. For each sample, the thickness is measure in the center (TS) and in two of their edges (ES). ES is calculated as the mean value for the two measurements. The thickness of the samples has to be measure before and after the 24 hours soaking in water. TS and ES are determined as the increment in thickness.

Water absorption is calculated as the increase in mass that the samples experience after soaking them in water.



Figure 1-11: Samples soaked in water for TS, ES and WA determination

Thickness swelling percentage is determined as the difference between the average thickness before and after soaking the samples in water:

$$\%TS = \left(\frac{t_2 - t_1}{t_1} \right) * 100$$

Been t_2 the thickness after soaking in water for 24 hours, in the center for TS and as the average of the other points for ES and t_1 the same points before soaking.

Water absorption percentage is determined as the difference in mass before and after soaking in water:

$$\%Water\ absorption = \frac{Final\ weight - Initial\ weight}{Initial\ weight} * 100$$

1.10 References

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Chapter 2 Analysis of Mechanical and Physical Properties of Particleboards manufactured with a resin synthesized during pressing

2.1 Introduction

Particleboards are wood-based composites that are manufactured using organic resins that are sprayed onto the surface of the wood chips or particles. These resins are often categorized as thermosetting adhesives; therefore, they require certain pressure and temperature combination to create a uniform and stable material. The bonding of the system is achieved through the curing of the resin inside the wood composite by creating physical and chemical bonds between the components. As a result, the final products can be used for many different applications such as shelving, cabinets, flooring, and structural sheathing (GÖKAY NEMLİ 2007; Hashemzadeh and Spanplattentechnik 2003). In order to be able to perform properly for these applications, the panels have to meet mechanical strength and dimensional stability requirements. Extensive research has been conducted in several variables that have an effect on the final properties of the panels. Among them pressing temperatures and times (Kelley et al. 1983; Papadopoulos 2006), resin type and curing behavior (Mantanis et al. 2018; Myers et al. 1991), size of the particle (Sackey, E. K., Semple, K. E., Oh, S. W., & Smith 2008).

Figure 2.1 shows the reaction of PF resins in acidic and basic media (Kiskan and Yagci 2020). As we can see, the reaction evolves creating methylene bridges between the phenol ring, mainly in the ortho and para positions. A series of condensation reaction with the elimination of water molecules occur during the final curing of the resins. Linear structures are generated and with growing condensation levels, crosslinking between the chains are created (Kloeser et al. 2007).

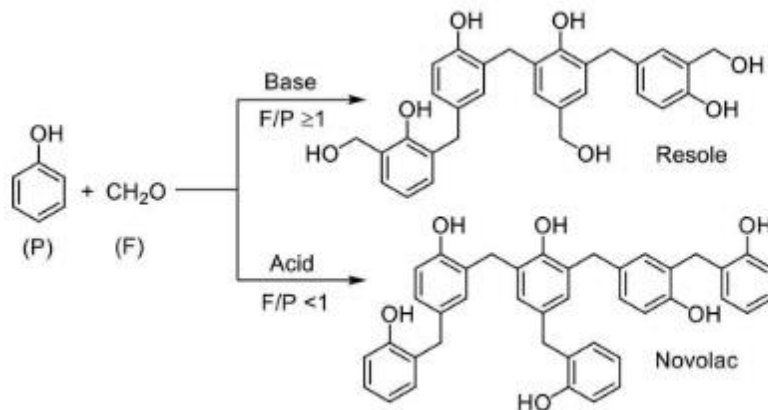


Figure 2-1: Reaction of phenol-formaldehyde resin in acidic and basic media

In order to obtain moisture-resistant wood composites, phenol-formaldehyde resins are one of the best choices. Urea-formaldehyde resins are another type of resins that are usually used to make particleboards. A negative side of these two systems is that they both emit formaldehyde gases during the manufacturing process as well as during the use of the final products. Polymeric diphenyl diisocyanate (p-MDI) constitutes a solution for this concern but this resin requires special safety precautions during the production of the panels because of the reactive isocyanate groups. These groups are associated can cause skin irritation and respiratory (Hashemzadeh and Spanplattentechnik 2003).

2.2 UF vs PF

Due to the fact that it was not possible to find any PF resin that is currently being used in a particleboard plant, we decided to compare the properties of our system with the commonly used Urea-Formaldehyde (UF). Both PF and UF are thermosetting adhesives that are used for exterior applications. Regarding the chemical reactions and curing times, the two of them present similar properties such as hardening temperature around 120°. On the other hand, some of the important differences about them are the color of the resin, in which case, UF is transparent and PF is typically dark brown. The

rheological behavior of UF also exhibits less flow than PF and the use of different hardeners (Mantanis et al. 2018).

The UF resin was provided by Hexion Inc, Columbus, Ohio, USA. This resin had a 70% solid content and used Ammonium sulfate ((NH₄)₂SO₄) as the catalyst. The catalyst was added according to the following percentage: 3% g/g resin. Because the solid content of the UF resin was lower than the values obtained for the PF (70vs90%), 38.6 grams of the resin had to be added in order to have the same quantity.

2.3 Hexamethylenetetramine

Hexamethylenetetramine (C₆H₁₂N₄), also called HMTA, hexamine, methenamine, or urotropine is used in the production of liquid or powdery synthesis of phenolic resins. It is formed by the reaction of four molecules of ammonia and six molecules of formaldehyde (Finch, 1994). Under room temperature and ambient conditions, HMTA is a white crystalline solid with a melting point of 280 °C that usually presents a fishy, ammonia-like smell. This compound has been used as a hardener for over fifty years because its effect on crosslinking different resin systems such as Novolacs can be seen on the final product when a high modulus, rigid cross-linked system is created (Kiskan and Yagci 2020).

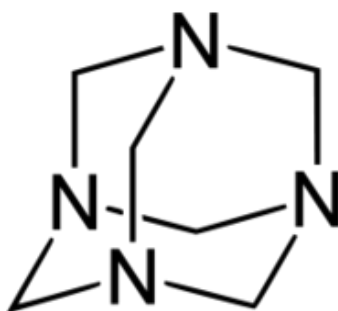


Figure 2-2: HMTA structure

One of the advantages that HMTA presents is that it is not a formaldehyde-yielding compound. Instead, its decomposition reaction leads to reactive imines that can react easily with nucleophiles where this hardener does not decompose in ammonia nor formaldehyde (Hemmilä et al. 2017; Iliev et al. 2006).

2.4 Hot – stacking

Hot-stacking is the activity of stacking particleboard panels with residual heat such that the temperature is slow to drop and the panel is allowed to continue to cure. The curing of PF resins and therefore the mechanical and physical properties of the wood-based products depend on the curing behavior of the adhesive. PF adhesives fully cure at a temperature of approximately 130 °C. Given that the curing speed is linked with temperature, pressing times used, and thickness of the panels, increasing the temperature has the effect of increasing the curing speed and therefore shorter times are needed. Hot-stacking is another option to fully cure the resins after the hot-pressing step (Kloeser et al. 2007).

This method is mostly used to complete the curing process of PF resins in the core layers of the panels, where the heat transferred is lower than in the surface (Czajkowski and Olek 2016; Thoemen 2010).

2.5 Materials and Methods

2.5.1 Chemicals and Materials

The present investigation involves the following phases: a) synthesis and study of the properties of selected resins, b) evaluation of the adhesive properties of the resins based on their lap shear strength, c) selection and optimization of the adhesive system that was used to obtain particleboards, d) evaluation of the mechanical properties and dimensional stability of the PB.

Six different phenol-formaldehyde (PF) resins were synthesized in a study aimed at establishing the effects of resin loading, hardener addition, and pressing time on the final properties that the final particleboard will present.

For all the synthesized resin and particleboard manufacture experiments, the following reactants were used:

Formaldehyde solution (37% w/w); ACS reagent grade, provided by RICCA. CAS number 50-00-0

Phenol (crystals), provided by VWR. ACS grade. CAS number 108-95-2

Hexamethylenetetramine (99+%), provided by Alfa Aesar. CAS number 100-97-0

Nitric Acid (69-70% concentration), provided by BDH. ACS grade. CAS number 7697-37-2

Sodium Hydroxide, beads provided by BDH. CAS number 1310-73-2

2.5.2 Resin synthesis and characterization

In order to determine which adhesive system, Novolac or Resol, present the best bonding performance, different P/F ratios were analyzed. Table 2.1 summarizes the combinations tested for resols:

F/P ratios	FI: 1.2
	FII: 1.34
	FIII: 2.45

Table 2-1: Basic media reaction conditions

Table 2.2 summarizes the Novolac resins that were synthesized and tested:

F/P ratios	FI: 0.8
	FII: 0.5
	FIII: 0.3

Table 2-2: Acidic media reaction conditions

The six different resins were synthesized in a glass reactor equipped with a stirrer, a thermometer, and a reflux condenser. Figure 2 shows the reactor where the mixture of phenol and an aqueous solution of the basis or acid was added carefully. At the same time, the formaldehyde was added, and the temperature was controlled until it reached 45 °C for 30 minutes. After adding all of the components, the reactor was heated up to 90°C and maintained for 60 minutes.

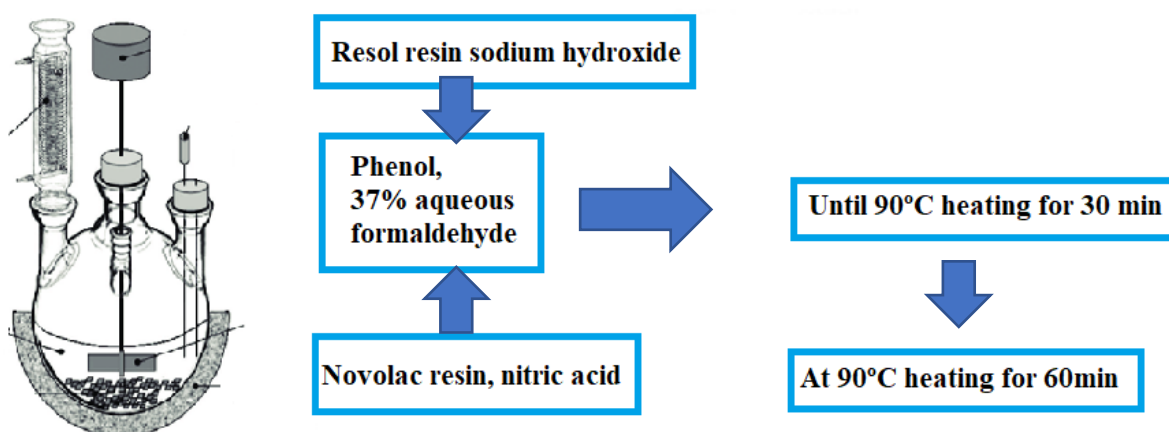


Figure 2-3: Reactor and reaction path

The solid contents of the different resins were determined according to ASTM D4426-01 method. The viscosity measurements were performed at room temperature (23°C) using a rotational viscometer Fungilab Inc. Expert Series. The shear rate used was 100 rpm and the spindle used was L3. In order to determine the pH of the resins, an AR20 pH/conductivity meter from Accumet Research was used.

2.5.3 Panel manufacture

Dried wood particles were blended in a small blender (Figure 2.4). The amount of resin and the wood particles were calculated so that three small particleboards could be made. Based on preliminary experiments, a 10% resin loading was used during the mixing stage. The resin was spread onto the particles using disposable pipettes of three milliliters, making sure that all the particles were in contact with the resin.



Figure 2-4 Blender used to mix the particleboard and the resin

For the pressing step, the material was placed in a molding box “stopper” with the following dimensions 15cm wide x 16cm long x 1.2 cm thick. By using the stopper, we were looking to obtain a homogeneous distribution of the material along with the panels, so that the variation in thickness and therefore density would be better controlled. After trimming the edges of each board, the final panels had the following target dimensions: 12.7cm long, 11.43cm wide, and 12mm thick.

2.5.4 Density determination

All particles used for the manufacture of the panels were conditioned in a humidity chamber at 22°C and 65% relative humidity. This procedure has to be followed because the moisture content (MC) of the particles is critical during hot-pressing operations (Youngquist 1999), especially when liquid resins are used. Before manufacturing the boards, the MC was measured in order to assure that values were 5.5 ± 0.5 %.

The density targeted for the particleboard was the low density (less than 640 kg/m^3) specified by the American National Standard Institute (ANSI) in the low range. The density is an important parameter that influences the mechanical and physical properties of the final panels. All densities of the boards were measured one by one before testing the properties or cutting the material into smaller sample sizes for the different measurements. The volume of the samples was calculated from the length, width, and thickness measured from a digital caliper (CD-800 C, Mitutoyo Co., Japan). All sample densities were determined by dividing the weight of the panels (kilograms) by their respective volume (m^3).

2.5.5 Water resistance

Because of the well-known water-resistant properties of the panels manufactured with PF resins, this was the first property that we screened for to determine the optimal pressing conditions and resin formulation. Panels 12.7×11.43 cm in dimension were soaked in water at room temperature for three different time spans: 2hs, 12hs, and 24 hours. Thickness and length measurements were taken before soaking the panels in water. The thickness after the different times was also measured and the thickness swelling (TS) was determined as follows:

$$TS_{2h} = (t_2 - t_1) / t_1 * 100$$

$$TS_{12h} = (t_{12} - t_1) / t_1 * 100$$

$$TS_{24h} = (t_{24} - t_1) / t_1 * 100$$

Where t_1 is the thickness at the middle of the sample before the experiment, and t_2 , t_{12} and t_{24} are the thickness measurement in the same point after the respective time in hours.

2.5.6 Mechanical Properties

Particleboard samples were tested to determine their mechanical properties according to ASTM D1037 standard. Because of the smaller sizes of the particleboards manufactured, adjustments had to be done in order to calculate adequate values for these properties. In the case of IB, TS and WA, the dimensions of the samples were correct. However, for MOR and MOE, the samples dimensions were 12.7 cm x 5.08 cm. This means that the length/ width was 2.5.

2.5.7 Experimental designs and data analysis

2.5.7.1 First experimental design

Screening work involved the adjustment of temperature, pressure, density, thickness, uniform distribution of the resin during the formation step of the panels.

During the first screening our goal was to determine what parameters yielded the best mechanical properties (Table 2.3).

Trial	Resin loading	% Hardener
1	10%	0%
2		5%
3	8%	0%
4		5%

Table 2-3: First experimental design

For the first experimental design, TS, WA and IB were determined. Since after making the panels during preliminary work, it was found that 10% of resin loading with a pressing time of 10 minutes presented good results, we decided to study if it was possible to reduce the resin loading to 8% and use the same amount of HMTA (hardener) in the mix.

Analysis of Variance ($\alpha= 0.05$) for all the properties was conducted using SSPS Software.

All panels were pressed for 10 minutes, at a temperature of 180 ± 5 °C and applying a pressure of 2.75 ± 0.25 MPa.

2.5.7.2 Final experimental design

The six properties (MOE, MOR, TS, WA, ES, and IB) were measured in the final experimental design. The comparisons of these properties were made considering the panels made with UF resin as a control. Table 2.4 states the conditions and hardener quantities used. For all treatments, the resin loadings were 10% of the final board weight and 2% in weight of wax. In the case of UF resin, the catalyst system used was ammonium sulfate.

All panels were pressed for 10 minutes, at a temperature of 180 ± 5 °C and applying a pressure of 2.75 ± 0.25 MPa.

Treatment	Hardener %	Post-treatment
UF control	No	No
Treat 1	5%	No
Treat 2	10%	No
Treat 3	10%	1 hour of simulated hot-stacking

Table 2-4: Final design conditions

Analysis of Variance ($\alpha= 0.05$) for all the properties was conducted using SSPS Software. The correlation between some of the properties of the manufactured PB and density was found to be significant, therefore an adjustment of covariance (ANCOVA) was performed. The goal of this analysis is to eliminate the effect of density variation on final sample properties.

2.6 Results and discussion

2.6.1 Resin Properties and lap shear analysis

Viscosity measurements, solid content (nonvolatile content), pH, and appearance were the characterization methods used to describe the physical and chemical properties of the synthesized resins. Tables 2-5 and 2-6 show all the values for these properties. Also, some images of the resins can be found in Figures 2-5 and 2-6.

Basic media	% solid content	Viscosity (mPa.s)	pH	Appearance
FI	91.51	140	8.1	Yellow solid with bubbles
FII	91.07	387	8.5	Brown solid with bubbles, brittle
FIII	90.91	1245	8.8	Colorless semisolid with bubbles

Table 2-5: Basic media conditions



Figure 2-5: Appearance of basic media resins

Acid media	% solid content	Viscosity (mPa.s)	pH	Appearance
FI	91.2	29.7	4.2	Brown plastic solid
FII	59.89	22.9	3.7	Brown solid plastic
FIII	44.79	13.2	2.1	Brown solid plastic

Table 2-6: Acidic media resins properties

We noticed that the values obtained for the properties of the different resins were in the same range as those found for Young-Kyu Lee et al. in the paper used as reference. The main difference between this paper and the present work was the use of nitric acid instead of oxalic acid.



Figure 2-6: Appearance of acid media resin

All lap shear samples tested for lap shear were conditioned at 65% RH and 22°C. The dimensions for the overlap area, where the adhesive was applied, was 20mm wide by 10mm long (Figure 1.3). The amount of resin applied in each sample was 0.05g. Considering the area of the samples, this equal 125 g/m² of adhesive loading.

The standard used for this test was DIN EN 205 (EN 205. Lap Shear test 2003).

Figure 2-7 shows the results for the different adhesive systems analyzed. As we can see, PF(HNO₃) and PF(Na (OH)) worked statistically as well as p-MDI, and better than UF . In the case of PF resins, the two systems using Na (OH) or HNO₃ were tested. Analysis of variance ($\alpha=0.05$) and Fisher's Least Significant Difference (LSD) tests were conducted using SSPS Software.

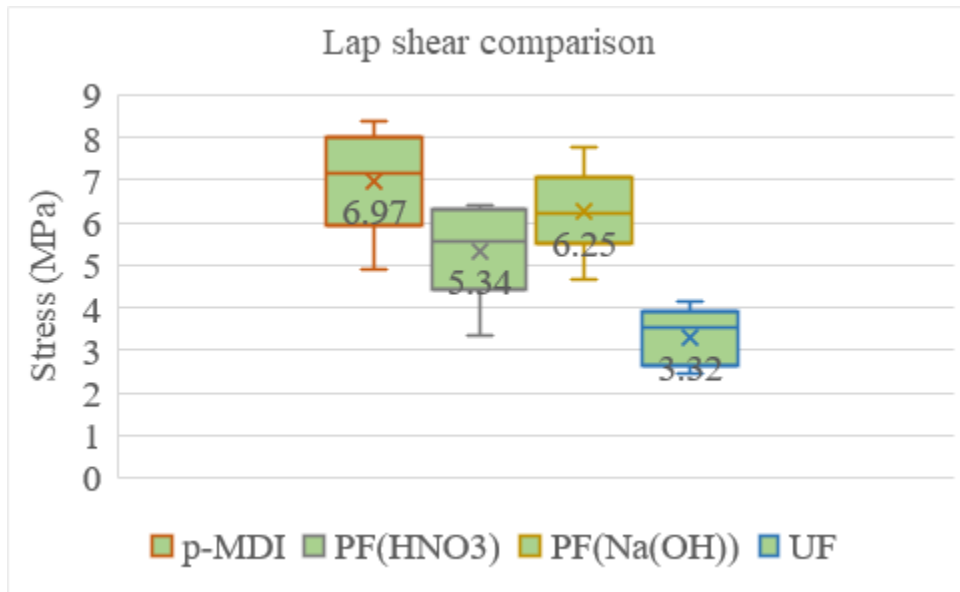


Figure 2-7: Lap shear comparison for different adhesive systems

As we can see in Table 2-7, p-MDI and PF synthesized with sodium hydroxide were found to be not significantly different. However, there was a significant difference between p-MDI and the PF synthesized with nitric acid. On the other hand, both PF resins performed similarly.

Lap shear (MPa)			
Resin	Mean	STD	LSD
p-MDI	6.97	1.24	A
PF(Na(OH))	6.25	1.05	AB
PF(HNO3)	5.34	1.14	B
UF	3.32	0.68	C

Table 2-7: Lap shear results for different adhesive systems and LSD

Figure 2-8 shows an example of lap shear sample after testing. As we can see, in this case we obtained a structural failure, where the adhesive bonding was strong enough to make the failure happened in the wood.

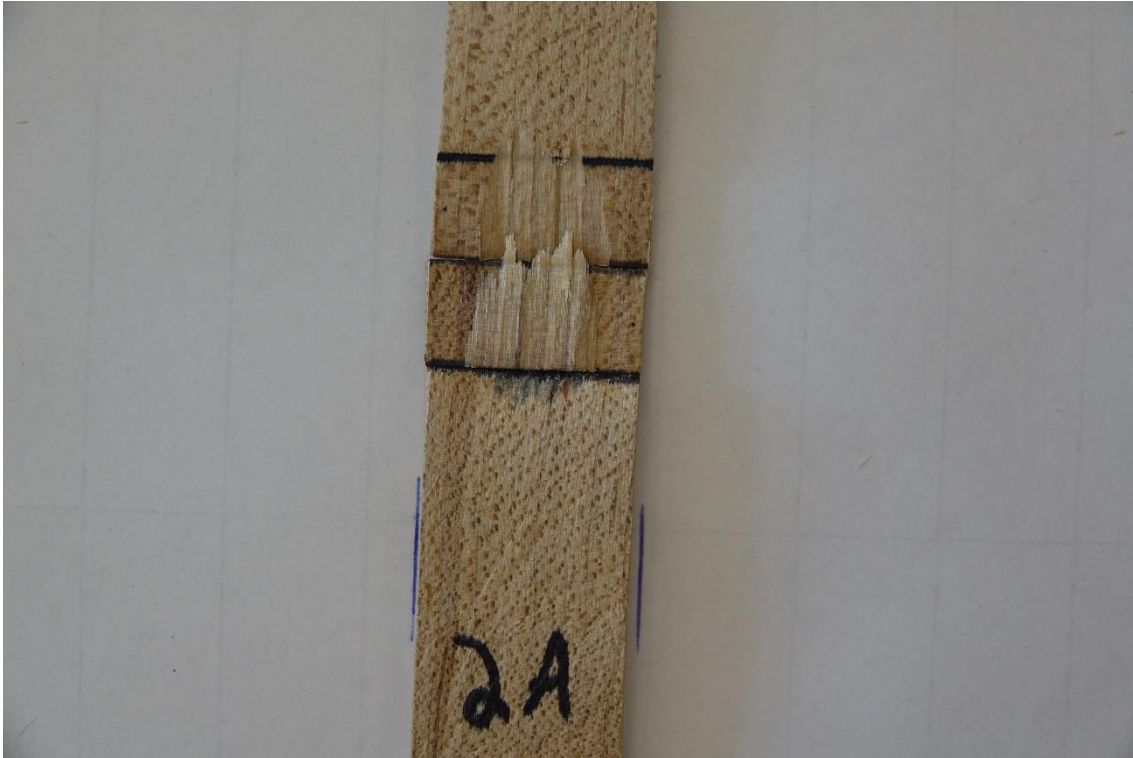


Figure 2-8: Lap shear sample after testing

After analyzing the results of the two different PF resins synthesized, Novolac resins catalyzed with HNO_3 were selected for the following experiments. The reasons for this were that it has been probed that wood pieces activated with nitric acid can reduce the gel time of PF resins, making it possible to reduce press time and possibly resin loading (Gardner and Elder 1988; Lee et al. 2003). Furthermore, some studies have demonstrated that nitric acid treatment can improve the strength of particleboard (Subramanian, Balaba, and Somasekharan 1982).

Figure 2-9 shows the results for the viscosity measurements of the selected resin by itself and adding different percentage of HMTA. Hexamine is added in quantities equals to 5 and 10 m% towards the total weight of the PF resin (Iliev et al. 2006).

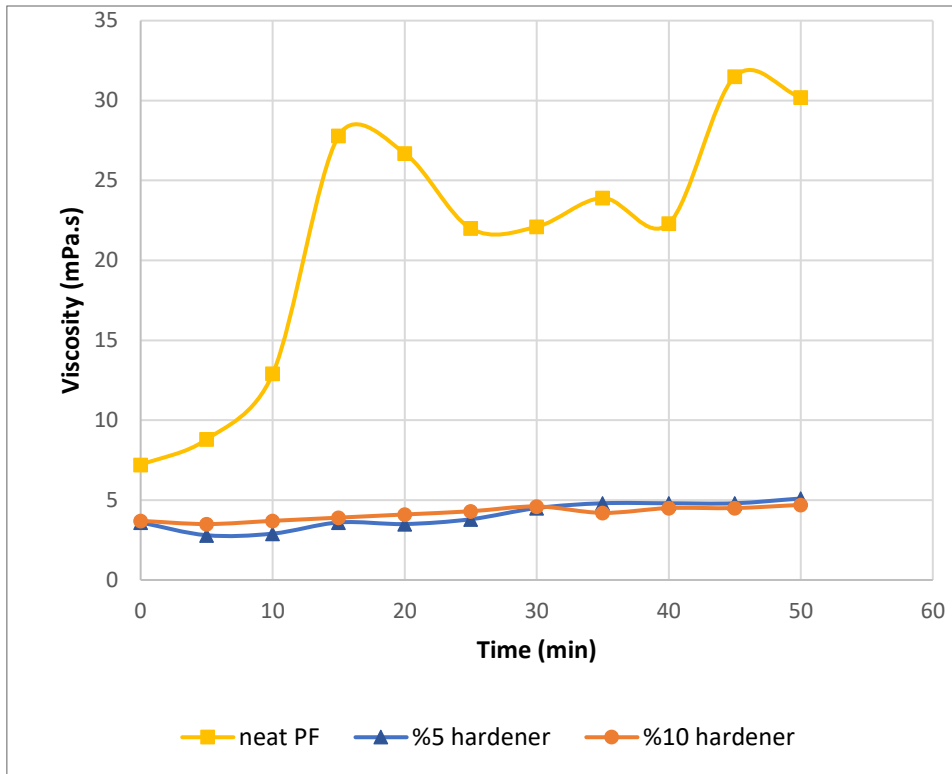


Figure 2-9: Viscosity measurements for PF(HNO₃) resin with and without HMTA(hardener)

Knop et al. described the interactions between phenolic resins and HMTA (Knop and Scheib 1979).

The highly exothermic reaction of nitric acid with phenol, increased the temperature of the PF resin at about 95°C. When dilute nitric acid is used, the formation of 2-nitrophenol and 4-nitrophenol is observed. It has been probed that when commercial PF resins react with HMTA the viscosity increases after 1 hour at 80°C, reaching values of 0.8 to 1 Pa.s. After this, the viscosity remained stable. (Iliev et al. 2006). For this project, the combined effects of adding the formaldehyde to the reaction dropwise, and the available hydroxyl group in the wood particles, was expected to create a good adhesion in the final PB. In Figure 2-9 we can see that the behavior of the neat PF resin is very unstable during the first hour of mixing the chemical. The opposite was observed when HMTA was added. In both cases, 5 and 10% of the viscosity measurements

showed that the structures formed in the resins generated a non-Newtonian system. Also, the resembling curves for the resins when we added HTMA could be attributable to a saturation of the system when 5% of hardener is applied. Similar behavior was observed for resol PF resins where synthesized at temperatures of 40°C (Kamarudin et al. 2020), where the excess of water in the system was thought to develop the viscosity values.

2.6.2 Characteristics of the PB manufactured

2.6.2.1 First experimental design

2.6.2.1.1 Thickness swelling and water absorption for first design

Considering that PF resins are known for their water absorption resistant, these two properties were the first target for our panels. Figure 2-10 shows the results for TS and WA for the different treatments. It should be noted that less TS and WA was desirable for improved performance.

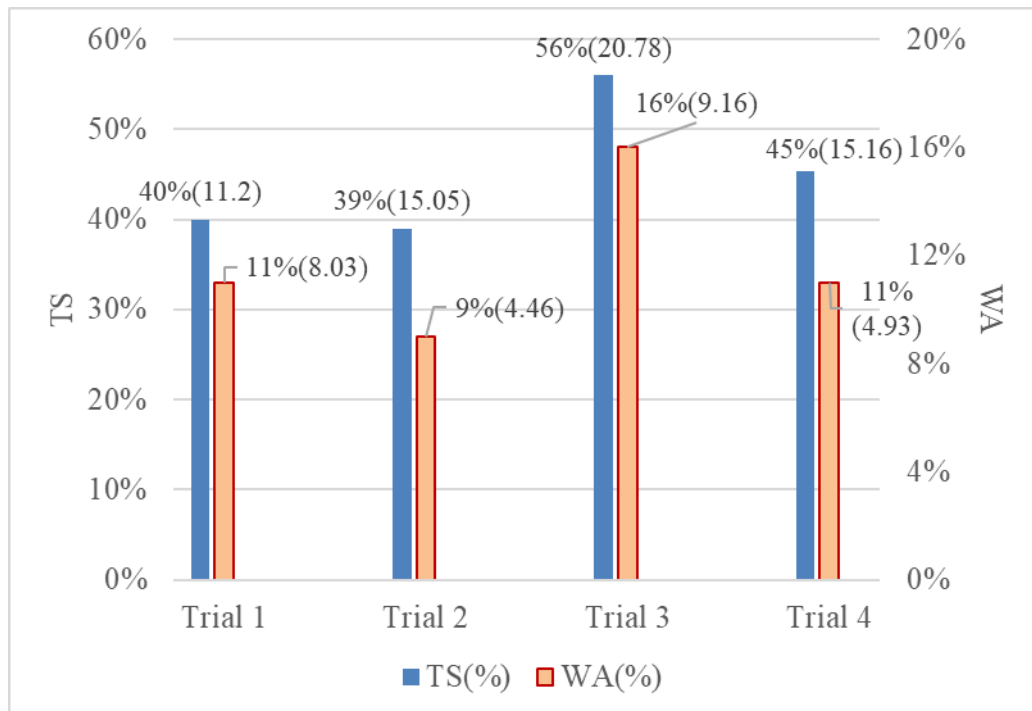


Figure 2-10: TS and WA results for the first design

We can see that Trial 2, were 10% of resin loading and 5% of hardener exhibited the best results for TS and WA, 39 and 9% respectively.

Considering that the results for all the trials for these two properties were acceptable, the analysis of variance was conducted only for the internal bonding.

2.6.2.1.2 Internal bonding for first design

Figure 2-11 shows the results for IB. Numbers in parenthesis are standard deviations.

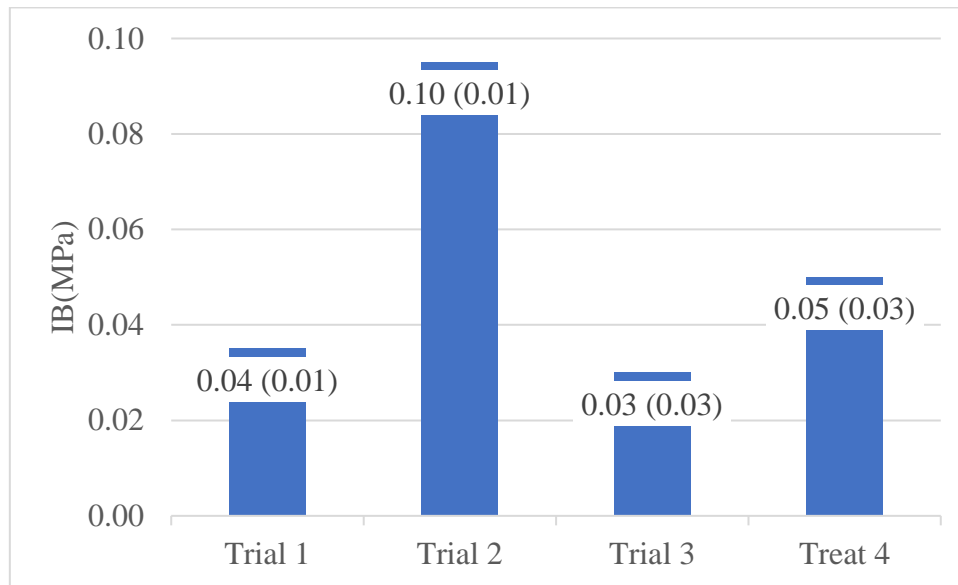


Figure 2-11: IB results.

The ANOVA results showed that both the resin loading and the use of hardener had significant effects on the internal bonding. However, in this case the interaction between these two factors was not significant. As we can see also on Figure 2-12, the results for the high resin loading (10%) and the use of hardener were the highest. Hence, these conditions were selected for the final experiment. Furthermore, due to the fact that low IB values could be demonstrating that the resin was not fully cured during the pressing step, hot-stacking and an increment of hardener from 5% to 10% was proposed for some of the treatments for the final experimental design.

Source	Sum of squares	df	Mean square	F	Sig
Main effects					
A:Hardener	0.0064	1	0.0064	13.71	0.0030
B:Resin Load	0.0025	1	0.0025	5.36	0.0392
Intercept					
AB	0.0016	1	0.0016	3.43	0.0888
error	0.0056	12	0.000466667		
Corrected total	0.0161	15			

Table 2-8: ANOVA results for IB

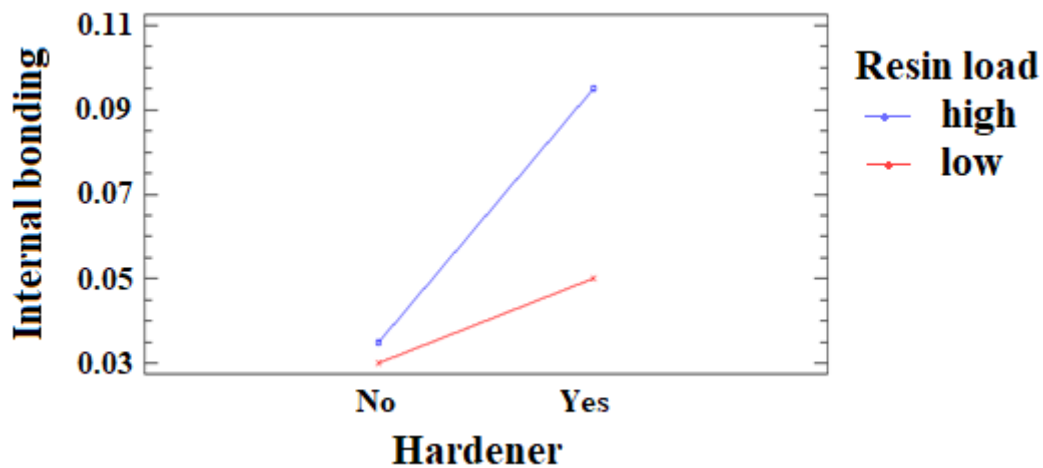


Figure 2-12: IB results for the different combinations tested in the first experimental design

2.6.2.2 Final experimental design

Tables 2-9 shows the results for the means and standard deviation for thickness swelling (TS), edge swelling (ES) and water absorption (WA).

		TS (%)		ES (%)		WA (%)	
		AVER	STDEV	AVER	STDEV	AVER	STDEV
Control	Hardener: no	36.77	10.07	27.41	10.07	89.4	4.8
	Post-treatment: no						
Treat 1	Hardener: 5%	23.99	9.25	39.38	9.25	10.29	5.11
	Post-treatment: no						
Treat 2	Hardener: 10%	32.47	12.05	30.86	12.05	8.42	7.45
	Post-treatment: no						
Treat 3	Hardener: 10%	37.46	12.62	26.39	12.62	12.69	10.3
	Post-treatment: 1hour hot-stacking						

Table 2-9: Average and standard deviation for thickness swelling, water absorption and edge swelling for the different treatments

Tables 2-10 shows the results for the means and standard deviation for modulus of elasticity (MOE), modulus of rupture (MOR) and internal bonding (IB).

		MOE (MPa)		MOR (MPa)		IB (N/mm ²)	
		AVER	STDEV	AVER	STDEV	AVER	STDEV
Control	Hardener: no						
	Post-treatmet: no	198.18	154.21	1.99	0.93	0.05	0.03
Treat 1	Hardener: 5%						
	Post-treatmet: no	152.70	85.25	0.85	0.41	0.04	0.03
Treat 2	Hardener: 10%						
	Post-treatmet: no	271.17	65.62	1.80	0.53	0.03	0.02
Treat 3	Hardener: 10%						
	Post-treatmet: 1hour hot-stacking	338.00	215.74	1.82	0.88	0.02	0.01

Table 2-10: Average and standard deviation for Modulus of rupture, Modulus of elasticity and Internal bonding for the different treatments

For the final experiment we can see that the property that showed the lower results was again the internal bonding. High standard deviations also claimed that the results were non consistent. This could have happened because the resins were not fully cured during the pressing step.

2.6.2.2.1 Thickness swelling

Figure 2-13 shows the results for thickness swelling for the treatments tested.

When we compared the results for the different treatments for TS, we observed that Treatment 1 (where 5% of hardener and no post treatment was applied), presented the best results.

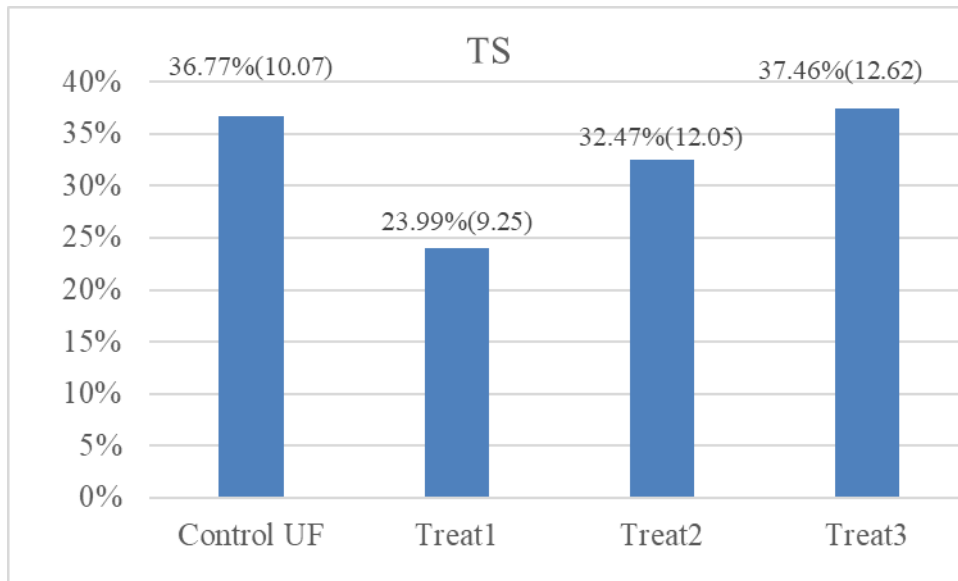


Figure 2-13: TS results. Numbers in parenthesis are standard deviations.

An analysis of thickness swelling with a t-test revealed that there is not significant difference between treatment 1 and 2 ($\alpha=0.05$). The difference between these two treatments was the amount of hardener used 5% for treatment 1 and 10% for treatment 2. For this property, we can suggest that the increase on the amount of hardener did not improve the values. Hence, treatment 1 would be the best option in this case.

2.6.2.2.2 *Edge swelling*

The values for means and standard deviations for ES are showed in Figure 2-14.

For the edge swelling we can see that treatment 3 performed as good as the control.

Since treatment 3 had the hot-stacking treatments (1hour) after pressing, we suggest that the edge swelling, the post treatment improved the values for the tested panels.

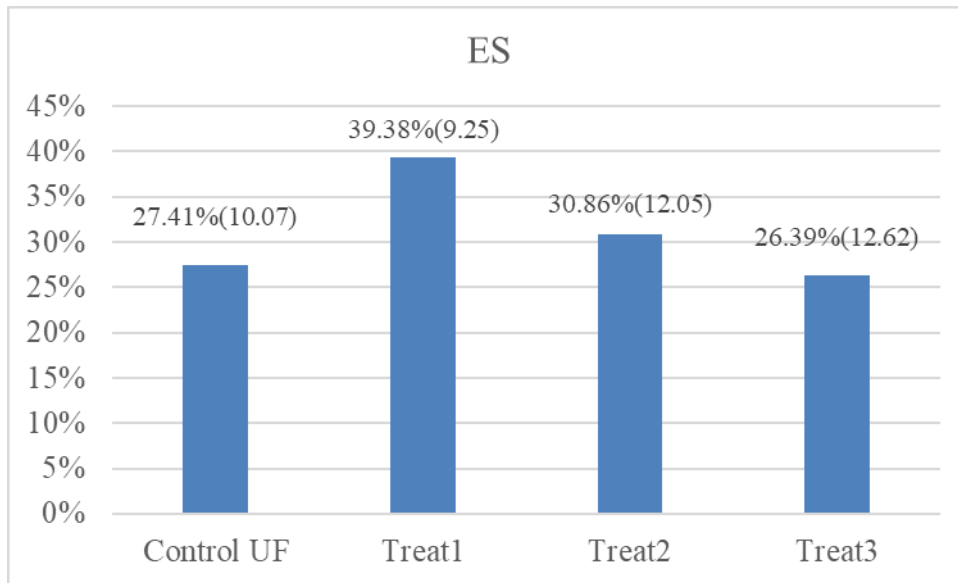


Figure 2-14: ES results. Numbers in parenthesis are standard deviations.

Since the difference between TS and ES were the points where we measured the panels, the results suggest that it is possible that the resins were not fully cured inside the panels. One of the phenomena that could have happened was the springback. During this phenomenon, an irreversible thickness swell caused by the release of compression stress is generated on the panels after the hot-pressing step (Báder and Németh 2019; Mohebby, Gorbani-kokandeh, and Soltani 2009). One of the possible consequences of springback is the debonding of the wood composites upon release of the press. This generates a decrease in the mechanical properties such as MOE and MOR, and on the other hand could also cause an increase in the TS and ES.

2.6.2.2.3 Water Absorption

Figure 2-15 shows the results for WA for the different treatments tested.

We can see that all the proposed treatments with PF resins outperformed the results of the control treatment with UF.

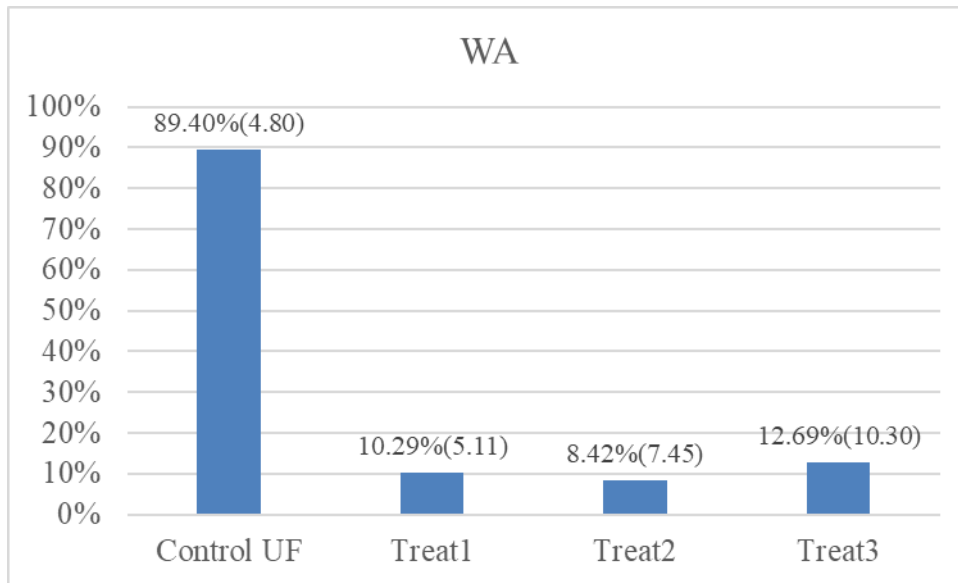


Figure 2-15: WA results. Numbers in parenthesis are standard deviations.

These results confirmed the excellent water absorption properties of PF resins. Even though the results for TS and ES were comparable for all the treatments, we can state that the panels manufactured with PF resins did not allow the absorption of a significant amount of water, which are the expected results for this type of wood composite.

Figure 2-16 shows some of the panels manufactured with UF resin, after soaking them in water for 24 hours.



Figure 2-16: UF panels after soaking in water for 24hs for TS,ES and WA

2.6.2.2.4 Bending Strength

In order to determine the MOE and MOR properties of the panels, the instrument was set up having a span of 10cm and rate of 0.79 cm/min. The results are shown in Figure 2-13.

Some researchers have probed the strong relationship between density and the mechanical properties of wood composites (He, Yu, and Dai 2007; Nemli et al. 2009; Wong et al. 1999). They claimed that the higher the density, the higher the mechanical properties. Overall, we can state that treatment 3 was the one that presented the best performance for MOE and MOR. Despite this, in order to determine if the density of the panels had an effect on all the properties measured, an ANCOVA test was performed.

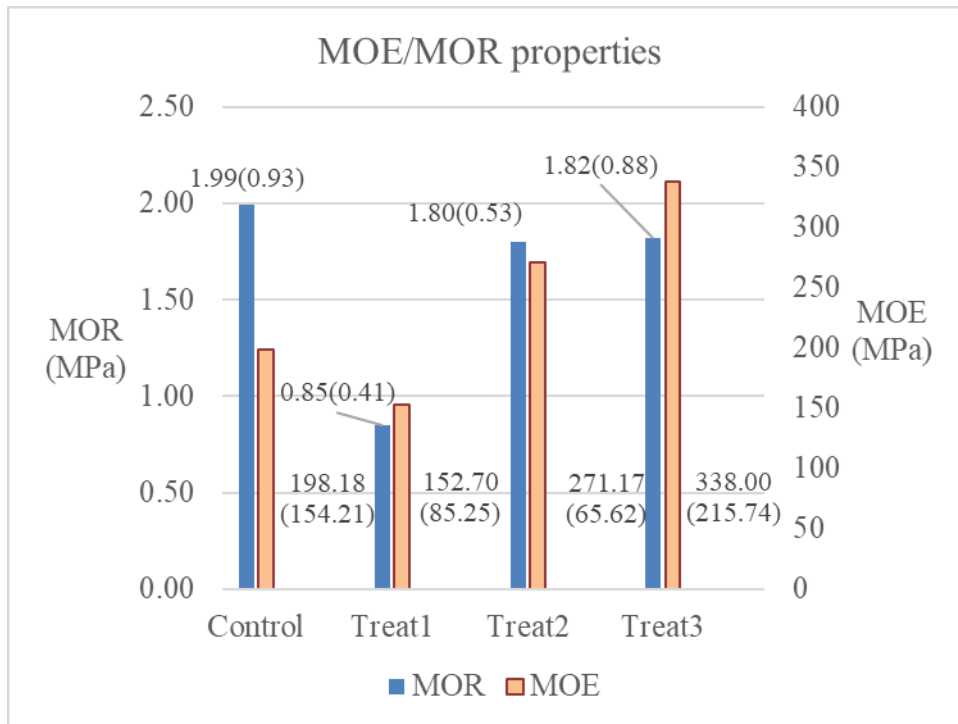


Figure 2-17: MOE and MOR results. Numbers in parenthesis are standard deviations.

2.6.2.2.5 Internal bonding

Figure 2-18 shows the results for the internal bonding measurements.

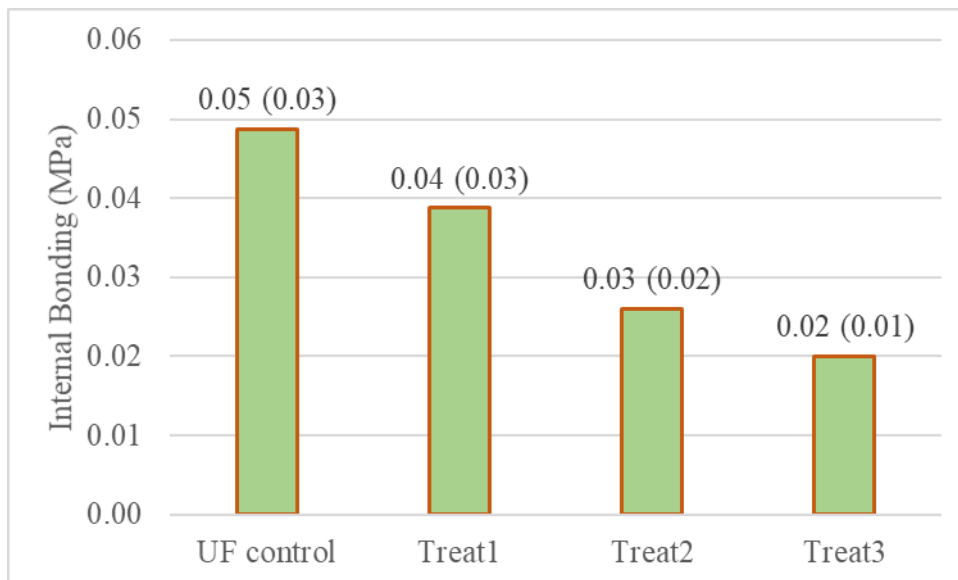


Figure 2-18: IB results. Numbers in parenthesis are standard deviations.

We can see for the results that even though the values for the different properties were closer to the ones found for the control, these values are still really low. For IB, eight samples were tested for each one of the treatments.

2.6.3 Statistical analysis with ANOVA and ANCOVA for the final design

Table 2.14 shows the results for the p-values for the ANOVA and ANCOVA tests.

As we can see, for most of the properties the p-values for the effect of the density showed no statistical difference if we eliminate this effect. In the case of MOR, after running the ANCOVA, we could see that the density had a significant effect on this property. At the same time, for the water absorption the results showed that there is statistical difference between treatments both before and after correcting for the effects of density.

Properties	p-values	
	ANOVA	ANCOVA
MOE	0.154	0.126
MOR	0.105	0.011
IB	0.080	0.080
TS	0.987	0.115
ES	0.895	0.218
WA	0.0001	0.0001

Table 2-11: p-values for ANOVA and ANCOVA tests

After running the tests, the means for all treatments for MOR and WA were adjusted to take into consideration the effect of density. Tables 2.15 and 2.16 show the adjusted means. Also, the same tables show the results for the comparison between means carried out by the Least Significant Difference (LSD) tests.

The results for the IB showed that even though the p-values were not significant, there were in both cases pretty close to the significance level ($\alpha=0.05$). According to these

results, the covariance density did not have an influence on this property. This was an interesting finding because it has been stated that the internal bonding of wood composites has a strong dependence on the density (He et al. 2007; Wong et al. 1999). This could suggest that the tested panels could either have experienced debonding due to springback, or a poor adhesion of the wood particles.

2.6.3.1 Analysis of the properties that demonstrated a strong dependence with density

2.6.3.1.1 Adjusted results for MOR

Tables 2-12 and 2-13 display the adjusted values for the MOR and WA properties, after accounting for the effect of density. This means that, after running the ANCOVA tests, these two properties showed that the results had a strong correlation between the densities measured for each individual panel and the MOR and WA properties.

Treatment	MOR	LSD
UF control	2.37 ± 0.50	A
Treat1: 5% hardener	0.82 ± 1.29	B
Treat2: 10% hardener	1.53 ± 0.61	AB
Treat3: 10% hardener + 1hour hot-stacking	1.24 ± 0.72	B

Table 2-12: Properties values after ANCOVA and LSD comparison for MOR.

Covariates appearing in the model are evaluated at the following values: Density = 494.46 kg/m³.

We can see that for MOR, treatment 2 performed as well as the control. Slightly lower values were found for treatment 3 and treatment 1. Despite of this, the chosen treatment should have to be treatment 2, because this was the only one that showed higher Modulus of Rupture.

2.6.3.1.2 Adjusted results for WA

Even before running the ANCOVA test, the difference between the results for the different treatments on WA were notable.

We can conclude that all treatments performed better than the control regarding the water absorption values found.

Treatment	WA	LSD
UF control	88.75 ± 8.05	A
Treat1: 5% hardener	14.7 ± 9.24	B
Treat2: 10% hardener	7.44 ± 8.09	B
Treat3: 10% hardener + 1hour hot-stacking	9.91 ± 8.52	B

Table 2-13: Properties values after ANCOVA and Tukey Kramer comparison for WA.

Covariates appearing in the model are evaluated at the following values: Density = 365.83 kg/m³.

2.7 Conclusions

The results showed that only for the Modulus of rupture, the control panels performed better than the suggested treatments. For all the other properties: thickness swelling, edge swelling, modulus of elasticity and internal bonding, there was not significant difference between the control and the treatments. The final analysis also demonstrated that for water absorption the suggested treatments outperformed the results for the UF resins.

What may be happening is that, since the production of PF is a step-growth polymerization reaction, the reaction time in our system was not sufficient to generate enough long chain high molecular weight polymers. This may have reduced the cross-linking density in situ the wood composite. Thus, low values for some of the properties like IB were observed.

The excess water in the system could have potentially reduced the IB because the steam generated in the core of the particle board may have not completely escaped during the hot pressing.

2.8 Future work

In order to continue this research, some advanced characterization techniques could be used in order to study the polymerization reaction in the resins. These techniques include: Nuclear Magnetic Resonance (NMR), Fourier-transform Infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Differential Scanning Calorimetry (DSC). DSC could also be used to further understand the curing of the resins during hot-stacking.

Also, an automatic hot press could be used to manufacture the boards, instead of using the small press that was used for this thesis.

2.9 References

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