BIOBASED PHENOLIC ADHESIVE
USING UNMODIFIED LIGNIN AND GLYOXAL

By

Sasha Emmanuel

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Forestry – Master of Science

2020

ABSTRACT

BIOBASED PHENOLIC ADHESIVE USING UNMODIFIED LIGNIN AND GLYOXAL

By

Sasha Emmanuel

Phenolic adhesives, primarily made of petroleum-based phenol and formaldehyde, have been used for many decades to manufacture wood composites such as plywood and oriented strand board (OSB) due to their superior performance. Phenol and formaldehyde are both made of fossil-fuel chemicals, and formaldehyde's toxicity and carcinogenic activity caused many researchers to focus on finding ways to replace it with biobased, less toxic raw materials. This study was focused on using lignin, a natural plant-based polymer, to replace phenol and used glyoxal, a biobased non-toxic chemical, to replace formaldehyde. The phenol was entirely replaced with an unmodified enzymatic hydrolysis corn stover lignin, while at the same time formaldehyde was substituted from 0 to 100% in increments of 10 with glyoxal. The resins were formulated under alkaline conditions using lignin to formaldehyde and/or glyoxal with a 1:2 molar ratio. The property and performance of resins and adhesives were measured and compared to a phenol-formaldehyde (PF) adhesive formulated in the lab. The pH, alkalinity, solid-content, free formaldehyde content of the formulated adhesives was similar to a commercially available PF adhesive. The dry lap shear strength of the developed lignin-glyoxal (LG) adhesive was 3.3 ± 0.4 MPa, which was comparable to the dry adhesion strength of the laboratory formulated PF adhesive (3.4 ± 0.2 MPa).

ACKNOWLEDGMENTS

First and foremost, I want to thank God for His ever-present favor in my life. Without Him, this would not have been possible. I want to thank my advisor, Dr. Mojgan Nejad, for giving me this opportunity. It all started back in 2017 when I came in as a Summer Research Opportunity Program (SROP) intern from Brooklyn with no research experience and no plans for graduate school. You saw my potential and gave me a chance to take my academic career beyond just my bachelor's degree. Thank you for always being available and thank you for pushing me to be a great researcher and even a better student. I want to thank my committee members Dr. Laurent Matuana, and Dr. Pascal Kamdem for sharing your knowledge, advice and just willingly being part of this journey.

This journey would not have been possible without my parents, Helena Emmanuel and Hilary Moise, my sounding boards. For showing me every day, the hard work, ambition, and determination needed to succeed in this life. Thank you mom, for your constant prayers, continuously encouraging me when I was at my lowest. You prayed for me even when I could not pray for myself, when I doubted my place in this world, you showed me the mark I already made and its continued growth. Thank you both for being fantastic parents. I also want to thank my undergraduate mentors at Medgar Evers College, Dr. Dereck Skeete, and Dr. Christopher Boxe, for believing in me. They made it their duty to ensure I was exposed to as many opportunities as possible to advance my academic career. I owe loads of gratitude to the excellent Forestry Graduate Secretary Katie James; from the very beginning, you have been an advocate and a friend. To Dr. Rothstein, from the beginning, you have been there, championing for the graduate students in all aspects, and for that, I will forever be grateful.

To my fantastic lab members Christian, Mona, Saeid, Mohsen, Akash, and of course, Isal, thank you for all the help with research from collecting to analyzing data, classes, and just being great friends. You have all made this journey here at MSU an amazing one. To my closest friends, thank you for daily encouragements and mental push. To you my dearest, thank you for the prayers, the love and understanding, the kind words of encouragement. I will always be grateful for your help during this journey.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

KEY TO ABBREVIATIONS

^{31}P-NMR	31 Nuclear Magnetic Resonance
CPF	Commercial Phenol-Formaldehyde
DMF	Anhydrous Dimethylformamide
DSC	Differential Scanning Calorimetry
FT-IR	Fourier-Transform Infrared
G	Guaiacyl
GPC	Gel Permeation Chromatography
H	Hydroxyphenyl
H_2SO_4	Sulfuric Acid
HCL	Hydrochloric Acid
HMTA	Hexamethylenetetramine
HPLC	High Performance Liquid Chromatography
HSO_3	Hydrogen Sulfite
IB	Internal Bond
iCAP	Inductively Coupled Argon Plasma
LD_{50}	Lethal Dose, 50%
LFG	Lignin Formaldehyde Glyoxal
LG	Lignin Glyoxal
LVL	Laminated Veneer Lumber
MDF	Medium Density Fiberboard

MF	Melamine Formaldehyde
M_n	Average molecular number
M_w	Average molecular weight
NaOH	Sodium hydroxide
OSB	Oriented Strand Board
PF	Phenol Formaldehyde
PG	Phenol Glyoxal
PLF	Phenol Lignin Formaldehyde
pMDI-	Polymeric diphenylmethane diisocyanate
PRF	Phenol Resorcinol Formaldehyde
S	Syringyl
SO_2	Sulfur Dioxide
T_g	Glass Transition Temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
UF	Urea Formaldehyde

CHAPTER 1: BACKGROUND

1.1 Phenolic Adhesive

Phenolic resins, also known as phenol-formaldehyde (PF) resins[1] were the first synthetic polymer ever developed.[1,2] With their first commercial use in 1908,[3] phenolic resins are used in numerous applications, such as fiber-reinforced composites, electric laminates, molding compounds, and adhesives.[4] Phenolic adhesives are primarily used as binders due to its high moisture and chemical resistance, mechanical and thermal stability, and electrical insulation properties.[4–8] In the adhesive industry, phenolic adhesives are widely used in wood composites, including laminated veneer lumber (LVL), plywood, and oriented strand board (OSB).[1] They are primarily made from the reaction of formaldehyde with phenol, and based on the molar ratio of formaldehyde to phenol and the type of catalyst used, the resin can be classified as either resole or novolac.[1,2,9] An increase in the molar ratio of formaldehyde to phenol increases the reactivity of the phenol to formaldehyde, hardening rate, degree of branching, and cross-linking of the resin.[1] Table 1 tabulates the differences between novolac and resole resin properties. Novolac phenolic resins are formed under acidic conditions, pH ranging between 4 to 6 [2] with phenol to formaldehyde ratio higher than one, as seen in Figure 1.[2,10] Bisphenol F is the purest form of novolac and occurs when formaldehyde is reacted with large amounts of phenol.[11] Novolacs are two-stage curing resins, cured at high temperatures (>150°C),[12] along with the addition of a hardener like hexamethylenetetramine (HMTA) or paraformaldehyde to aid in forming additional methylene bridges.[13,14]

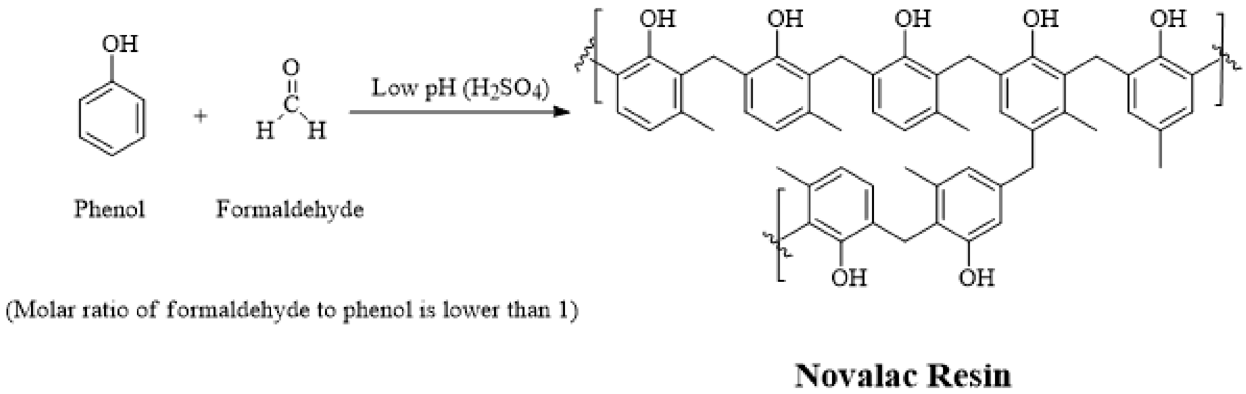

Figure 1. Reaction Mechanism for the Synthesis of Novolac Phenolic Resins. (Formaldehyde = F, Phenol = P)

Without the introduction of the curing agent or hardener, novolac resins are thermoplastics,[9] and can be used as thermoplastic polymers for the production of belts, tubes, and tires.[13] However, when cured using HMTA, novolac resins go from a thermoplastics resin to a thermoset.[15]

Table 1. Properties of Novolac Resins Vs. Resole Resins

Novolac Resin	Resole Resin
Acidic catalysts (H_2S0_4) with a pH range 1 – 4	Basic catalyst (NaOH) with a pH range 7 to 13
Phenol in excess	Formaldehyde in excess
Requires hardener to cure	Requires only heat to cure
Two-stage resin	Single-stage resin
Produces a thermoplastic polymer before adding HMTA [15]	Produces a 3-D cross-linked insoluble polymer[16]

Resole phenolic resins are produced by a condensation polymerization reaction between formaldehyde and phenol at temperatures ranging from 40°C to 100°C,[13] with the pH ranging from 10 to 13[1] using an alkaline catalyst, usually sodium hydroxide, with a molar ratio of phenol to formaldehyde of less than one.[2] Resole resin production occurs in two phases, shown in Figure 2; addition and condensation.[2] Below 60°C, the addition phase occurs where the formaldehyde will react with the phenol to produce hydroxymethyl phenols on either the two para positions or on the ortho position, which will then react with methylene glycol to form methylol phenols compounds.[9] At temperatures above 60°C, methylolphenol reacts with both phenol and other methylolphenol compounds in the condensation phase producing a prepolymer.[2,11] Unlike novolac resins, resole resins only require heat to start curing and crosslinking.[14]

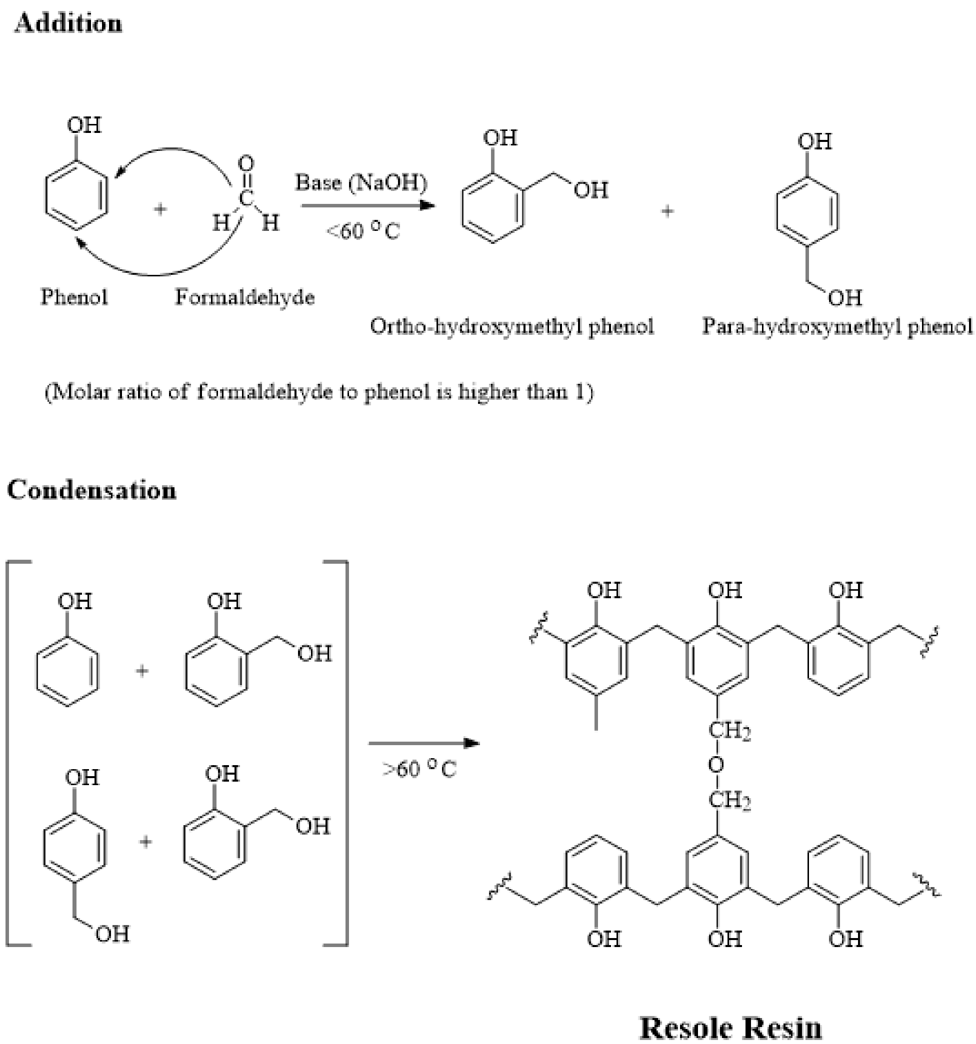

Figure 2. Reaction Mechanism for the Synthesis of Resole Phenolic Resin. (Formaldehyde = F, Phenol = P)

It must be noted that there are some differences between the resin and the adhesive. The resin is the prepolymer produced by reacting the phenol with formaldehyde and is uncured.[17] The resin is then used to formulate the phenolic adhesive, also known as glue mix, which will then be used to manufacture bio-composite like OSB and plywood.

Plywood and OSB are the primary wood composites that are made using phenolic adhesives.[2] Typically, it is made with southern yellow pine and Douglas fir, but sometimes they are also made from western hemlock, western pines, red pines (in Michigan), maples, and yellow poplar.[18] Plywood is produced using up to at least three layers of veneers, which are adhered together with an adhesive under high pressure about 220psi (1500kPa), for dense species and 110 psi (750 kPa) for low-density species.[18] They are pressed under temperature ranging from 132°C to 165°C and 107° to 135°C for softwood and hardwood, respectively.[18,19] It can be used for both interior and exterior applications.[20] Oriented strand board (OSB) are made of thin strands of wood with low to medium density like southern pine, yellow poplar, sassafras, white birch, and aspen.[18] Core and surface boards are typically 4′ × 8′ with strands arranged in the cross-machine direction or parallel to the length of the board in the core layer and are placed in the machine direction or parallel to the width of the board in the surface boards.[21] This arrangement allows for better mechanical properties. These boards will then be compressed under pressure ranging from 4.8 to 5.5 MPa (700 to 800 psi) at temperatures ranging from 177 to 204 °C (350 to 400 °F) for 3 to 6 minutes.[18] At this time, pressure and temperature, the adhesive curing, or hardening process will occur. OSB is widely used for roofing, siding, subfloors, wall sheathing, and web-stock for wood I-beams.[2] Majority (85%) of the world’s OSB production is produced in the United States and Canada with a growing interest in European countries like France, Germany, Spain, and Poland.[22] Typically, in the United States, there are two types of resins used in OSB: the core resin for the middle layers made with polymeric diphenylmethane diisocyanate (pMDI) and the surface resin for the outer layers are usually phenolic resins.[20] However, European manufacturers primarily use pMDI in their OSB production due to their stricter regulations for formaldehyde usage.[23]

The composition and chemistry of wood vary based on the species, properties of the wood (adherend) like extractives content, porosity, moisture content, grain orientation, and density, which can all affect the performance of the adhesive.[24] Extractives, which are non-structural substances[25] in the wood, can disperse to the surface when exposed to high temperatures, reducing the adhesives' ability to penetrate the wood and form interfacial bonds.[26] For instance, wood species with high amounts of extractives like starches, alcohols, tannins, resinous materials, and proteins can affect the adhesive's wettability.[20,26] Another effect resinous extractive has on the performance of the adhesive is the ability to repel water (hydrophobic properties), which can pose a problem for water-based adhesives.[26] Extractives can also impact the adhesive's bond-ability and the adherend through its acidic level, [27] which will decrease the curing rate of alkaline phenolic resins while increasing the cure rate of acidic-phenolic resins like urea-formaldehyde (UF) resins.[25] The wettability of the adhesive is another critical factor that will impact the adhesion performance. Wettability is measured as the speed by which the adhesive will wet the surface or spread over the surface of adherend (wood).[24] This happens when the contact angle between the surface of the adherend (wood) and a drop of adhesive approaches zero.[24,26] The wettability of a wood surface with an adhesive is the initial step in creating the bond.[25] Many factors can affect the wetting of the wood; consequently, the adhesion performance of the adhesive (glue mix). Penetration is also a critical factor in the application of the adhesive on the wood specimen. Porous wood species can show high amounts of overpenetration of the adhesive. There are two types of adhesive penetration: 1) gross/lumen penetration and 2) cell wall penetration.[28] Gross or lumen penetration occurs when the adhesive flows into and through the pores of the wood filling the lumens.[24,28] This type of penetration depends on the adhesive's contact angle on the wood specimen and its viscosity.[29] Selecting hardwood specimens may lead to higher gross penetration due to its more porous nature and larger vessel presence.[18] Cell wall penetration depends more on the adhesive's molecular weight.[24] The cell wall penetration can affect the mechanical strength between the adhesive and wood but cell wall penetration of adhesives in the cells could lead to nanomechanical interlocking by enhancing the contact area of the adhesive and the wood.[24,26] A wood specimen's moisture content, density, and grain orientation can affect its wettability.[24] The moisture content of wood ranging from 6% to 14% allows for satisfactory bonding with the adhesive, and below 3% will reduce adhesive wetting.[26] The high amount of moisture above the fiber saturation point in wood, which is averaged about 30%, can also lead to loss of adhesive due to the reduced amount of adhesive and water that can be absorbed by the wood.[26,30] This loss occurs when pressure is applied to the adhered wood veneers together causing the adhesive to be more fluid leading to adhesive spillage on the sides of the panel (squeeze-out).[26] Changes in the moisture content of the wood can also lead to shrinking and swelling, which can result in interfacial stresses between the adhered wood.[31] The density of the wood species can also affect the adhesive's performance and penetration. The low-density wood species have large lumen volumes and thinner walls,[18] which allows for better adhesive penetration to create strong interfacial bonding[26] while also resulting in loss of adhesive on the bond line due to excessive penetration. Although adhesive penetration is vital in forming strong bonds, over-penetration can occur, resulting in weaker bonding between the wood and adhesive and resulting in a waste of adhesive.[24,26] Adhesive shear strength of joint wood is the strongest when the grain runs parallel to the applied force.[32] The lap shear strength testing, which is one way of determining the pressed panels' mechanical properties, measures the amount of stress it can withstand when force is applied in opposite directions. The greater the lap shear strength, the stronger the bond between the wood and the adhesive, leading to greater wood failure. Percentage of wood failure can help determine the bonding strength between the wood and the adhesive, where a higher percent.[33] This can be determined by visual analyzing the panels after lap shear testing or using image analysis software. The more visible damage seen on the panels, the stronger the adhesive, which can be seen easily with the PF adhesives due to its darker color. The alkali content of the resin is also an essential parameter. The higher the adhesives' alkalinity, the greater its reactivity and hardening rate, resulting in the need for shorter press time.[1]

1.2 Research Motivation

According to market research, global formaldehyde consumption has increased exponentially.[34] By the end of 2026, it is anticipated to increase to 36.6 million tons, with the majority of it being used for formulating resins such as phenol-formaldehyde (PF), melamine-formaldehyde (MF), and urea-formaldehyde (UF).[34] This increase in consumption of formaldehyde will result in higher use and dependency on petrochemicals. Formaldehyde is produced from the catalytic oxidation of methanol and is used as a precursor of PF, UF, and MF resins.[2] Moreover, formaldehyde is used in many sectors ranging from automotive to healthcare industries.[2] It is a highly flammable colorless gas. Although there are serious concerns about formaldehyde's impact on human health, it is still being used in many different applications.[4,7,35–38] Formaldehyde is considered a highly toxic chemical with a lethal dosage (LD50) higher than 100mg/kg in rats and 42mg/kg in mice.[2,36,37,39,40] Formaldehyde is known to cause certain health risks like eye, nose, throat, and skin irritation at a concentration higher than one ppm (1.25 mg/m^3).[2,12] In 2010, formaldehyde was classified as carcinogenic to humans through inhalation exposure by the Environmental Protection Agency (EPA).[41] Formaldehyde has been concluded to have a causal association with nasopharyngeal, leukemia, nasal, and paranasal cancers.[41] This very concern is why many countries are introducing stricter restrictions and regulations for the use of formaldehyde. Countries like Japan, Germany, Austria, Sweden, and the United States all began forging more stringent regulations on reducing formaldehyde emissions.[42] For decades, European countries have been gradually decreasing the acceptable formaldehyde emissions level in OSB, medium-density fiberboard (MDF), and particleboard with the highest emission level permitted at 8mg/100g board.[23] While countries like the US continue to use formaldehyde in the production of OSB panels, albeit with stricter regulations, in Europe, almost all OSB producers use pMDI, especially in the core layer.[23] The United States Congress passed a bill in July 2010, setting restrictions on the number of formaldehyde emissions allowed in plywood, MDF, and particleboard manufacturing.[43] Formaldehyde emissions were set to 0.05ppm for plywood, 0.11 ppm for MDF, and 0.09 for particleboard.[43] Formaldehyde emissions have decreased significantly due to all these regulations, which will be subjected to even stricter regulations since formaldehyde was classified as a carcinogenic chemical.[23]

CHAPTER 2: LITERATURE REVIEW

In recent years, many researchers have found comparable replacements to help alleviate our dependency on nonrenewable petroleum-based chemicals. [6,10,44–50] Biomass sources like a cashew-nut shell, tannin, and lignin have been used as substitutes for phenol to formulate phenolic adhesive.[2,20,49] These biomass feedstocks are used as replacements due to their renewability, availability typically as waste biomass, and their comparatively lower prices.[51]

2.1 Tannin

Tannin has been a favorable raw material used to partially or entirely substitute phenol in the phenolic adhesive formulations due to its phenolic structure.[48,52–54] Tannins are biomaterials extractable from leaves, bark, and wood from various wood species.[51,55] Due to the phenolic nature of tannins and its ability to form cross-linkages with formaldehyde, it has been a suitable substitute for phenol. Its reactivity is determined by the reactive position sites. There are two different types of tannins, condensed, also called polyflavonoid tannins and hydrolyzable tannins.[56] Condensed (polyflavonoid) tannins comprise 90% of the world's commercially produced tannins, which is up to 200,000 tons per year.[55,57] They are made of flavonoid units with two types of phenolic nuclei A- ring, which includes phloroglucinol and resorcinol, and B-ring, which includes catechol and pyrogallol.[55,57] Depending on the tannin type, they can contain up to 8 reactive locations to react with formaldehyde and form methylene bridges.[55] The type A rings have higher reactivity toward aldehydes like formaldehyde than the B-type tannin. The most commonly used tannin type is the condensed tannins and is mainly extracted from wattle or mimosa bark (*Acacia*), hemlock bark *(Tsuga*), quebracho (*Schinopsis*), sumach (*Rhus*), and different *Pinus* bark species.[54,57] Hydrolyzable tannins are nonpolymeric structures that comprise simple phenols such as gallic, digallic, and ellagic acid and sugar esters, usually in the form of glucose.[57] These tannins are less common in adhesive production due to their lower reactivity, limited availability, and higher price than condensed tannins.[58]

2.2 Lignin

Lignin is another major naturally available polymer that has been used to replace phenol in the formulation of phenolic adhesives due to its phenolic structure. Lignin is one of the most commonly found biobased amorphous polymeric material second to cellulose in the world.[47,59–61]

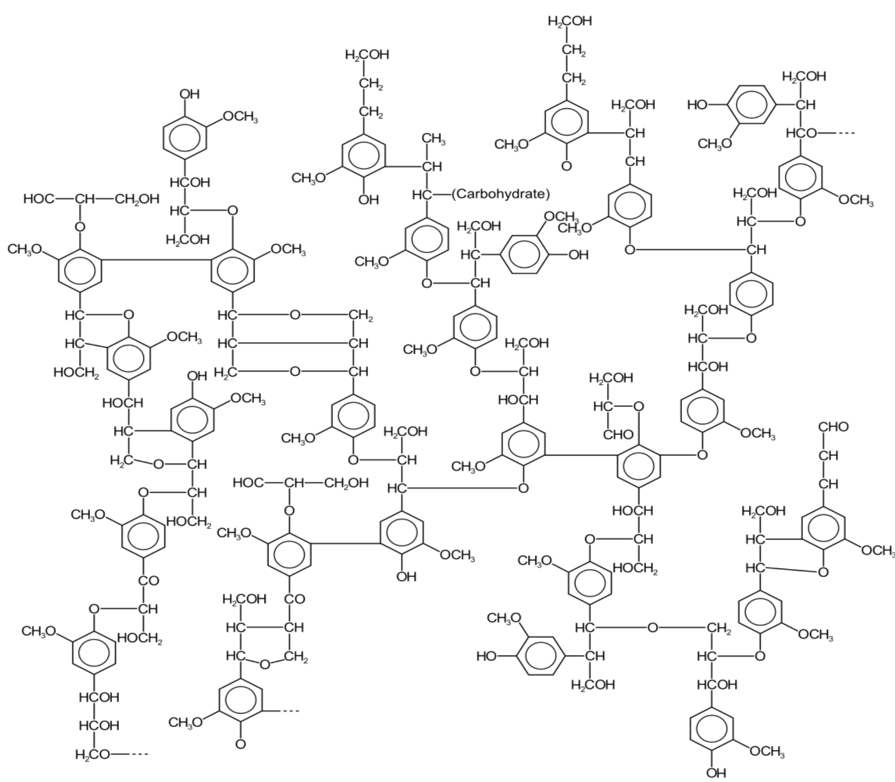

Figure 3. Lignin Structure

Karol Głąbpl.wiki: Karol007commons: Karol007e-mail: kamikaze007 (at) tlen.pl - own work from: Glazer, A. W., and Nikaido, H. (1995). Microbial Biotechnology: fundamentals of applied microbiology. San Francisco: W. H. Freeman, p. 340. ISBN 0-71672608-4This W3C-unspecified vector image was created with Inkscape., CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=1993633

Lignin's complex structure seen in Figure 3 consists of three basic phenyl propane units called monolignols, which includes sinapyl alcohol, coniferyl alcohol, and *p*-coumaryl alcohol. These three monolignols shown in Figure 4[59,63] produce aromatic residues, including syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units, respectively.[59] The presence of these monolignols and aromatic residues differs depending on the lignin source in various plants,[64] shown in Table 2.

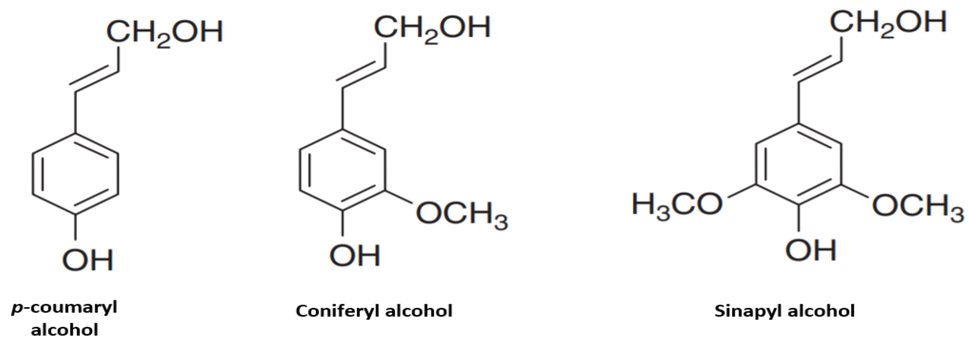

Figure 4. Three basic phenylpropane units (Monolignols)

The lignin's performance and suitability for different applications are contingent on the source of the lignin and the isolation method.[65] The lignin content varies based on the source hardwood (angiosperms), softwood (gymnosperms), and annual crops (Table 3).[63]

Table 2. Lignin Source And Its Monolignols Content (%)[64]

Lignin Source	Coniferyl Alcohol (%)	Sinapyl alcohol (%)	*p* -coumaryl alcohol (%)
Hardwoods	25 – 50	45 – 75	0 – 8
Softwoods	> 95	0	< 5
Herbaceous crops	35 – 80	20 – 55	5 – 35

Table 3. Lignin sources and its lignin content (%)[63]

Lignin Source	Lignin Content (%)
Hardwood	18 - 25
Softwood	25 - 40
Herbaceous crops (grasses)	10-20

In pulp and paper manufacturing, the wood's cellulose portion is used to prepare pulp and paper products. In consequence, more than 95% of lignin and other lignocellulosic waste from the wood are burnt to generate energy for the pulping process.[64,66]To be able to utilize the lignin component of the waste; first, lignin needs to be isolated from pulping liquor. The pulping process techniques can be divided into two categories: sulfur-based or sulfur-free isolation techniques.[67] Sulfur-based processes include kraft pulping and sulfite pulping..[67,68] Sulfur-free methods include soda pulping and organosolv pulping processes.[68] The lignins derived from these processes are considered technical lignins[68], including kraft, sulfite, soda, and organosolv lignins.[60] Kraft lignin is developed by the kraft process, which involves the delignification of wood and other biomass > 95%, under high temperature around 170°C with a solution of sodium sulfide and sodium hydroxide.[64,69] The resulting kraft lignin makes up 85% of the world's total lignin production.[70] This process results in lignin with high amounts of phenolic hydroxylic groups and condensed structures and a low number-average molecular weight (M_n) ranging from 1000-3000 $g.mol^{-1}$.[67] Kraft lignin has a low sulfur content (2-3%) despite the high sulfur extraction method used and also has high levels of phenolic hydroxyl groups.[68] Sulfite lignin or lignosulfonate lignin is derived from the sulfite pulping process of wood using a high temperature of 140-170°C with sulfur dioxide (SO_2^-) and hydrogen sulfite (HSO_3^-).[68] Lignosulfonate consequently contains high amounts of sulfur, resulting in higher ash content leading to a darker color. It is water-soluble, with a broad polydispersity index ranging from 6 to 8, and a higher number-average molecular weight ranging from 15,000 to 50,000 g.mol^{-1} than the kraft lignin.[67,68] Soda lignin is produced through a soda pulping process that is usually used for non-wood fibrous feedstocks such as straw, flax, and sugarcane.[68,71] Sodium hydroxide solution is used to digest the fibrous feedstocks at a temperature of 160°C or lower.[68] Soda lignins are insoluble in water, sulfur-free, and have low molecular weight and broad molecular weight distribution ranging from 800-3000 g/mole.[67,68,72] Soda lignin extracted from herbaceous sources also contains high silicate and nitrogen contents.[71,73] Organosolv lignin is produced through the organosolv pulping process using an acidic or nonacidic organic solvent like ethanol or methanol with water and acetic acid, with the addition of small amounts of acids like hydrochloric acid (HCL) or sulfuric acid (H_2SO_4) used as a catalyst.[67] The resulting lignin is highly soluble in organic solvents, but because of its hydrophobic nature, they are insoluble in water and is considered the purest commercial lignin.[67,68] Diluted–acid enzymatic hydrolysis lignin, which is the lignin utilized in this research, is a primary by-product of the bioethanol process resulting in lignin yield ranging from 10-30% of the lignocellulosic biomass depending on the source.[74,75] In this method, the biomass is pretreated using dilute acid (H_2SO_4) and then processed enzymatically using cellulolytic enzymes like exo-glucanases, endo-glucanases, and β-glucosidases.[75] Pretreatment of lignocellulosic material is typically performed before conducting the enzymatic hydrolysis to increase the efficiency of the process in extracting the sugars by weakening the structure of the biomass.[76–79] This allows for the tightly packed cellulose and hemicellulose content between layers of lignin to be more exposed and available for the enzymes and chemicals.[76] This step is essential because lignin and hemicellulose reduce the effectiveness of enzymes from separating the cellulose component during the enzymatic hydrolysis process.[80] Diluted-acid pretreatment, the most beneficial pretreatment technique which is performed at high temperatures for a short time (<30 min) or low temperature for longer processing time (30-90 min).[80] This pretreatment procedure may be used as either the main method in hydrolyzing lignocellulosic material to sugars or used as a precursor to the enzymatic hydrolysis of the material.[75] Corn stover lignin extracted using dilute acid enzymatic hydrolysis tend to have fewer ether linkages resulting in added reactive sites (H and G).[81] Also note, the phenolic content of enzymatic hydrolysis corn stover pretreated using dilute acid can also be higher by increasing the pretreatment conditions like reaction temperature and residence time.[78]

2.2.1 Lignin Modification

Lignin's complex structure, however, poses limitations for its use as a phenol replacement in these adhesives.[10,82] Due to steric hindrance in lignin structure, formaldehyde's reactivity is significantly lower. Compared to monomeric phenol, which has three available reactive sites (one para and two ortho), there are fewer available reactive aromatic sites in the lignin structure for reaction with formaldehyde.[83,84] This will then reduce the degree of cross-linking during the polymerization stage,[83] which may result in unfavorable adhesive properties like lower mechanical strength and higher free formaldehyde content. To combat this issue, lignin modification has been introduced to increase lignin's reactivity with formaldehyde through hydroxymethylation, demethylation, and phenolation.[47,85] Methylation, also known as hydroxymethylation, is the most straightforward modification technique.[86] In this technique, lignin is dissolved in an alkaline medium, then reacts with formaldehyde, which results in hydroxymethyl groups attached that are attached to the aromatic rings of lignin via the Lederer-Manasse reaction.[65,67,86] Phenolation, also known as phenolysis, entails thermally treating lignin with phenol in an acidic solution like sulfuric acid (H_2SO_4).[86] The phenolation process does not only increase the phenolic content; it also decreases the lignin's molecular weight by cleaving ether bonds during the process.[86] Demethoxylation, which is the most expensive process,[50] increases lignin's reactivity by removing one or two methoxy groups from the ortho positions, creating available sites for reaction with formaldehyde.[84] Subsequently, increasing lignin's reactivity with formaldehyde or other aldehydes by adding additional hydroxyl groups.[84,86] Despite the ability to increase lignin's reactivity with formaldehyde and other aldehydes, these modification methods require added cost, time, and toxic organic chemicals, making it undesirable to industry and also impeding the purpose of developing sustainable means of reducing our dependency on petroleum-based chemicals.[47,82]

2.3 Partial or Total Replacement of Phenol

In many research studies, partial replacement of phenol was conducted to develop resole phenolic adhesives.[6,10,44,45,47,87] Khan et al.[44] developed a lignin phenol-formaldehyde adhesive replacing phenol with Eucalyptus bark lignin (10, 25, 35, 50, and 60% (w/w%)). They concluded that replacing 50% of phenol with eucalyptus bark based on a 1:2 ratio, lignin-phenol to formaldehyde using a 10 wt.% catalyst (NaOH), at 80°C for 4 hours would produce an adhesive with enhanced mechanical properties comparable to PF adhesives. This study noted that as the lignin concentration increased, the non-volatile solid content decreased and remained constant after 25 wt.% substitutions; gel time also decreased when lignin content was increased from 0 to

50 wt.%. Also, as the lignin concentration increased, there was an increase in the shear and adhesive strength. This study showed that an increase in cross-linking occurred which was also confirmed by the decrease in gelation time.[44] Yang et al.[45] conducted a study using four different biorefinery technical lignins, wheat straw, corn cob, and two poplar lignins to replace 50% of phenol in PF adhesive formulation. They reported that adhesives made with high molecular weight lignins like the wheat straw and corn cob showed significantly higher viscosity than commercial PF adhesives. The solid content of the formulated adhesives was higher than the commercial PF too. The cure temperature of resins analyzed via differential scanning calorimetry (DSC) showed slightly higher (124 – 130°C) than the cure temperature of commercial PF (118°C). The bonding strength of LPF adhesive formulated using corn cob lignin was the highest at 1.18 MPa compared to CPF adhesive 1.53 MPa, which is extremely lower than the adhesion strength of phenol-formaldehyde adhesives (3.5MPa). Jin et al.[5] also used modified enzymatic hydrolysis cornstalk lignin to replace 5 to 20% of phenol with formaldehyde to prepare an adhesive. This study showed that by replacing 20% of phenol with EHL, the dry shear strength was 1.5 MPa and 1.80 MPa for the wet strength, which met the Chinese standards of ≥1 and ≥0.7, respectively. They were able to determine that by increasing the NaOH content from 2.5 to 5%, the dry strength increases for the 20% phenol replacement adhesive, but with the same formulation, the wet strength decreases.[5]

Many researchers have made significant improvements by successfully replacing phenol with modified or unmodified lignin up to 50%. However, Kalami et al.[47] (our group) were the first, which successfully replaced 100% of phenol with an unmodified enzymatic hydrolysis corn stover lignin producing an adhesive with mechanical properties similar to that of a commercially formulated phenol resorcinol formaldehyde (PRF) adhesive. The dry lap shear strength of 3.4 MPa and the wet shear strength of 2.6 MPa showed no significant difference when compared to the formulated PRF adhesives, which was 3.6 MPa and 3.0 MPa, respectively. Furthermore, by substituting phenol with the unmodified corn stover lignin, formaldehyde consumption was reduced by 50%. The use of corn stover lignin as a suitable phenol replacement was further proven to be best by another study performed by Kalami et al.[10] This study analyzed different lignin sources and various extraction methods to determine the most suitable lignin for replacing phenol.

2.4 Partial or Total Replacement of Formaldehyde

Glyoxal, $C_2H_2O_2$, (40 wt.%) is the simplest dialdehyde, which has been used as a substitution for formaldehyde.[7,36,88,89] It is produced from oxidation (gas-phase) of ethylene glycol with a copper or silver catalyst, or oxidation (liquid phase) of acetaldehyde with nitric acid or as a secondary product of biological processes.[90,91] It is considered non-volatile based on the Henry Law constant ($\leq 3.38 \times 10^{-4}$ Pa.m^3/mol) in its aqueous state,[91–93] biodegradable,[7,88,91] and is less toxic than formaldehyde.[92,94] Glyoxal is considered to be a non-toxic chemical due to its low acute toxicity levels. According to studies conducted on rats, the lethal oral dosage (LD_{50}) in rats ranged from 3000 to 9000 mg/kg body weight, and the dermal LD_{50} was greater than 2000mg/kg body weight.[91] As mentioned earlier, formaldehyde's toxicity (100mg/kg in rats and 42mg/kg in mice) is much higher than glyoxal (LD50).[2] Also, with its two adjacent carbonyl groups, glyoxal's high reactivity with phenol, which is similar to that of formaldehyde and phenol, makes it a suitable formaldehyde replacement.[51,93,95] Glyoxal is used in many applications including, the textile industry, paper coating, adhesives, pharmaceuticals, cosmetics and electronics.[96] According to global market trends, glyoxal production was USD 265 million in 2019 and is predicted to increase by 2024 to USD 326 million at a compound annual growth rate (CAGR) of 4.3%.

Researchers have attempted and succeeded in partially replacing formaldehyde with glyoxal in phenolic resin formulations.[7,35,36,88,89] Hussin et al.[35] successfully developed a lignin-based phenolic adhesive replacing 100% of formaldehyde with glyoxal and up to 30% of phenol using two hibiscus cannabinus (kenaf core) extracted through kraft and soda processes. They reported that their 30% soda kenaf lignin-phenol-glyoxal (SLPG) had higher glass transition temperature (T_g) and higher phenolic-OH content than kenaf kraft lignin, which resulted in greater crosslinking and producing a favorable adhesive. Hussin and his colleagues also reported that their soda lignin-based adhesive performed better than their kraft lignin-based adhesive with higher viscosity, solid content, and tensile strength.[35] Ballerini et al. [88] studied the substitution of phenol and formaldehyde with pine tannin and glyoxal, respectively. They discovered that at pH around 8-9.5, tannin glyoxal had similar performance (gel time and rate of cure) to that of tannin-formaldehyde adhesive at a pH range of 6-7. Also, with the aid of pMDI, adhesive formulated using pine tannin and glyoxal (70% Tannin, 9% glyoxal, and 21% pMDI) internal bond (IB) strength was increased from 0.44 MPa in the tannin and glyoxal (88%Tannin with 12%glyoxal), to 0.60 MPa. Additionally, formaldehyde emission decreased dramatically from 4.7mg/100g 95% tannin/5% paraformaldehyde adhesive compared to 0.6mg/100g in the formulations without paraformaldehyde. Lei et al.[48] formulated a formaldehyde-free adhesive using glyoxal and lignin (acetic acid wheat straw lignin) along with pMDI 20 to 40%. In this study, mimosa tannin extract was also used as a replacement for PF resin in the formulation of the mixed adhesive. Lei and his colleagues focused on the properties of formulated resins when formaldehyde is replaced with glyoxal and when low molecular weight lignins were used as phenol replacement. For these adhesives, 55% and 60% glyoxalated lignin (GL), which is pre-reacted lignin with glyoxal, were mixed with different ratios of pMDI (20,25, 30, and 40%) and mimosa tannin (0, 15, 20, and 25) was used to replace PF resin in the adhesive formulation. This study showed the adhesives formulated with 60% of glyoxalated lignin and with 40% pMDI (60/40 GL/pMDI) using neither PF resin and mimosa tannin had a higher internal bond strength of 0.53 MPa. This was compared to their control adhesives using glyoxalated lignin, pMDI, and PF resin 55/25/20 and 55/20/25, which had an internal bond strength of 0.35 MPa and 0.31 MPa, respectively. This study also used triacetin and resorcinol, which are used as an accelerator to help increase the performance of the adhesive. The addition of triacetin did not improve the performance and cure temperature of the GL/MDI adhesive, but resorcinol did. With the growing interest in reducing our dependency on petroleum-based chemicals and reducing our exposure to toxic chemicals, few researchers have explored replacing both phenol and formaldehyde with lignin and glyoxal. Mansouri et al.[36] were able to substitute 100% of formaldehyde with glyoxal, replacing phenol with modified lignin and mixed it with PMDI. This study showed that the formulated adhesive could meet the adhesion strength/IB strength required by the international standard for exterior grade panels. However, as a result of the low reactivity of both lignin and glyoxal, they used modified lignin. They used a combination of lignosulfonate with petrochemical adhesive diphenylmethane-diisocyanate (pMDI) with a ratio of glyoxal to pMDI of 60:40. Diphenylmethane-diisocyanate was used as an accelerator to aid in increasing the mechanical strength of the adhesive.

2.5 Possible Challenges and Drawbacks

As stated earlier, replacing 100% of phenol with unmodified lignin is difficult due to lignin's complex 3D-structure and its lower reactivity with formaldehyde than phenol. Kalami et al.[10] compared nine different lignin samples as a phenol substitute and reported that the enzymatic hydrolysis corn stover lignin was the most suitable lignin for replacing 100% of phenol in the phenol-formaldehyde adhesive formulation. However, it is very challenging to replace 100% of both phenol and formaldehyde simultaneously with unmodified lignin and glyoxal that have lower reactivity than both phenol and formaldehyde. Due to the two carbonyl groups in glyoxal and its tendency to undergo side reactions like the Cannizzaro reaction leading to a more acidic medium, more in-depth research is needed to determine optimal parameters to address these concerns.

2.6 Objectives

This study's objective was to replace the formaldehyde portion of lignin-based phenolic adhesive with a biobased aldehyde such as glyoxal in a way that would not negatively affect the performance of the formulated adhesive. This was accomplished by gradually substituting formaldehyde with glyoxal in 10% increments starting from a 0% substitution, which was the control (LF and PF) to 100% substitution of formaldehyde. However, since both the phenol and formaldehyde portions of the adhesive were replaced with biobased, less reactive compounds, the challenge was to maintain the adhesion performance comparable with petroleum-based adhesive. The goal was to reduce the formaldehyde consumption in this biobased resin as low as possible by optimizing the resin formulation to achieve similar or superior performance to the commercially available phenolic resin. Any attempt in this line would improve the environmental aspect of the products by minimizing the adverse health effect for both workers at the manufacturing site and consumers using produced panels by significantly reducing the formaldehyde emission. This project's ultimate goal was to formulate a 100% biobased adhesive with similar or superior performance as of commercially formulated phenol-formaldehyde adhesive currently used in exterior grade plywood and OSB panels.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

Phenol 99.5 wt.% was purchased from Acros Organics and used as received. The lignin sample used for this research was isolated from corn stover lignin provided by POET LLC, produced as a by-product of the bioethanol synthesis through dilute acid pretreatment[97] and enzymatic hydrolysis of corn stover. Corn stover entails the stalks, leaves, and husks left behind after harvest.[78] Corn stover (*Zea Mays*) contains 15 -21% of lignin[97] and is the most produced popular biomass produced in the United States.[98] It contains high amounts of all three monolignols, including guaiacyl (G), hydroxyphenyl (H), and syringyl (S).[97] Corn stover lignin was selected for this research because, according to previously published work in our group[10], it was proven to be the best candidate for the substitution of phenol in the lignin-based phenolic adhesives since this lignin contains high *p*-coumaric and ferulic acid in addition to a higher amount of *p*-hydroxyphenyl (H-lignin).[10] Corn stover lignin processed through enzymatic hydrolysis process of corn stover contains high H-lignin, which has two vacant ortho positions in its phenolic structure that can react with aldehyde resulting in less free formaldehyde emission and higher bond strength.[10] Formaldehyde 37 wt.% and glyoxal 40 wt.% were purchased from Acros Organics and Fisher Scientific Inc, respectively. Both chemicals were used as received. Sodium hydroxide (NaOH) is the most common basic catalyst used in the preparation of resole resin. Sodium hydroxide (1N) solution was purchased from Fisher Scientific Inc. and was used as a solvent to dissolve the lignin and also as a catalyst. Wheat flour and plywood bark extender are used in adhesive formulations as a filler or extender to improve adhesive properties, control viscosity,

[99]and avoid excessive penetration of adhesive into the wood.[99] Southern yellow pine (SYP) veneer samples measuring 25.4 mm × 101.6 mm × 3.17 mm (1in × 4in × 0.12in) were used for the lap shear strength testing of the formulated adhesives.

3.2 Methodology

3.2.1 Lignin Characterization

Moisture Content

The lignin sample's moisture content was measured by drying lignin samples in an oven at 105°C for 1 hour and at 80°C for 3 hours. Samples were dried at 80°C to remove moisture (water) without partially degrading specific lignin components.[10] A mass of 0.5 g of the lignin was weighed in a dry, pre-weighed, aluminum pan and heated in an oven for 3 hours. Samples were cooled in a desiccator to room temperature and then weighed. The analysis was done using five replicates, and moisture content was calculated using equation 1.

$$\%Moisture\ Content = \frac{original\ weight - oven\ dried\ weight}{oven\ dried\ weight} \times 100\% \qquad \textit{[Equation 1]}$$

Ash Content

The ash content of the lignin was analyzed according to TAPPI-T 211 om-93 method. Crucibles were dried at 250 °C using a Thermolyne benchtop muffle furnace and which was then weighed to the nearest 0.1 mg after cooling to room temperature in a desiccator. Lignin samples were first dried for 3 hours at 105°C, then 1 g of the oven-dried lignin was added to each weighed crucible. The crucibles were then transferred to the furnace and heated at 525°C for 4 hours. Using a desiccator, samples were then cooled to room temperature and weighed. This test was performed in five replicates. Ash content was calculated using equation 2.

$$\%Ash\ Content = \frac{weight\ of\ Ash\ (g)}{weight\ of\ the\ oven{-}dried\ sample(g)} \times 100\% \qquad \textit{[Equation 2]}$$

Elemental Analysis

Elemental analysis of the lignin sample was determined by A&L, Great Lakes Laboratories (Fort Wayne, Indiana, USA). Following U.S EPA method 3051A (SW-846), for microwave extraction, [100] the lignin sample was first mineral-digested via open vessel microwave. /Mineral content was then determined based on a method from the Association of Official Analytical Chemists (AOAC 985.01) using a Thermo Scientific's Inductively Coupled Argon Plasma (iCAP) Duo 6000 series instrument.

Molecular Weight Distribution

To determine the molecular mass distribution of the lignin sample, it was first acetylated to increase its solubility in the tetrahydrofuran (THF) solution used as the mobile phase.[65] One gram of oven-dried lignin was acetylated by adding it to 40 mL of a 50/50 v/v% solution of acetic anhydride and pyridine and was mixed at 600 rpm for 24 hours at room temperature. A total of 150 mL hydrochloric acid (pH=1) was used to precipitate the acetylated lignin. The precipitates were then vacuum filtered, and the residual solids were washed with hydrochloric acid (0.05M) solution three times and with deionized water several times. The washed acetylated lignin sample was then dried using a vacuum oven at 40 °C overnight. Gel permeation chromatography (GPC) was used to determine the molecular weight, molecular number, and polydispersity index (PDI) of the acetylated lignin. The dried acetylated lignin was dissolved in THF (HPLC grade, 5 mg/ml concentration) and was filtered using a syringe filter (PTFE, 0.45 µm); the filtrate sample was used for GPC analysis. The GPC system from Waters, Milford, MA, USA included a separations module (Waters e2695), had a mobile phase (THF) at a flow rate of 1 mL/min at 35°C and three columns (300 mm × 7.8 mm Ultyragel THF 500 Å from Waters). Polystyrene standards were used for calibration standards with molecular weights from 162, 370, 580, 945, 1440, 1920, 3090, 4730, 6320, 9590, 10400 to 16200 Da. Using a 2414 Refractive Index (RI) Detector, 25 µL of the lignin solution was injected into the GPC system, which was constantly maintained at 35°C same as the columns. Chromatograms were analyzed using Empower GPC Software.

Hydroxyl Content Using ^{31}P-NMR

Hydroxyl content of the lignin sample was quantitatively determined using phosphorous-31 nuclear magnetic resonance (^{31}P-NMR). A mass of 40 mg of dried lignin was first dissolved in a mixture of 325 µL of anhydrous pyridine/deuterated chloroform (1.6:1, v/v) and 300 µL anhydrous dimethylformamide (DMF). Cyclohexanol and chromium (III) acetylacetonate were purchased and used as internal standard and relaxation reagent.[10] They were both dissolved in anhydrous pyridine and deuterated chloroform at a ratio of 1.6:1.0 (v/v) separately. A volume of 100 µL of cyclohexanol (22mg/mL concentration) and 50 µL of chromium (III) acetylacetonate solution (5.8 mg/mL concentration) solution was added to the dissolved lignin mixture. Finally, 100 µL of (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, (TMDP) a phosphitylation reagent was used to assist with tagging the hydroxyl groups during the analysis. A total of 600 µL of the mixture was then transferred to a 5mm NMR tube. ^{31}P NMR spectra were obtained using an Agilent DDR2 500 MHz NMR spectrometer combined with 7600AS, running VnmrJ 3.2A, and a pulse delay of 5 s and 128 scans was used. The different hydroxyl groups were determined using the chemical shifts reported in Table 4.[101]

Table 4. ^{31}P-NMR chemical shifts of lignin's functional groups

Hydroxyl Group	Chemical Shift Span (ppm) (^{31}P- NMR Spectra)
Aliphatic OH	149.1 -145.4
Condensed Phenolic OH	144.6 - 143.3 and 142.0- 141.2
OH from Syringyl OH	143.3 - 142.0
OH from Guaiacyl OH	140.5 - 138.6
OH from Hydroxyphenyl	138.5 - 137.3
OH from Carboxylic acid	135.9 - 134.0

3.2.2 Resin and Adhesive Formulation

For this research, phenolic resin was formulated by substituting 100% of phenol with an unmodified corn stover lignin and using different ratios of formaldehyde and/or glyoxal (0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100% molar ratio). The molar ratio of phenolic hydroxyl content of lignin to formaldehyde/glyoxal was kept 1:2 for all the samples.

Lignin formaldehyde (LF) resin was formulated using 100% unmodified lignin and formaldehyde. A mass of 15 g of lignin was dissolved gradually in 55mL of 0.1 N sodium hydroxide stirred at 150 rpm. The amounts of lignin and formaldehyde were measured based on the total phenolic content of our lignin sample, which was 3.89 mmol/g using a 1:2 molar ratio of lignin to formaldehyde. A round bottom flask equipped with a thermometer, condenser, stir bar, and dry bath stacker was used, as seen in Figure 5. A dry bath stacker was used to have a uniform temperature around the flask along with the thermometer. In a round bottom flask, 9.5 g of formaldehyde was added, followed by the addition of the dissolved lignin. Gradually the temperature of the system was increased to 65° C within 30 minutes at constant stirring (600 rpm). At 65° C, the system was kept constant for 10 minutes. The remaining NaOH solution, 20 mL (approximately 1/3 of the determined amount), was added to the flask. The temperature was steadily increased to 85° C, kept at that temperature for 1 hr. The resin was then cooled to room temperature; some of the resin was stored in a freezer to prevent further polymerization that can be used later to prepare adhesive. The remaining resin was used to measure its properties.

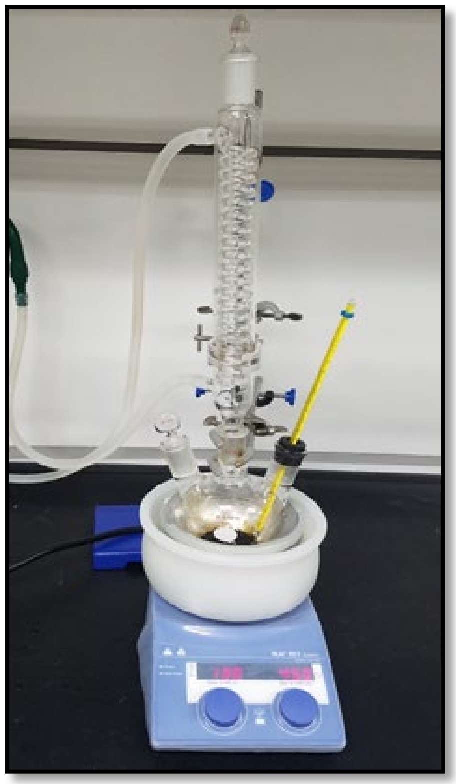

Figure 5. Resin formulation equipment setting, equipped with a thermometer, condenser, dry bath stacker, and digital heater and stirrer.

Lignin Formaldehyde and/or Glyoxal Resins

The same procedure explained above was used for the formulation of lignin formaldehyde/glyoxal (LFG). Formaldehyde was substituted in 10% increments from 0% to 100%. These formulations were denoted LFG-10, LFG-20, LFG-30, LFG-40, LFG-50, LFG-60, LFG-70, LFG-80, LFG-90, and LG.

Adhesive Preparation

The formulated resin was used to prepare the adhesive using the same procedure recommended for commercial phenol-formaldehyde adhesive, also known as glue mix preparation by industry, which was applied by Kalami et al.[10] First, 6.5 % (wt%) wheat flour was dissolved in 18% (wt%) distilled water, followed by gradually adding a 6.5 % (wt%) plywood extender (modal) to the mixture. Next, a mix of 3 % (wt%) sodium hydroxide and 66 % (wt%) thawed resin was added to the solution gradually. The solution was stirred until the mixture became homogenous, using a high-speed mixer at 800 rpm for 5 minutes.

3.2.3 Resin and Adhesive Properties

pH and Alkalinity

The pH of the formulated resin and adhesives were analyzed using a Mettler Toledo S220 digital pH meter at room temperature. Samples were first mixed using a stir plate and stir bar for 10 seconds, and then pH was measured. The alkalinity of resins and adhesives determines the amount of acid needed to reduce the acidity to a pH of 3.[102] Alkalinity of samples were tested based on ASTM D1067. About 6 g of sample was diluted in 100mL distilled water. The solution was titrated to a pH of 3.5, using 0.1 N hydrochloric acid (HCl). Alkalinity was then determined based on the consumed amount of HCl used, which was calculated using equation 3.

$$\% \, Alkalinity = \frac{Vml(HCl) \times 0.4}{weight\ of\ sample(g)} \times 100\% \qquad \textit{[Equation 3]}$$

Solid content

The solid content (SC%) or non-volatile content of the formulated resin and adhesive was analyzed following ASTM D4426-01 procedure (5 replicates). Aluminum pans were placed in a digital oven at 270 °C to burn off any excess oils on the pans from manufacturing. After cooling the pans to room temperature, they were weighed and labeled. Then 1 g of the sample (resin or adhesive) was added to each pan and placed in an oven for 105 minutes at 125°C. Samples were then cooled down to room temperature in a desiccator and weighed. The solid content was determined using equation 4.

$$SC\% \quad = \frac{weight\ of\ oven\ dried\ resin\ (g)}{weight\ of\ initial\ resin\ (g)} \times 100\% \qquad \textit{[Equation 4]}$$

Viscosity

The viscosity of the formulated resin was measured at room temperature using a Brookfield DV2T Viscometer. Using spindle number 63, the viscosity of the adhesive was measured in triplicates and reported in centipoise (cp).

Gelation Time

The gelation time was measured by adding about 1g of the resin in a glass test tube and immersed it in boiling water. The time was measured instantly using a stopwatch. The gelation time was recorded from the time the test tube was submerged in the boiling water to the time that the resin held to the rod. The resin was stirred in the tube and by raising and lowering the glass rod until a gel forms around the rod. This was done in triplicate to determine the average gel time for each sample.

Free Formaldehyde Content

To determine the free formaldehyde content (%CH_2O), a hydroxylamine hydrochloride method was used according to the European Standard DIN EN ISO 9397. Five grams of sample was dissolved in 100ml distilled water and using 0.1N HCl, the pH of the solution was titrated to pH 4.0 while stirred on a stir plate at 250 rpm. When the solution was at a stable pH of around 4.0, 20 ml of 10% (w/v) hydroxylamine hydrochloride was added to the solution. The reaction between hydroxylamine hydrochloride with formaldehyde produced formaldoxime and hydrochloric acid:[10]

$$HCHO + NH_2OH \cdot HCl \longrightarrow H_2O + CH_2NOH + HCl.$$

After 5 minutes of mixing, to ensure the reaction was complete, the solution was then titrated again to a pH of 4.0 using 0.1N sodium hydroxide. The amount of HCl formed was used to determine the amount of formaldehyde reacted with hydroxylamine hydrochloride. Free formaldehyde content was calculated using equation 5.

$$\%\,CH2O = \frac{(Vml\ (NaOH) \times N(NaOH) \times 3.003))}{(\ weight\ of\ resin\ sample\ (g)} \times 100\% \qquad \textit{[Equation 5]}$$

3.2.4 Resin and Adhesive Performance

Water Resistance of the Resin

The formulated resin's water-resistance was measured using an industry-recommended technique to determine the quality of resin bond strength quickly. Samples passed the test if the cured mixture of sawdust and resin samples remained intact and did not dissolve while submerged in the water for a specific period of time. Approximately 5 ml of resin was placed in aluminum dishes. In two dishes, 0.5g of sawdust was mixed with the resin. The third dish, with only a resin sample, was used as a control. The samples were cured in a conventional oven for 1 hour at 130°C. Afterward, the cured samples were cooled, and 0.5g of each sample was submerged in a beaker containing 100 ml of distilled water, which was kept for one week at room temperature. Formulated resin samples were evaluated periodically after every hour for 4 hours, then every 24 hours for up to a week.

Adhesion Strength of Adhesives

The dry lap shear strengths of the produced adhesives were evaluated according to ASTM D5868-01 standard test method to determine the adhesion strength of plywood samples when pressed under similar parameters as recommended by industry curing of commercial phenol resorcinol formaldehyde adhesive. Using southern yellow pine, veneer samples measuring at 25.4 mm × 101.6 mm × 5.6 mm (1 in × 4 in × 0.22 in), as shown in Figure 6. About 0.10- 0.12 g of the prepared adhesive was applied on one-fourth of the veneer's surface (1 in^2). Ten replicates of each formulated adhesive were tested. Using a PHI heated press, two veneers were pressed at 175°C under 1250 kPa (180 psi) for 4 min according to industry recommendation. Veneer samples were cooled down to room temperature in a desiccator for 24 hrs before testing.

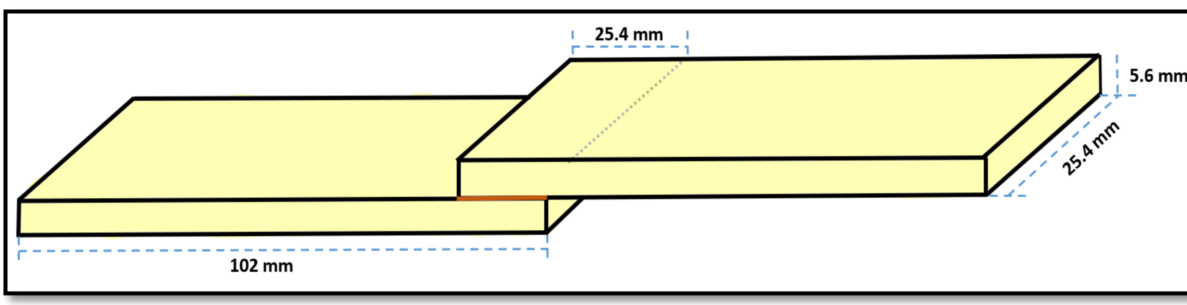

Figure 6. Image of veneer specimens for lap shear strength testing.

The adhesion strength was determined using an Instron 5565 universal testing machine. To measure the adhesion strength (maximum shear strength in PSI was recorded) of developed biobased adhesives. Specimens were loaded with a minimum of 1 inch of the veneer held in the test grip at each end. The samples were analyzed at a loading rate of 0.5 in/min, as seen in Figure

7. Results were recorded as maximum shear stress, calculated by dividing the maximum force by shear area in MPa.

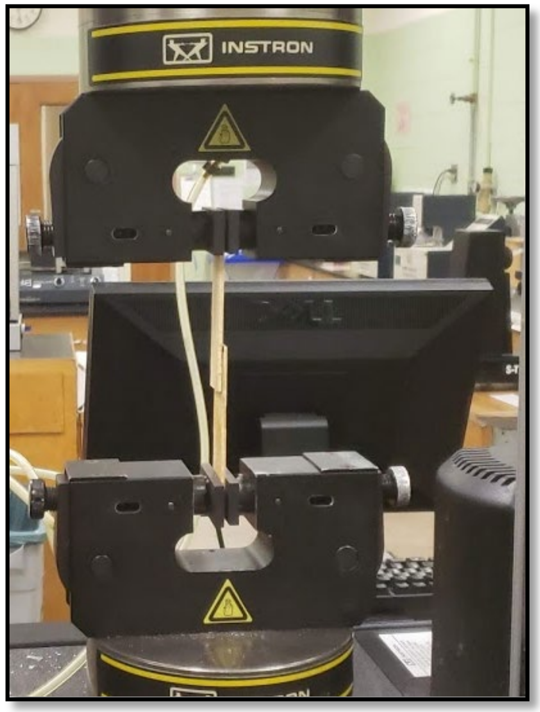

Figure 7. Universal Instron testing of pressed veneer specimen

Wet Lap Shear Strength

Wet lap shear strength of samples was evaluated according to ASTM D-3434 test method. Veneer samples were submerged in boiling water for 4 hours and then placed in an oven at 65°C for 20 hours. Samples were then immersed in boiling water again for another 4 hours. These samples were dried using a paper towel to remove excess water and tested right away using the same procedure performed for the dry lap shear strength.

Image Analysis (Percent Failure)

Using the procedure reported by Kalami et al.[10], the percentage of wood failure for tested lap shear samples was determined quantitatively using ImageJ software for image analysis. This analysis was conducted to determine what percentage of the veneer samples failed due to adhesive failure or wood failure. These samples were photographed, and the image was adjusted in Photoshop by first cropping the area to be analyzed using the cropping tool. Images were further cropped to specific dimensions of 7.5 ×7.5 inches using the “canvas size” in the “image” tab seen in Figure 8.

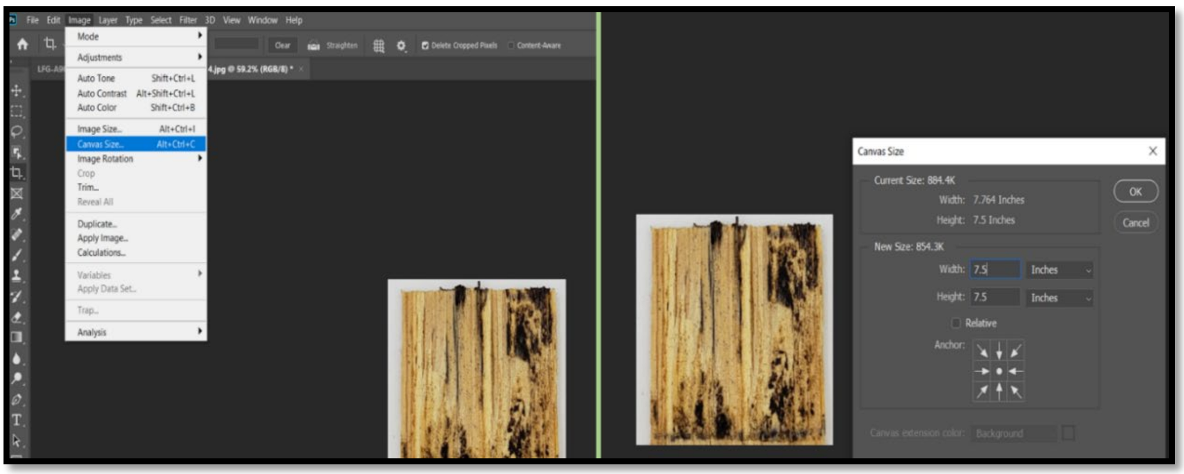

Figure 8. Wood specimen adjusted in Photoshop. 7.5 × 7.5 inches of veneer specimen was cropped for analysis.

The contrast and color were adjusted by first selecting “auto contrast” and “auto color” in the “image” tab seen in the image on the left in Figure 9. Using the “adjustment” tab under the “image” function shown in the middle image in Figure 9., the brightness and contrast were set to 100. The images were then saved as a tiff file for ImageJ analysis.

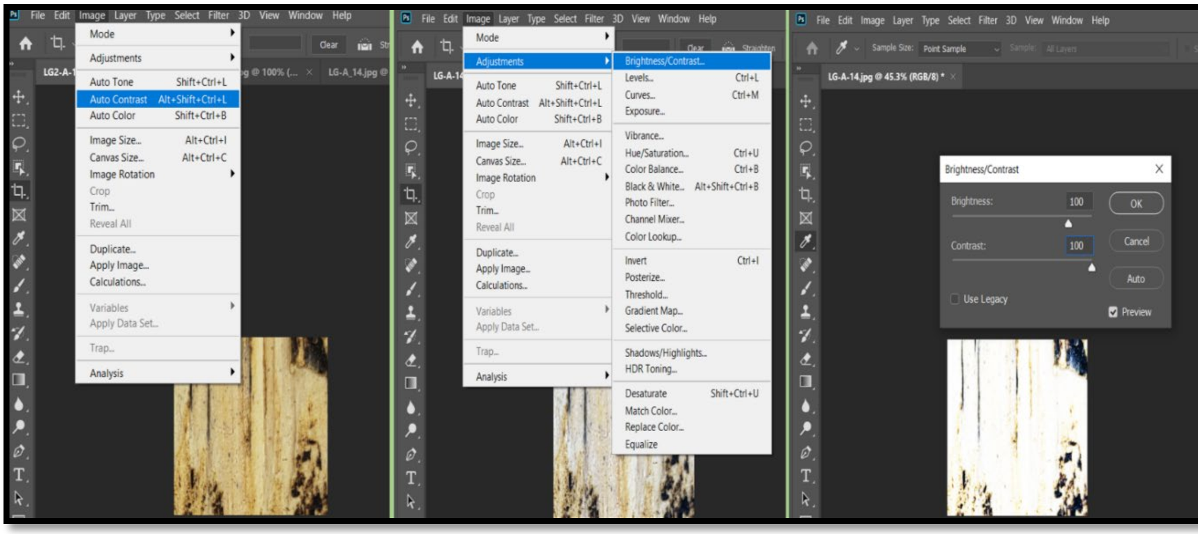

Figure 9. Wood Specimen adjusted in Photoshop. Image (left) were adjusted for auto contrast and auto color and then adjusted for brightness and contrast (100%) (middle and right)

In the ImageJ software, adjusted images were made binary by selecting "make binary" in the "process" tab, as seen in Figure 10. The next step was to select the desired information in the results, which were area fraction, standard deviation, and area in the "set measurements" option in the "analyze" tab shown in Figure 11.

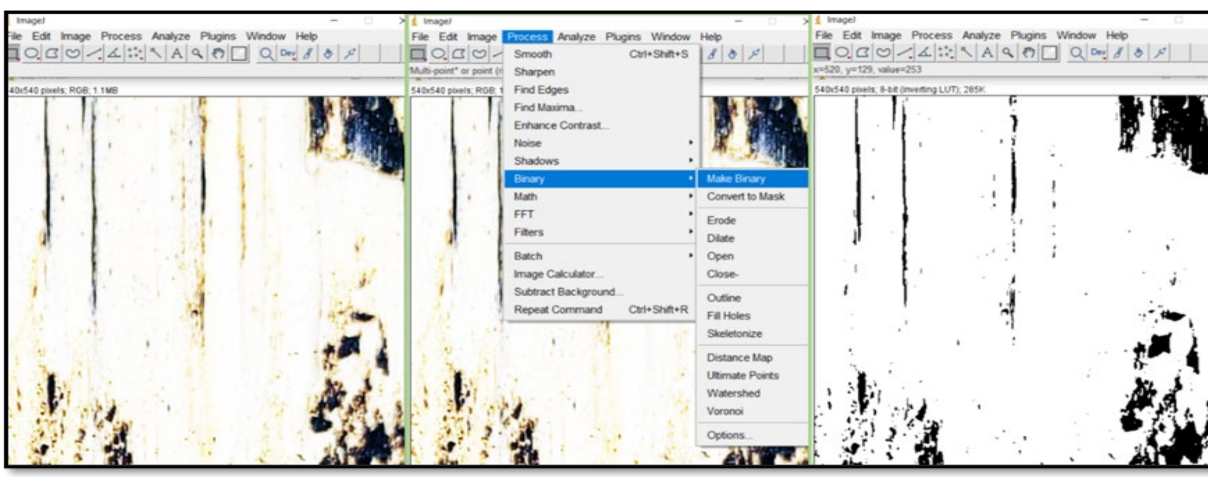

Figure 10. ImageJ software analysis of veneer for wood failure. The tiff file of the image was opened in ImageJ software (left), and using the software (middle) image was made binary for analysis. (right).

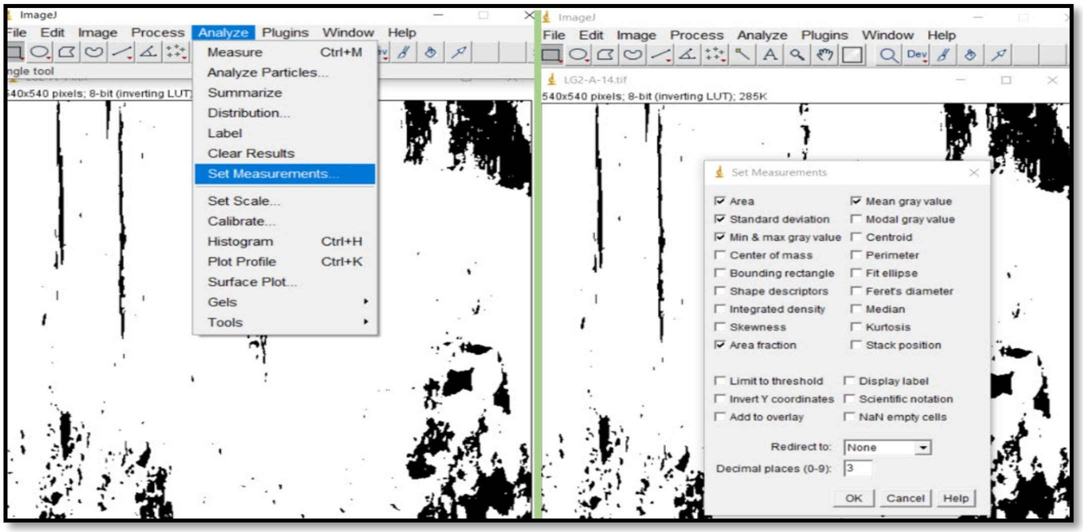

Figure 11. ImageJ software analysis of veneer for wood failure. Set measurements (left) are chosen for specific results needed to determine the wood failure of wood samples. (right)

After setting the desired measurements, the image was then analyzed using the "measure" option in the "analyze" tab displayed in Figure 12. The resulting area fraction value was the total area shaded black, which corresponded to resin failure. The wood failure, which was shaded white, was determined by subtracting that value from 100%, as seen in the right image in Figure 12. This wood failure analysis was performed on each wood specimen for each adhesive formulation and averaged.

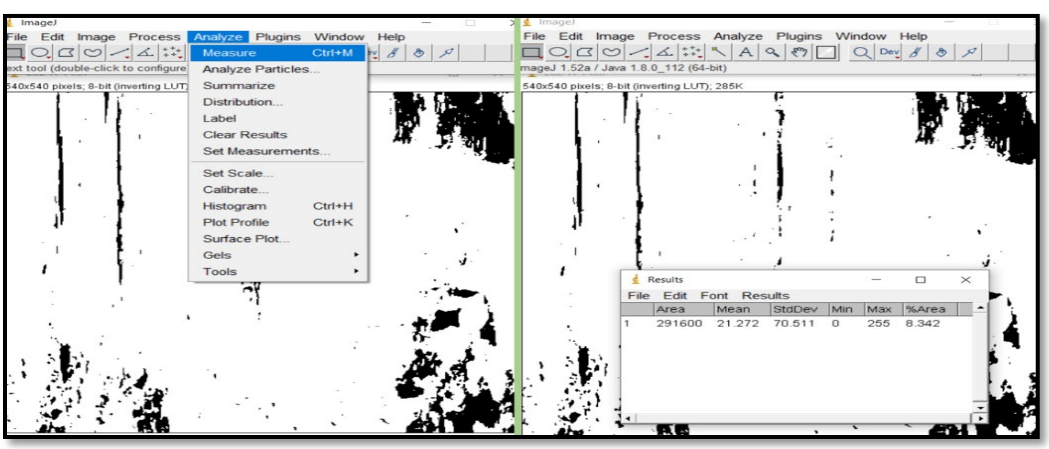

Figure 12. ImageJ Software Analysis of Wood Failure. Image Is Analyzed (Left) And Value Displayed Under % Area Represents Resin Failure (Right).

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Lignin Characterization

Ash and Moisture Content

The ash content of the corn stover lignin sample was at 0.7% (Table 5). Although sulfuric acid was used during pretreatment of biomass and used to isolate pure lignin from lignin cake, the proper washing with distilled water helped ensure the removal of most residual ash. Moisture content (MC%) of the lignin was measured using two different parameters (times and temperatures). The moisture content of lignin was 3±0.04 % when measured at 100°C after 1 hour, while it was 2.3±0.2 % when measured at 80°C after 3 hours. As expected, drying lignin at 80°C for 3 hours had a lower moisture content than higher temperatures. This could be sue to potential lignin degradation at higher temperature and loss of VOC.[47,103]

Table 5. Ash Content (%), Sulfur Content (%), Moisture Content (%), Molecular weight and PDI of Lignin Sample

Sample	%N	%S	% MC: 100°C, 1h	% MC: 80°C, 3h	% Ash Content	Mn (g/mol)	Mw (g/mol)	PDI
Lignin	2.19	0.4	3.0 (0.04)	2.3 (0.2)	0.7 (0.07)	1550	6400	4.12

Elemental Analysis

Based on the elemental analysis performed on the lignin sample, 0.4% of sulfur was detected, which can also correspond with the low ash content (0.7%) of this lignin. Sulfur content in lignin is dependent on the extraction method used to isolate lignin from biomass. The nitrogen content of the lignin in this study was 2.19%, which was similar to an enzymatic hydrolysis corn stover lignin reported by da Costa Sousa et al.[104] Lignin isolated from annual crops contain higher nitrogen content probably due to the use of nitrogen-based fertilizers, or enzymes used in the bioethanol process. [104,105]

Molar Mass Distribution Analysis of Lignin Sample

The average molecular weight M_w (6400 g/mol), the average molecular number M_n (1550 g/mol), and the polydispersity index (PDI=4.2) of corn stover lignin were measured using GPC and are reported in Table 5. The high PDI of lignin might negatively impact the homogeneity of the formulated adhesives.

Hydroxyl Functional Groups of Lignin (^{31}PNMR Data)

Using ^{31} phosphorous Nuclear magnetic resonance spectroscopy (^{31}P NMR), the lignin sample's hydroxyl content was determined, which can include aliphatic, phenolic, and carboxylic acid groups. For phenol-formaldehyde formulation, lignin's total phenolic hydroxyl content is needed to calculate the formulation's required formaldehyde amount. The total phenolic hydroxyl content of the corn stover lignin used for this research, as shown in the ^{31}P NMR spectra (Figure 13), was 2.37 mmol/g.

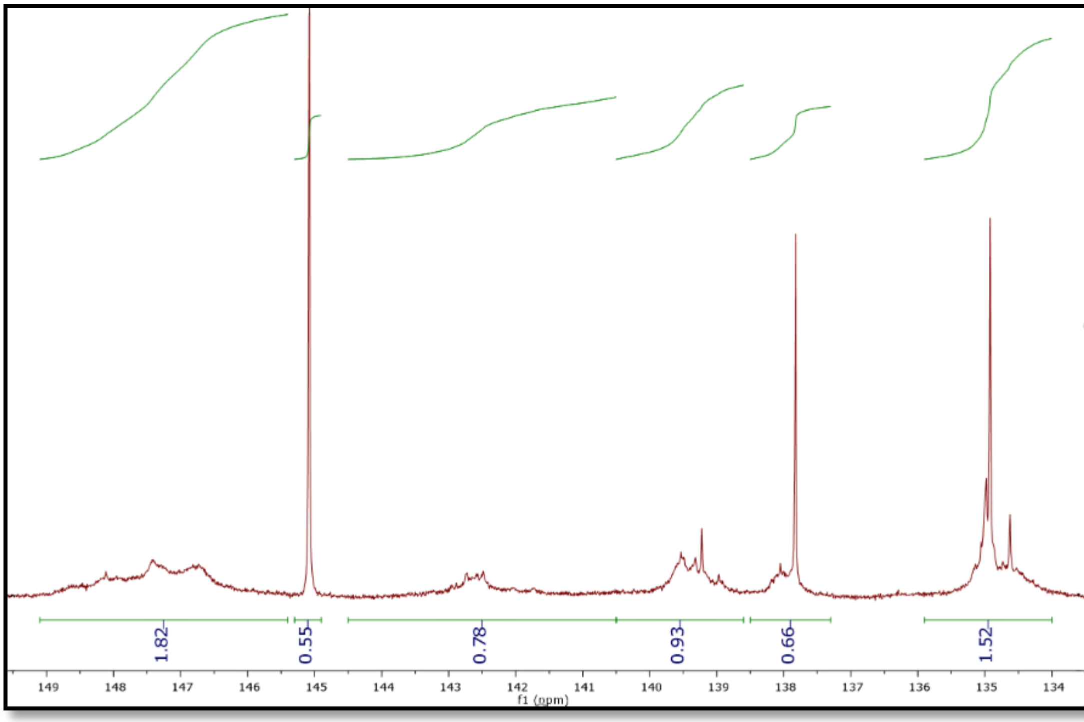

Figure 13. ^{31}PNMR Spectra of Lignin Sample

This value was used to measure the amount lignin needed to react with glyoxal and formaldehyde using a molar ratio of 1:2 lignin to formaldehyde or glyoxal. As aforementioned, based on the source of the lignin and the extraction process, the reactivity of lignin with formaldehyde may differ. Corn stover lignin extracted via enzymatic hydrolysis had been shown to have a higher *p*-hydroxyphenyl content, H (0.66 mmol/g), and guaiacyl content, G (0.93 mmol/g) compared to nine other lignins.[10]

Table 6. ^{31}P-NMR analysis results for corn stover lignin.

Lignin ID	Aliphatic OH (mmol/g)	Syringyl (mmol/g)	Guaiacyl (mmol/g)	*p*-hydroxy-phenyl (mmol/g)	Carboxylic Acid (mmol/g)
EH-CS	1.82	0.78	0.93	0.66	1.52

4.2 Resin and Adhesive Properties and Performance

pH and Alkalinity

For this research, the goal was to produce a resole phenolic adhesive, formulated under basic conditions typically in the range of 9 to 13.[20] The desired pH for lignin-based resins should be between the range of 9 to 11 to avoid lignin precipitation.[106] As shown in Table 7, the pH of the PF and LF resins were 10.2 and 10.66, respectively.

Table 7. Physical and Chemical Properties of Formulated Resins

Sample ID	pH	Alkalinity (%)	Solid Content (%)	Gelation Time (min)	Free Formaldehyde Content (%)	Water Resistance
LF	10.66 ± 0.03	2.42 ± 0.04	19.98 ± 0.08	2.6 ± 0.02	0.79 ± 0.02	+ 24 hours
LFG-10	10.16 ± 0.01	2.44 ± 0.03	21.00 ± 0.14	3.04 ± 0.5	0.55 ± 0.01	Dissolved in <24 hrs
LFG-20	9.71 ± 0.005	2.32 ± 0.03	21.20 ± 0.50	3.14 ± 0.7	0.91 ± 0.02	Dissolved in <24 hrs
LFG-30	9.14 ± 0.02	2.05 ± 0.01	20.85 ± 0.28	3.93 ± 0.4	1.07 ± 0.001	Dissolved in <24 hrs
LFG-40	8.16 ± 0.01	1.80 ± 0.03	20.79 ± 0.15	2.13 ± 0.9	1.55 ± 0.06	Dissolved in <24 hrs
LFG-50	6.88 ± 0.02	1.71 ± 0.03	21.40 ± 0.03	Gelled	1.65 ± 0.02	Dissolved in <24 hrs
LFG-60	6.35 ± 0.02	1.68 ± 0.03	21.03 ± 0.07	Gelled	1.76 ± 0.05	+ 24 hrs
LFG-70	6.12 ± 0.01	1.79 ± 0.05	21.44 ± 0.04	Gelled	2.06 ± 0.01	1 week
LFG-80	5.82 ± 0.01	1.72 ± 0.05	22.12 ± 0.08	Gelled	1.79 ±0.01	1 week
LFG-90	5.62 ± 0.01	1.72 ± 0.05	22.64 ± 0.27	Gelled	2.02 ± 0.07	1 week
LG	5.52 ± 0.005	1.59 ± 0.01	22.09 ± 0.06	Gelled	1.61 ± 0.04	1 week
PF[10]	10.2	2.6 ± 0.1	30 ± 0.5	18.7 ± 0.3	0.3 ± 0.03	1 week

Still, as the formaldehyde substitution increased, the pH gradually decreases to a recorded pH of 5.52 for the LG resin. This trend in decreasing pH may have occurred due to the Cannizzaro reaction.[107] Under alkaline conditions, typically with sodium hydroxide, two aldehydes molecules without alpha hydrogens will react with itself to produce a carboxylic acid and an alcohol, oxidation, and reduction products, respectively, as seen below.[107] However, the pH of the formulated adhesives, as seen in Figure 14, were all within the standard range.[106] Although our formulated resins resulted in lower pH, and the adhesive (known by the industry as glue mix) had pH higher than 9.[20] The formulated LF adhesive had a pH of 13.24, which was similar to the pH of the formulated PF resin in the lab of 13.2 as reported by Kalami et al.[10] However, it should be noted that as the formaldehyde substitution increased, the pH of the formulated adhesive similar to resin decreased. Nonetheless, the LG adhesive had a pH of 12.54, performing well above the expected range (10 to 13) for resole phenolic adhesives. The alkalinity of the adhesives ranged between 3.85% to 4.58%, with a slight decrease as the formaldehyde substitution increased.

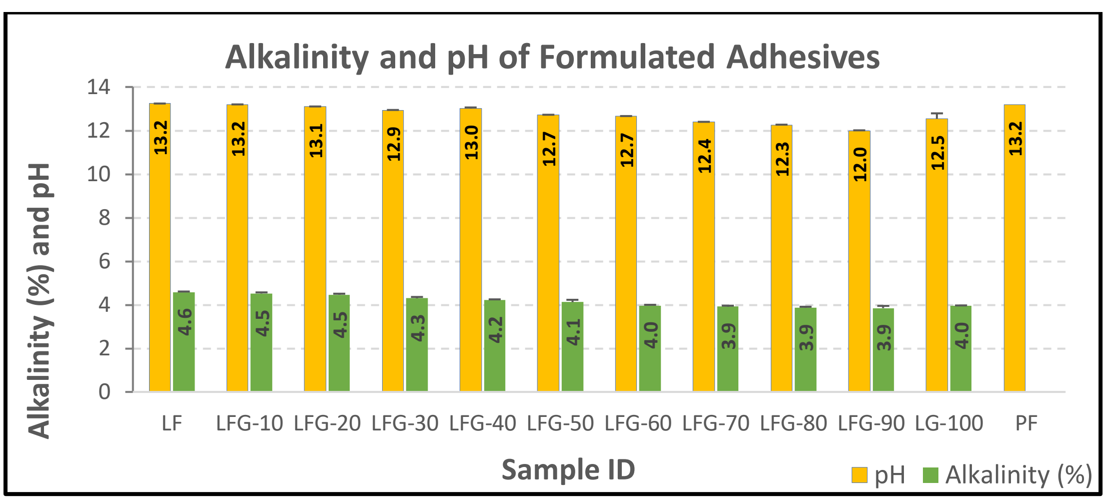

Figure 14. Alkalinity and pH of formulated adhesives.

Solid Content

The solid content (SC) of the resin had comparable results to a phenol-formaldehyde resin, as seen in Table 7. The solid content of the formulated adhesives can impact mechanical interlocking and can also affect the adhesive spread rate. As shown in Table 7, the formulated resins showed a slight increase in solid content as the glyoxal incorporation increased from 19.98% in the LF to 22.1% in the LG. However, these values are significantly lower than the solid content PF resin (30%). Although the percent solid content of LG adhesive increased to 30.2%, after the addition of extender and filler, it is still significantly lower than the solid content of PF adhesive (42%) and below the expected range of phenolic adhesives of 40 to 50%. [20] Nonetheless, if needed, the solid content can easily be adjusted by adding more fillers in the adhesive formulation.

Viscosity and Gelation Time

The viscosity of formulated adhesives was lower than the PF adhesive. The viscosity for the LF adhesive was 672 cP (Table 8), while the viscosity of PF adhesive was 2179 cP as reported by Kalami et al.[10] However, it is recommended that resole phenolic adhesive have a viscosity ranging between 400 and 600 cP for easy application.[108,109]

The gelation times of the resins are reported in Table 7. After substituting 40% of formaldehyde with glyoxal, resin gelled right away. In the future, a rheometer can be used to determine the viscosity and gelation time of the formulated resins and adhesives more accurately. Gelation time and viscosity are two critical parameters in determining the properties and performance of these adhesives. As gel time is the point where the resin is no longer a viscous liquid, a shorter gelation time can affect the application time, leaving less time for application and negatively affecting the adhesives' mobility and ability to penetrate the wood. Additionally, a longer gelation time will require longer curing time, needing more energy and time during processing. Viscosity is also critical during processing affecting the application and penetration of the adhesive in the wood, which, along with the gelation time, can affect the mechanical properties of the adhesive. Both are essential for the application process; therefore, they need more in-depth examination.

Free Formaldehyde Content

The free formaldehyde content of the resole phenolic adhesives relates to the unreacted formaldehyde that did not participate in the reaction with phenol or lignin in this case. As seen in Table 7, the free formaldehyde is much higher than that of the PF resin, which was 0.3%. This may be the result of the lower reactivity of both glyoxal and lignin. However, there is an unusual trend in the data which requires repeating this test. Nonetheless, it is safe to say that the free formaldehyde content increases as the formaldehyde substitution increases.

Regarding the developed adhesives, the free formaldehyde content decreased significantly lower than that of the resin shown in Table 8. The free formaldehyde content reduced from 1.61% in the LG resins to 0.17% in the adhesive, which is slightly above the requirement (<0.1%) for phenolic resins.[54] This decrease may be a result of further polymerization when formulating the adhesive. It must be noted that this test requires further investigation to determine the cause.

Water Resistance of the Resin

The water-resistance testing on the formulated resin was a simple qualitative industry performance test to determine its resistance in room temperature water. Based on the results shown in Table 7 above, the adhesive performance increased as the amount of glyoxal was increased. PF, LF, and LFG-60 to LG did not dissolve in the water and remained intact for up to a week. LFG-10 to LFG-50 dissolved in less than 24hrs after being immersed in water.

Table 8. Physical and chemical properties of formulated adhesives

Sample ID	pH	Alkalinity (%)	Solid Content (%)	Free Formaldehyde Content (%)	Viscosity (cPs)
LF	13.2 ± 0.01	4.58 ± 0.03	29.9 ± 0.4	0.17 ± 0.01	672 ± 10
LFG-10	13.2 ± 0.02	4.52 ± 0.05	32 ± 0.4	0.17 ± 0.01	673 ± 6
LFG-20	13.1 ± 0.005	4.46 ± 0.05	30.8 ± 0.2	0.17 ± 0.01	688 ± 10
LFG-30	12.9 ± 0.005	4.30 ± 0.06	30.2 ± 0.4	0.18 ± 0.01	618 ± 7
LFG-40	13.0 ± 0.05	4.22 ± 0.03	29.6 ± 0.1	---	665 ± 8
LFG-50	12.7 ± 0.01	4.12 ± 0.11	30.8 ± 0.2	0.47 ± 0.02	746 ± 1
LFG-60	12.7 ± 0.01	3.97 ± 0.03	31.6 ± 0.2	0.30 ± 0.01	695 ± 4
LFG-70	12.4 ± 0.01	3.92 ± 0.04	31.1 ± 0.1	0.25 ± 0.01	437 ± 2
LFG-80	12.3 ± 0.01	3.86 ± 0.05	30.7 ± 0.1	0.26 ± 0.04	---
LFG-90	12 ± 0.02	3.85 ± 0.10	32.3 ± 0.7	0.16 ± 0.01	157 ± 4
LG	12.5 ± 0.25	3.95 ± 0.02	30.2 ± 0.5	0.17 ± 0.01	131 ± 3
PF[10]	13.1	---	42 ± 0.6	---	2180

Lignin Glyoxal (LG) Optimized

From 50% formaldehyde substitution, there was a drop in pH resulting in an acidic resin. Due to this increased acidity of the resin, lignin began to precipitate, as shown in Figure 15.

Gelation of the resin occurs at a point during the chemical reaction when the viscous liquid resin converts irreversibly to an elastic gel[110] and the molecular weight reaches a maximum, which is when the monomers are all now chemically bonded, forming one chain[111] causing the viscosity of the resin to reach infinity.[110,111] It is vital to prevent the gelation of the resin during processing.

This process should take place during heating after being applied to the veneer specimen. The onset of gelation reduced the viability of the adhesive during processing, which had adverse effects on the resin's mechanical properties, including adhesion and the processability of the resin.[111] To solve this, the amount of NaOH solution was increased to help to reduce the viscosity, thereby preventing gelation of the resin. The NaOH addition was also added gradually at a slower rate. This change, along with the addition of lignin to the NaOH slowly at a slower pace, increased the time to dissolve the lignin in the NaOH. Also, changing the mixing speed of the stir plate from 150 to 250 rpm helped ensure that the lignin was dissolved entirely, which reduced the initial viscosity of the lignin solution. The time and temperature of the system were kept the same as LF formulation.

Figure 15. Image of precipitated lignin in LG resin during formulation

Dry Lap Shear and Wood Failure Results

The adhesion strength of developed adhesives was analyzed using a lap shear test. The analysis was performed on the plywood samples glued using the formulated lignin-based adhesives from 0 to 100% substitution of formaldehyde with glyoxal shown in Figure 16. Wood failure analysis results on the wood specimen after the lap shear test are presented in Figure 17. Dry lap shear strength of the lignin formaldehyde adhesive was 3.49 MPa, and wood failure was around 71%. In the LFG-10 adhesive, there was a sharp increase in shear strength of 4.51 MPa but a decline in the wood failure 62.7%. As the amount of formaldehyde substitution continued to increase, the adhesive shear strength decreased but was still within the industry standards for plywood specimens. Before optimization, the lignin glyoxal (LG) adhesive had a lap shear strength of 2.83 MPa, the lowest shear strength, and a wood failure of 53%.

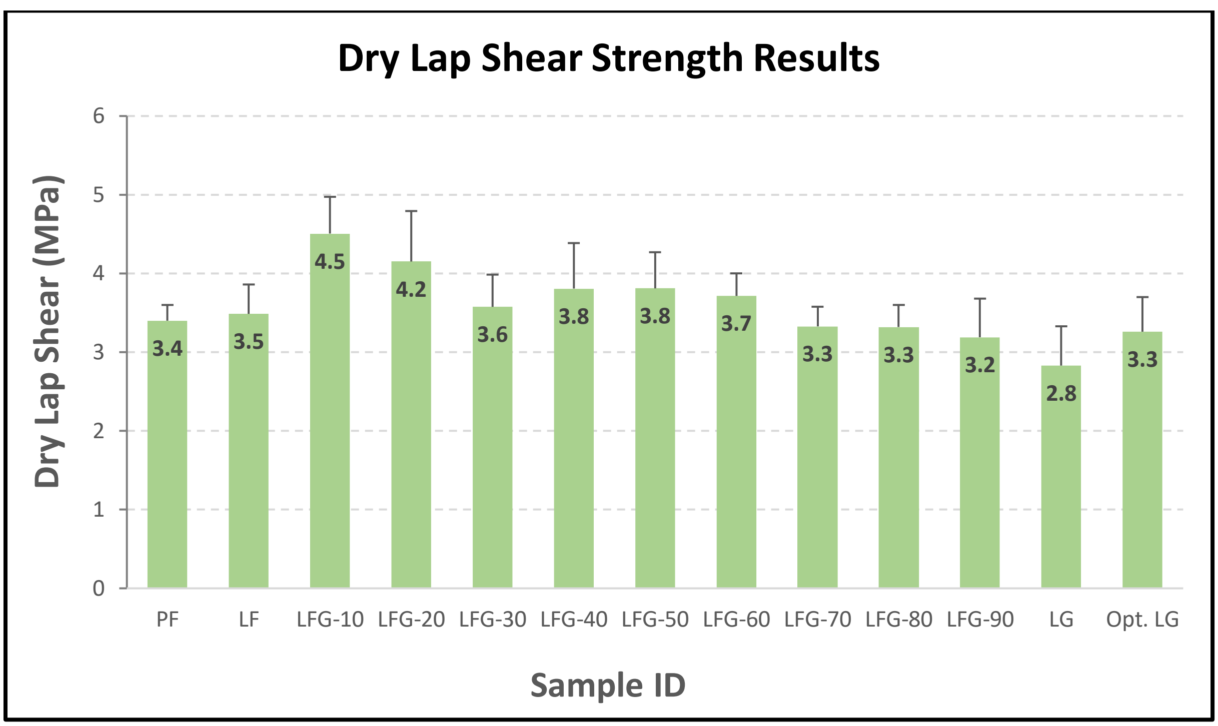

Figure 16. Dry lap shear strength results for formulated adhesives

After optimization, the LG adhesive had a lap shear strength of 3.26 MPa and a wood failure of 81%; these values are relatively close to the adhesion strength of PF adhesive formulated by Kalami et al.[10] 3.4 MPa and 88% wood failure. This improvement was due to the adhesive's increased viscosity, allowing lower penetration and possibly reducing glue line starvation, which resulted in improved adhesion strength.

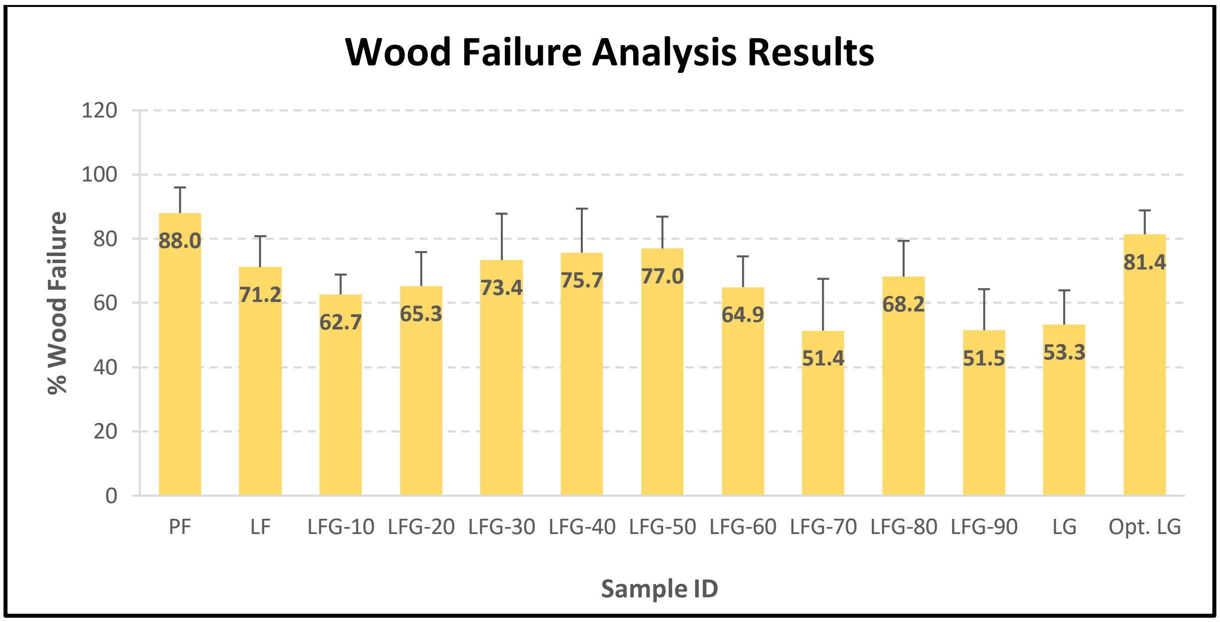

Figure 17. Percent wood failure, Image analysis results

Wet Lap Shear Test for PF, LF, and LG.

Wet lap shear testing was conducted on the PF, LF, and LG samples. PF and LF adhesives performed as expected, which is shown in Table 9. However, the plywood veneer samples prepared with the LG adhesive performed poorly. After placing samples in boiling water, the veneer samples glued with LG adhesives separated in less than 30 minutes. Despite the high dry lap shear (3.26 MPa) reported for the optimized LG adhesive, the developed adhesive failed the wet lap shear strength. This could be due to the lower reactivity of glyoxal and lignin, which requires further investigation in the future. It must be noted that the glued veneers remained intact when the samples were immersed in the cold (room temperature) water. We believe the increased temperature (100°C) might have played a significant role in causing the LG adhesive to fail.

Table 9. Wet lap shear strength and wood failure result for LF, PF, and LG adhesives.

Sample ID	Adhesive amount (g)	Wet Lap Shear Stress (MPa)	Wood Failure (%)
Lignin Formaldehyde	0.12	2.03 ± 0.3	63 ± 7
Phenol Formaldehyde	0.12	3.0 ± 0.7	87 ± 5
Lignin Glyoxal	0.12	Failed	----

CHAPTER 5: CONCLUSIONS AND FUTURE RECOMMENDATION

5.1 Conclusions

1. For this study, an unmodified corn stover lignin extracted via dilute acid pretreatment-enzymatic hydrolysis was used. 100% of phenol was successfully substituted with an unmodified corn stover biorefinery lignin. Replacing 100% of phenol with unmodified lignin reduced formaldehyde consumption by 58%. The formulated phenol-formaldehyde adhesive contained about 17g of formaldehyde, while the same amount of formulated lignin formaldehyde (LF) resin only contained 7g of formaldehyde.

2. Additionally, 100% of formaldehyde was replaced with non-toxic, biobased glyoxal to develop lignin glyoxal (LG) adhesive. This adhesive showed similar properties compared to that of commercial resole phenolic adhesive, while some properties like viscosity, gel time, and free formaldehyde content call for further optimization and analysis. The dry lap shear strength of the LG adhesive was 3.26 MPa, which performed similarly to the PF adhesive at 3.4 MPa.

3. Although the dry adhesion strength of the formulated LG adhesive was comparable to the PF adhesive, the developed LG adhesive failed the wet shear strength tests when submerged in hot water (in less than 30 minutes) during the first boiling stage of the wet shear strength test. Further investigation is required to better understand the reaction mechanism between lignin and glyoxal, which will help to improve the LG wet adhesive performance.

5.2 Future Recommendation

This research resulted in a biobased adhesive that has comparable performance to the commercially available phenol-formaldehyde adhesive with a dry lap shear strength of 3.26 MPa. This is an excellent step in the right direction in eliminating the use of petroleum-based phenol and formaldehyde using biobased lignin and glyoxal. More analysis and optimization are needed to better understand the potential chemical reaction between lignin and glyoxal and to increase the performance of the developed LG adhesive.

1. An in-depth analysis of the cure kinetics is also important to better understand the characteristics of the adhesive. Differential Scanning Calorimetry (DSC) can be used to better understand the curing behavior and reaction kinetic of developed LG adhesives. Also, nuclear magnetic resonance (NMR) spectroscopy and Fourier-transform infrared (FT-IR) spectroscopy can be used to determine the extent of cure.[112]
2. A more accurate rheology analysis using a Rheometer will help to accurately measure the rheology and gelation time of the resins and adhesives. This rheology analysis will aid in optimizing the amount of catalyst and fillers required in the formulation of both the resin and the adhesives. Using a Rheometer will reduce any margin of error, which is expected when using the gelation time procedure applied for this study.
3. The formulated resin and adhesive molecular weights can be analyzed by gel permeation chromatography (GPC) to understand the adhesive’s ability to penetrate into the wood’s cell wall. Since lignin has a much larger molecular weight than phenol, it can impact the formulated biobased adhesive penetration.[5] More optimization is needed to develop an

LG adhesive that can perform according to the industrial standards for the wet lap shear strength. This will require more elaborate analytical testing like DSC and TGA.

4. With further investigation, this 100% biobased resole adhesive can be a suitable replacement for phenol-formaldehyde adhesive for both interior and exterior applications. It will reduce our dependency on toxic, petroleum-based chemicals and adhesives.

REFERENCES

REFERENCES

1. Dunky, M. Adhesives in the Wood Industry. in *Handbook of Adhesive Technology, Revised and Expanded* (ed. Pizzi, A., Mittal, K. L.) 872–931 (CRC Press, 2003). doi:10.1080/10426919008953291

2. Pilato, L. Resin Chemistry. in *Phenolic Resins: A Century of Progress* (ed. Pilato, L.) 41–88 (Springer Berlin Heidelberg, 2010). doi:10.1007/978-3-642-04714-5

3. Pizzi, A. & Mittal, K. L. *Wood Adhesives*. *Wood Adhesives* (2011). doi:10.1201/9780080928692-10

4. Foyer, G., Chanfi, B.-H., Boutevin, B., Caillol, S. & David, G. New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors. *Eur. Polym. J.* **74**, 296–309 (2016).

5. Jin, Y., Cheng, X. & Zheng, Z. Preparation and characterization of phenol–formaldehyde adhesives modified with enzymatic hydrolysis lignin. *Bioresour. Technol.* **101**, 2046–2048 (2010).

6. Mansouri, E., Mansouri, N.-E. El, Yuan, Q. & Huang, F. Preparation and Characterization of Phenol Formaldehyde resins modified with Alkaline Rice Straw Lignin. *BioResources* **13**, 8061–8075 (2018).

7. Younesi-Kordkheili, H. Ionic liquid modified lignin-phenol-glyoxal resin: a green alternative resin for production of particleboards. *J. Adhes.* **95**, 1–13 (2018).

8. Ferdosian, F., Pan, Z., Gao, G. & Zhao, B. Bio-based adhesives and evaluation for wood composites application. *Polymers (Basel).* **9**, (2017).

9. Qureshi, S. P. ASM Handbook: Phenolic Resins. in *ASM Handbook* (eds. Miracle, D. B. & Donaldson, S. L.) **21**, 120–125 (ASM International, 2010).

10. Kalami, S., Chen, N., Borazjani, H. & Nejad, M. Comparative analysis of different lignins as phenol replacement in phenolic adhesive formulations. *Ind. Crops Prod.* **125**, 520–528 (2018).

11. Kiskan, B. & Yagci, Y. The Journey of Phenolics from the First Spark to Advanced Materials. *Isr. J. Chem.* **60**, 20–32 (2020).

12. Pizzl, A. *Wood : Adhesives Chemistry and Technology*. *CRC* (Routledge, 2018). doi:10.1016/B978-0-444-51140-9.50023-8

13. Fink, J. K. Phenol/Formaldehyde Resins. in *Reactive Polymers Fundamentals and Applications* (Elsevier Inc., 2018). doi:10.1016/c2017-0-01641-5

14. Brydson, J. A. Phenolic Resins. in *Plastics Materials* 1–18 (Butterworth-Heinemann, 1999). doi:10.1016/b978-0-323-35824-8.00001-3

15. Conner, A. Wood: Adhesives. Encyclopedia of Materials: Science and Technology. *Adhes. wood* 17 (2001).

16. Fink, J. K. Phenol/Formaldehyde Resins. in *Reactive Polymers Fundamentals and Applications* (ed. Fink, J. K.) 155–177 (Williams Andrew Publishing, 2013). doi:10.1016/b978-1-4557-3149-7.00004-8

17. Frihart, C. R. Wood Adhesion and Adhesives. *Handb. Wood Chem. Wood Compos.* 216–265 (2005). doi:doi:10.1201/b12487-13

18. Shmulsky, R. & Jones, P. D. *Forest Products and Wood Science An Introduction: Sixth Edition*. *Forest Products and Wood Science An Introduction: Sixth Edition* (Wiley-Blackwell, 2011). doi:10.1002/9780470960035

19. United States Environmental Protection Agency, (USEPA). AP 42, Fifth Edition, Volume I Chapter 10: Wood Products Industry. *Technol. Transf. Netw.* 1–36 (2002).

20. Gardziella, A., Pilato, L. A. & Knop, A. *Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology (Google eBook)*. (2000).

21. Milner, H. R. & Woodard, A. C. *Sustainability of engineered wood products*. *Sustainability of Construction Materials* (Elsevier Ltd., 2016). doi:10.1016/b978-0-08-100370-1.00008-1

22. Dumitrascu, A.-E., Lunguleasa, A., Salca, E.-A. & Ciobanu, V. D. Evaluation of Selected Properties of Oriented Strand Boards Made from Fast Growing Wood species. *BioResources* **15**, 199–210 (2020).

23. Mantanis, G. I., Athanassiadou, E. T., Barbu, M. C. & Wijnendaele, K. Adhesive systems used in the European particleboard, MDF and OSB industries*. *Wood Mater. Sci. Eng.* **13**, 104–116 (2018).

24. Sutrisno, Widyorini, R., Syamsudin, T. S., Alamsyah, E. M. & Purwasasmita, B. S. Bonding strength of plywood bonded using phenol formaldehyde mixed with wood bark powder nanofiller. *J. Indian Acad. Wood Sci.* **17**, 21–33 (2020).

25. Roffael, E. Significance of wood extractives for wood bonding. *Appl. Microbiol. Biotechnol.* **100**, 1589–1596 (2016).

26. Vick, C. B. Adhesive Bonding of Wood Materials. *Wood Handb. - Wood as an Eng. Mater.* 9-1-9–24 (1999).

27. Bockel, S. *et al.* The role of wood extractives in structural hardwood bonding and their influence on different adhesive systems. *Int. J. Adhes. Adhes.* **91**, 43–53 (2019).

28. Ulker, O. Wood adhesive and Bonding Theory. *Intech* **i**, 13 (2016).

29. Frihart, C. R. Adhesive bonding and performance testing of bonded wood products. *J. ASTM Int.* **2**, 455–466 (2005).

30. St-Pierre, B., Beauregard, R., Mohammad, M. & Bustos, C. Effect of moisture content and temperature on tension strength of fingerjointed black spruce lumber. *For. Prod. J.* **55**, 9–

16 (2005).

31. Rindler, A., Hansmann, C. & Konnerth, J. The effect of moisture on the mechanical response of wood, adhesive and their interphase by means of nanoindentation. *Wood Sci. Technol.* **53**, 729–746 (2019).

32. River, B. Fracture of Adhesive-Bonded Wood Joints. in *Handbook of Adhesive Technology, Revised and Expanded* (eds. Pizzi, A. & Mittal, K. L.) (2003). doi:10.1201/9780203912225.ch15

33. Kariz, M. & Sernek, M. Determination of the percentage of wood failure by 3D scanning of the adhesive bondline. 551–553 (2014). doi:https://doi.org/10.3390/polym12102237

34. Bhisey, R. Global Formaldehyde Market is expected to reach 36.6 million tons towards the end of 2026 - Transparency Market Research. 2018–2020 (2020).

35. Hazwan Hussin, M., Aziz, A. A., Iqbal, A., Ibrahim, M. N. M. & Latif, N. H. A. Development and characterization novel bio-adhesive for wood using kenaf core (Hibiscus cannabinus) lignin and glyoxal. *Int. J. Biol. Macromol.* **122**, 713–722 (2019).

36. El Mansouri, N. E., Pizzi, A. & Salvadó, J. Lignin-based wood panel adhesives without formaldehyde. *Holz als Roh - und Werkst.* **65**, 65–70 (2007).

37. Amaral-Labat, G. A. *et al.* Environment-friendly soy flour-based resins without formaldehyde. *J. Appl. Polym. Sci.* **108**, 624–632 (2008).

38. Zhang, Y., Yuan, Z. & Xu, C. Engineering biomass into formaldehyde-free phenolic resin for composite materials. *AIChE J.* **61**, 1275–1283 (2015).

39. Alonso, M. V., Oliet, M., Pérez, J. M., Rodríguez, F. & Echeverría, J. Determination of curing kinetic parameters of lignin–phenol–formaldehyde resol resins by several dynamic differential scanning calorimetry methods. *Thermochim. Acta* **419**, 161–167 (2004).

40. Deng, S., Du, G., Li, X. & Pizzi, A. Performance and reaction mechanism of zero formaldehyde-emission urea-glyoxal (UG) resin. *J. Taiwan Inst. Chem. Eng.* **45**, 2029–2038 (2014).

41. U.S EPA. IRIS Toxicological Review of Formaldehyde (Inhalation) (External Review Draft 2010). *U.S Environ. Prot. Agency* 1–16 (2010).

42. Octavia, Z. Standards and Regulations Concerning the Formaldehyde Emissions from Wood Panels. 266–271 (2016).

43. S.1660-111TH Congress: Formaldehyde Standards for Composite Wood Products. *www.GovTrack.us* **H.R. 4173**, HR 3801 (2009).

44. Khan, M. A., Ashraf, S. M. & Malhotra, V. P. Eucalyptus bark lignin substituted phenol formaldehyde adhesives: A study on optimization of reaction parameters and characterization. *J. Appl. Polym. Sci.* **92**, 3514–3523 (2004).

45. Yang, S., Zhang, Y., Yuan, T.-Q. & Sun, R.-C. Lignin-phenol-formaldehyde resin adhesives

prepared with biorefinery technical lignins. *J. Appl. Polym. Sci.* **132**, n/a-n/a (2015).

46. Qiao, W. *et al.* Synthesis and characterization of phenol-formaldehyde resin using enzymatic hydrolysis lignin. *J. Ind. Eng. Chem.* **21**, 1417–1422 (2015).

47. Kalami, S., Arefmanesh, M., Master, E. & Nejad, M. Replacing 100% of phenol in phenolic adhesive formulations with lignin. *J. Appl. Polym. Sci.* **45124**, 2–10 (2017).

48. Lei, H., Pizzi, A. & Du, G. Environmentally friendly mixed tannin/lignin wood resins. *J. Appl. Polym. Sci.* **107**, 203–209 (2007).

49. Siddiqui, H. *et al.* Sustainable Bio-Based Phenol-Formaldehyde Resoles Using Hydrolytically Depolymerized Kraft Lignin. *Molecules* **22**, 1850 (2017).

50. Alonso, M. V., Oliet, M., Rodríguez, F., Astarloa, G. & Echeverría, J. M. Use of a methylolated softwood ammonium lignosulfonate as partial substitute of phenol in resol resins manufacture. *J. Appl. Polym. Sci.* **94**, 643–650 (2004).

51. Sarika, P. R., Nancarrow, P., Khansaheb, A. & Ibrahim, T. Bio-Based Alternatives to Phenol and Formaldehyde for the Production of Resins. 1–24 (2020).

52. Trosa, A. & Pizzi, A. A no-aldehyde emission hardener for tannin-based wood adhesives for exterior panels. *Holz als Roh - und Werkst.* **59**, 266–271 (2001).

53. Moubarik, A., Pizzi, A., Allal, A., Charrier, F. & Charrier, B. Cornstarch and tannin in phenol-formaldehyde resins for plywood production. *Ind. Crops Prod.* **30**, 188–193 (2009).

54. Gomez-Bueso, J. & Haupt, R. Wood Composite Adhesive. in *Phenolic Resins: A Century of Progress* (ed. Pilato, L.) 155–187 (Springer Berlin Heidelberg, 2010).

55. Zhou, X. & Du, G. Applications of Tannin Resin Adhesives in the Wood Industry. *Tann. - Struct. Prop. Biol. Prop. Curr. Knowl.* 1–19 (2020). doi:10.5772/intechopen.86424

56. Fradinho, D. M. *et al.* Chemical characterisation of bark and of alkaline bark extracts from maritime pine grown in Portugal. *Ind. Crops Prod.* **16**, 23–32 (2002).

57. Pizzi, A. Tannins: Major sources, properties and applications. *Monomers, Polym. Compos. from Renew. Resour.* 179–199 (2008). doi:10.1016/B978-0-08-045316-3.00008-9

58. Pizzi, A. Natural Phenolin Adhesives: Tannin. in *Handbook of Adhesive Technology, Revised and Expanded* (2003).

59. Calvo-Flores, F. G. & Dobado, J. A. Lignin as renewable raw material. *ChemSusChem* **3**, 1227–1235 (2010).

60. Gadhave, R. V., Srivastava, S., Mahanwar, P. A. & Gadekar, P. T. Lignin: Renewable Raw Material for Adhesive. *Open J. Polym. Chem.* **09**, 27–38 (2019).

61. El Mansouri, N. E., Yuan, Q. & Huang, F. Characterization of alkaline lignins for use in phenol-formaldehyde and epoxy resins. *BioResources* **6**, 2647–2662 (2011).

62. Palonen, H. Role of lignin in the enzymatic hydrolysis of lignocellulose. *VTT Publ.* 3–80 (2004).

63. Zheng, Y., Shi, J., Tu, M. & Cheng, Y.-S. *Principles and Development of Lignocellulosic Biomass Pretreatment for Biofuels*. *Advances in Bioenergy* **2**, (Elsevier Ltd, 2017).

64. Gellerstedt, G. & Henriksson, G. Lignins: Major Sources, Structure and Properties. in *Monomers, Polymers and Composites from Renewable Resources* 201–224 (Elsevier, 2008). doi:10.1016/B978-0-08-045316-3.00009-0

65. Fang, Z. & Smith, R. *Production of Biofuels and Chemicals from Lignin*. (Springer Singapore, 2016). doi:10.1007/978-981-10-1965-4

66. Feldman, D. Lignin and Its Polyblends — A Review. *Chem. Modif. Prop. Usage Lignin* 81–99 (2002). doi:10.1007/978-1-4615-0643-0_5

67. Laurichesse, S. & Avérous, L. Chemical modification of lignins: Towards biobased polymers. *Prog. Polym. Sci.* **39**, 1266–1290 (2014).

68. Mandlekar, N. *et al.* An Overview on the Use of Lignin and Its Derivatives in Fire Retardant Polymer Systems. in *Lignin - Trends and Applications* (ed. Poletto, M.) 207–231 (InTech, 2018). doi:10.5772/intechopen.72963

69. Chakar, F. S. & Ragauskas, A. J. Review of current and future softwood kraft lignin process chemistry. *Ind. Crops Prod.* **20**, 131–141 (2004).

70. Tejado, A., Peña, C., Labidi, J., Echeverria, J. M. & Mondragon, I. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresour. Technol.* **98**, 1655–1663 (2007).

71. Lora, J. H. Industrial commercial lignins: Sources, properties and applications. *Monomers, Polym. Compos. from Renew. Resour.* 225–241 (2008). doi:10.1016/B978-0-08-045316-3.00010-7

72. Mousavioun, P. & Doherty, W. O. S. Chemical and thermal properties of fractionated bagasse soda lignin. *Ind. Crops Prod.* **31**, 52–58 (2010).

73. Nasrullah, A., Bhat, A. H., Sada Khan, A. & Ajab, H. *Comprehensive approach on the structure, production, processing, and application of lignin*. *Lignocellulosic Fibre and Biomass-Based Composite Materials: Processing, Properties and Applications* (Elsevier Ltd., 2017). doi:10.1016/B978-0-08-100959-8.00009-3

74. Mansouri, N. E. El & Salvadó, J. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. *Ind. Crops Prod.* **24**, 8–16 (2006).

75. Taherzadeh, M. J. & Karimi, K. *Enzyme-based hydrolysis processes for ethanol from lignocellulosic materials: A review*. *BioResources* **2**, (2007).

76. Jędrzejczyk, M., Soszka, E., Czapnik, M., Ruppert, A. M. & Grams, J. *Physical and chemical*

pretreatment of lignocellulosic biomass. *Second and Third Generation of Feedstocks: The Evolution of Biofuels* (2019). doi:10.1016/B978-0-12-815162-4.00006-9

77. He, X., Miao, Y., Jiang, X., Xu, Z. & Ouyang, P. Enhancing the enzymatic hydrolysis of corn stover by an integrated wet-milling and alkali pretreatment. *Appl. Biochem. Biotechnol.* **160**, 2449–2457 (2010).

78. Moxley, G., Gaspar, A. R., Higgins, D. & Xu, H. Structural changes of corn stover lignin during acid pretreatment. *J. Ind. Microbiol. Biotechnol.* **39**, 1289–1299 (2012).

79. Zhao, C., Qiao, X., Shao, Q., Hassan, M. & Ma, Z. Evolution of the Lignin Chemical Structure during the Bioethanol Production Process and Its Inhibition to Enzymatic Hydrolysis. (2020). doi:10.1021/acs.energyfuels.0c00293

80. Alvira, P., Tomás-Pejó, E., Ballesteros, M. & Negro, M. J. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresour. Technol.* **101**, 4851–4861 (2010).

81. Crestini, C. & Argyropoulos, D. S. Structural Analysis of Wheat Straw Lignin by Quantitative 31P and 2D NMR Spectroscopy. The Occurrence of Ester Bonds and α-O-4 Substructures. *J. Agric. Food Chem.* **45**, 1212–1219 (1997).

82. Qu, Y., Luo, H., Li, H. & Xu, J. Comparison on structural modification of industrial lignin by wet ball milling and ionic liquid pretreatment. *Biotechnol. Reports* **6**, 1–7 (2015).

83. Ghorbani, M. *et al.* Lignin phenol formaldehyde resoles: The impact of lignin type on adhesive properties. *BioResources* **11**, 6727–6741 (2016).

84. Wang, M., Zhao, Y. & Li, J. Demethylation and other modifications of industrial softwood kraft lignin by laccase-mediators. *Holzforschung* **72**, 357–365 (2018).

85. El Mansouri, N.-E., Yuan, Q. L. & Huang, F. Study of chemical modification of alkaline lignin by the glyoxylation reaction. *Mater. Sci.* **6**, 4523–4536 (2011).

86. Hu, L., Pan, H., Zhou, Y. & Zhang, M. Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review. *BioResources* **6**, 3515–3525 (2011).

87. Danielson, B. & Simonson, R. Kraft lignin in phenol formaldehyde resin. Part 1. Partial replacement of phenol by kraft lignin in phenol formaldehyde adhesives for plywood. *J. Adhes. Sci. Technol.* **12**, 923–939 (1998).

88. Ballerini, A., Despres, A. & Pizzi, A. Non-toxic, zero emission tannin-glyoxal adhesives for wood panels. *Holz als Roh- und Werkst.* **63**, 477–478 (2005).

89. Ramires, E. C., Megiatto, J. D., Gardrat, C., Castellan, A. & Frollini, E. Biobased composites from glyoxal–phenolic resins and sisal fibers. *Bioresour. Technol.* **101**, 1998–2006 (2010).

90. Wang, S., Yu, Y. & Di, M. Green modification of corn stalk lignin and preparation of environmentally friendly lignin-based wood adhesive. *Polymers (Basel).* **10**, (2018).

91. Kielhorn, J., Pohlenz-Michel, C., Schmidt, S. & Mangelsdorf, I. Concise International Chemical Assessment Document 57, Glyoxal. *World Heal. Organ.* (2004).

92. Navarrete, P., Pizzi, A., Pasch, H. & Delmotte, L. Study on lignin-glyoxal reaction by MALDI-TOF and CP-MAS 13C-NMR. *J. Adhes. Sci. Technol.* **26**, 1069–1082 (2012).

93. Bussolati, G. *et al.* Acid-free glyoxal as a substitute of formalin for structural and molecular preservation in tissue samples. *PLoS One* **12**, 1–16 (2017).

94. Ramires, E. C. & Frollini, E. Resol and novolac glyoxal-phenol resins : use as matrices in bio-based composites. *16th Int. Conf. Compos. Struct. (ICCS 16)* 30–31 (2011).

95. Frollini, E., Silva, C. G. & Ramires, E. C. *Phenolic resins as a matrix material in advanced fiber-reinforced polymer (FRP) composites*. *Advanced Fibre-Reinforced Polymer (FRP) Composites for Structural Applications* (2013). doi:10.1533/9780857098641.1.7

96. Information, N. C. for B. PubChem Compound Summary for CID 7860, Glyoxal. (2020).

97. Buranov, A. U. & Mazza, G. Lignin in straw of herbaceous crops. *Ind. Crops Prod.* **28**, 237–259 (2008).

98. Vikram, K. Corn Stover. *Ag Marketing Resource center* (2009). Available at: https://www.agmrc.org/renewable-energy/feedstocks-biofuels/annual-crops/corn-stover.

99. Sahoo, S. C., Sill, A. & Pandey, C. N. A Natural Additive Approaches to Enhance the Performance of Formaldehyde Based Adhesive for Plywood manufacturing. *Int. J. Innov. Sci. Mod. Eng.* **3**, 22–28 (2014).

100. U.S EPA. Method 3015A: Microwave assited acid digestion of sediments, sludges,soils and oils. Test Methods for Evaluating Solid Wast. **67**, 1–30 (2007).

101. Li, M., Yoo, C. G., Pu, Y. & Ragauskas, A. J. 31P NMR Chemical Shifts of Solvents and Products Impurities in Biomass Pretreatments. *ACS Sustain. Chem. Eng.* **6**, 1265–1270 (2018).

102. Wang, X., Huang, Z., Cooper, P., Zhang, Y. & Casilla, R. The Ability of Wood to Buffer Highly Acidic and Alkaline Adhesives THE ABILITY OF WOOD TO BUFFER HIGHLY ACIDIC AND ALKALINE ADHESIVES Zeen Huang Postdoctoral Fellow Romulo Casilla. *Wood Fiber Sci.* 398–405 (2010).

103. Ház, A., Jablonský, M. & Orságová, A. Determination of Temperature Regions in Thermal Degradation of Lignin. *4nd Int. Conf. Renew. Energy Sources* **200280301**, 1–6 (2013).

104. Da Costa Sousa, L. *et al.* Isolation and characterization of new lignin streams derived from extractive-ammonia (EA) pretreatment. *Green Chem.* **18**, 4205–4215 (2016).

105. Lei, M. *et al.* Characterization of lignins isolated from alkali treated prehydrolysate of corn stover. *Chinese J. Chem. Eng.* **21**, 427–433 (2013).

106. Pizzi, A., Mittal, K. & Pizzi, A. Phenolic Resin Adhesives. in *Handbook of Adhesive*

Technology, Revised and Expanded (2003). doi:10.1201/9780203912225.ch26

107. Hauptt, R. A. & Sellers, T. Characterizations of Phenol-Formaldehyde Resol Resins. *Ind. Eng. Chem. Res.* **33**, 693–697 (1994).

108. Gillern, M.F.; Oita, K. ; Teng, RJ.; Tiedeman, G. T. Phenol Formaldehyde Resoles and Laminates. U.S. Patent. (1981).

109. Kamarudin, N., Biak, D. R. A., Abidin, Z. Z., Cardona, F. & Sapuan, S. M. Rheological study of phenol formaldehyde resole resin synthesized for laminate application. *Materials (Basel).* **13**, 14–19 (2020).

110. Alonso, M. V., Oliet, M., García, J., Rodríguez, F. & Echeverría, J. Gelation and isoconversional kinetic analysis of lignin-phenol-formaldehyde resol resins cure. *Chem. Eng. J.* **122**, 159–166 (2006).

111. Brostow, W., Goodman, S. H. & Wahrmund, J. Epoxies. in *Handbook of Thermoset Plastics* 191–252 (2014). doi:10.1016/B978-1-4557-3107-7.00008-7

112. Ratna, D. *Handbook of Thermoset Resins*. (iSmithers Rapra Publishing, 2010).

113. Karol Głąbpl.wiki: Karol007commons: Karol007e-mail: kamikaze007 (at) tlen.pl - own work from: Glazer, A. W., and Nikaido, H. (1995). Microbial Biotechnology: fundamentals of applied microbiology. San Francisco: W. H. Freeman, p. 340. ISBN 0-71672608-4This W3C-unspecified vector image was created with Inkscape., CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=1993633