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Lignin-Glyoxal Bio-Adhesive Based on Lignin from Sugarcane Bagasse: Characterization and Application

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Abstract

This study explores the potential of lignin extracted from sugarcane bagasse as an eco-friendly alternative to petroleum-derived phenol-formaldehyde (PF) adhesives. PF adhesives are widely used in plywood manufacturing, but their reliance on non-renewable resources and the toxicity of phenol and formaldehyde pose sustainability and health concerns. The researchers aimed to develop a lignin-glyoxal (LG) bio-adhesive that could match the performance of commercial PF adhesives. Lignin was isolated through alkali treatment, yielding 17.46 ± 3.61 %. FT-IR spectrophotometry and GPC characterization confirmed typical lignin functional groups, with Mn and Mw values of 1068.0 and 1196.0 g/mol, respectively. UV-Vis spectrophotometry revealed active sites with a total phenolic hydroxyl content of 0.35 ± 0.01 mmol/g. The optimal LG bio-adhesive composition was 1:2, achieving a tensile strength of 0.45 ± 0.06 N/mm², comparable to PF standards. While the LG 1:2 bio-adhesive exhibited suitable physicochemical properties and passed water resistance tests, it failed wet tensile strength tests, indicating its potential for interior wood product applications. This research contributes to the development of sustainable industrial applications utilizing lignin-based bio-adhesives.

Keywords: Alkali treatment, Bio-adhesives, Glyoxal, Lignin, Lignin-glyoxal, Sugarcane bagasse

Introduction

PF adhesives, widely used in plywood manufacturing, rely on non-renewable petroleum-derived components [1]. Their future availability and cost are threatened by diminishing hydrocarbon resources, while health concerns arise from the toxicity and carcinogenicity of phenol and formaldehyde [2]. Bio-adhesives offer a promising, eco-friendly alternative to traditional PF adhesives, addressing sustainability and safety issues in wood bonding applications. Researchers have investigated eco-friendly alternatives to PF adhesives. Due to structural similarities, Glyoxal, the simplest dialdehyde, shows promise as a formaldehyde substitute [3]. Formaldehyde, a known carcinogen, exhibits high toxicity (LD50, rat ≥ 100 mg/kg; LD50, mouse ≥ 42 mg/kg). Glyoxal, while a suspected carcinogen, is less toxic (LD50, rat > 2960 mg/kg; LD50, mouse > 1280 mg/kg) [4]. Higher LD50 values indicate lower toxicity. Glyoxal is non-volatile and potentially derivable from natural sources [5]. As a formaldehyde alternative in adhesives, glyoxal addresses health and environmental concerns.

Concurrently, lignin, a primary constituent of plant cell walls, demonstrates significant potential to replace phenol in phenolic resin production [5,6]. LG bio-adhesives reduce reliance on fossil-fuel-based and formaldehyde-containing adhesives, offering more sustainable and safer solutions [3,6]. Lignin, a phenolic macromolecule prevalent in biomass cell walls, exhibits structural similarity to phenol due to its aromatic rings and phenolic hydroxyl groups [5]. This biopolymer comprises three monomers, namely guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) (**Figure 1**). The G and H units are pivotal in determining lignin's reactivity and efficacy in adhesive applications. In phenolic adhesive systems, aldehyde reactivity is confined to the G and H units, which possess 1 and 2 reactive sites at the C3 and C5 positions of their phenolic

hydroxyl groups, respectively. Consequently, lignin with elevated G and H content offers a higher density of reactive sites for aldehyde interaction, thereby enhancing adhesive performance [3].

Lignin derived from sugarcane bagasse (*Saccharum officinarum*) is particularly noteworthy due to its relatively high ratio of G monomers, making it an excellent source for lignin isolation in adhesive applications[7]. Sugarcane bagasse contains 38 % G lignin monomers and 2 % H monomers, highlighting its significant potential as a lignin source for producing environmentally friendly LG bio-adhesives [8]. Boussetta *et al.* [9] successfully isolated lignin from sugarcane bagasse using alkali treatment with 10 - 20 % (w/v) NaOH at 98 °C, and precipitated it with 1.5 - 3 M H_2SO_4 to reach pH 2. The highest lignin yield was achieved with 16 % NaOH and 1.5 M H_2SO_4. Similarly, Siahkamari *et al.* [3] used 0.5 M NaOH for delignification and 1 M H_2SO_4 for precipitation.

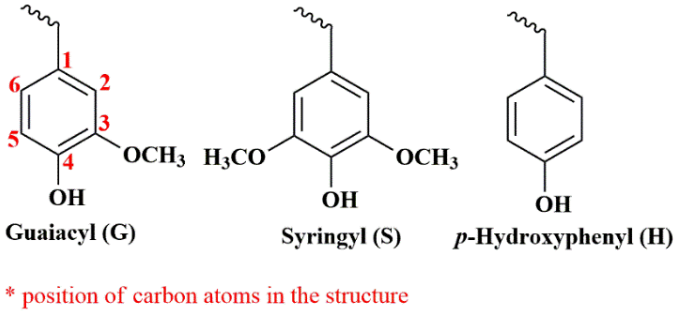

Figure 1 Chemical structures of various monomers of lignin (guaiacyl (G), syringil (S), and *p*-hydroxyphenyl (H)) [9].

These studies confirm that alkali treatment is effective for lignin isolation. Kalami *et al.* [10] demonstrated that lignin from corn stalks can replace phenol in PF adhesives. The bio-adhesive showed similar properties to commercial PF resins, with a solid content of 24.7 %, pH 9.2, viscosity 0.4 Pa·s, gelation time 432 s, and comparable shear strength. Prior investigations into LG bio-adhesives have not encompassed lignin extracted from bagasse sources. This study aims to isolate lignin from sugarcane bagasse obtained in Pontianak City, West Kalimantan, to enhance the efficacy of LG bio-adhesives as a phenol substitute in PF adhesive formulations. Furthermore, this research endeavors to evaluate the physicochemical properties of the synthesized LG bio-adhesives to ascertain their compliance with the Indonesian National Standard (SNI) No. 06-4567-1998, which delineates specifications for liquid PF adhesives utilized in plywood manufacturing.

Materials and methods

Materials

The equipment utilized in this research includes a centrifuge LC-04S (Oregon), Fourier-transform infrared (FT-IR) spectroscopy 8400 (Shimadzu), gel permeation chromatography HLC-8320 (TOSOH), hot press, microscope, oven, universal pH indicator (Merck 1.09535.0001), universal testing machine UH-X (Shimadzu), UV-Visible spectroscopy UV2600 (Shimadzu), and *viscotester* VT-06. The materials employed in this study were distilled water (H_2O), sugarcane bagasse, acetic anhydride (Merck 100042), hydrochloric acid (HCl) 37 % (Merck 258148), sulfuric acid (H_2SO_4) 95 - 97 %, pH 6 buffer (Merck 109437), 1,4 dioxane (Merck 109671), phenol (Merck 100206), formaldehyde 37 % (Sigma-Aldrich 1.04003), glyoxal 40 % (Sigma-Aldrich 128465), wood veneer, filter paper, commercial lignin (Sigma-Aldrich 471003), sodium hydroxide (NaOH) (Merck 106498), pyridine (Merck 109728), wood powder, alder bark flour, and wheat flour.

Methods

Pretreatment and isolation of lignin from sugarcane bagasse

The physical pretreatment of sugarcane bagasse commenced with a series of thorough washings, repeated five times using running water, to ensure the removal of odors. Following this, the bagasse was subjected to sun-drying for a duration of 3 to 4 days.

Subsequently, it was cut into smaller fragments, approximately 2 cm in length, to facilitate further processing. These pieces were pulverized using a blender and sieved through a 100-mesh sieve. Lignin isolation from bagasse was conducted chemically via the alkali treatment method, as described by Boussetta *et al*. [9]. The ratio of sample powder to NaOH was 1:10. Specifically, 50 g of bagasse powder was refluxed in 500 mL of 16 % (w/v) NaOH at 98 °C for 2 h. The refluxed solution was filtered through filter paper to separate the precipitate from the black leachate solution containing lignin. The black liquor was then treated with 1.5 M H_2SO_4 solution to adjust the pH to 2, precipitating the lignin. The acidified solution was centrifuged at 3000 rpm for 20 min to separate the precipitate from the solution. The lignin precipitate underwent a purification process involving washing with distilled water, followed by thermal drying in an oven at 60 °C for a duration of 16 h. Subsequently, the dried lignin was subjected to mechanical size reduction via pulverization using a blender to achieve a fine particulate form. The dried lignin obtained is typically brown in color, varying from light to dark shades depending on the source and extraction process [11]. It will be in a powder form.

Lignin characterization

FT-IR spectroscopy was conducted on lignin samples over 4000 - 400 cm^{-1} (resolution: 2 cm^{-1}), emphasizing fingerprint regions (1700 - 400 cm^{-1}). Molecular weight determination utilized gel permeation chromatography (GPC) following lignin acetylation. This process involved reacting 1 g lignin with 20 mL pyridine and 20 mL acetic anhydride (24 h, room temperature, 600 rpm), precipitation with 150 mL of 0.1 M HCl, filtration, washing (0.05 M HCl, distilled water), and drying (40 °C, 16 h). The acetylated lignin then underwent GPC analysis for molecular weight determination. The results of this characterization are the Mn, Mw, and PDI values of the lignin samples. Mn (Number-average molecular weight) is the total molecular weight of all polymer chains divided by the number of chains. Mw (Weight-average molecular weight) gives more weight to higher molecular weight chains and is always greater than Mn. The Polydispersity Index (PDI), calculated as Mw/Mn, measures the breadth of molecular weight distribution. A PDI near 1 indicates a narrow distribution [3,12,13].

Phenolic hydroxyl content determination

Phenolic hydroxyl (OH_{ph}) content in lignin samples was quantified via UV-Vis spectrophotometry, adapting previously established methods [12-14] using Ultraviolet Ionization Difference Spectrophotometry (Δε-IDUS). Lignin (10 mg) was dissolved in 5 mL dioxane:0.2 M NaOH (1:1). Subsequently, 0.8 mL of this lignin solution was diluted to 10 mL with pH 6 buffer and 0.2 M NaOH separately. Absorbance was measured from 200 - 400 nm against respective blanks. The absorbance of the lignin solution in the alkaline medium was subtracted from the absorbance in the neutral medium. The phenolic hydroxyl content was calculated using Eq. (1) [12].

$$OH_{ph}\,(\text{mmol/g}) = \frac{(0.25\times \text{Abs } 300\text{ nm}) + (0.107\times \text{Abs } 350\text{ nm})}{c} \quad (1)$$

Abs 300 nm: Absorbance value at 300 nm
Abs 350 nm: Absorbance value at 350 nm
C: Lignin solution concentration (g/L)

Preparation of lignin-glyoxal (LG) resin

The LG bio-adhesive was synthesized by modifying methodologies previously established by other researchers [9,10]. The bio-adhesives were formulated with varying concentrations of lignin, specifically at 0, 50, and 100 %. The molar ratio of lignin, represented by its phenolic hydroxyl groups, to glyoxal, was consistently maintained at 1:2, indicating that 2 moles of glyoxal were utilized for each mole of phenolic hydroxyl group present in lignin. In the preparation procedure, 10 g of lignin powder was dissolved in 34 mL of a 1 M sodium hydroxide (NaOH) solution. Glyoxal was subsequently introduced incrementally into the lignin solution. The mixture's temperature was elevated to 65 °C and held constant for 30 min. Following this period, an additional 16 mL of 1 M NaOH solution was added. The temperature was then increased to 90 °C and maintained for 2 h. The resultant resin was subsequently stored in a refrigerator for future use. The resin has distinct physical characteristics, typically brown or dark brown in color, similar to lignin due to its natural pigmentation. It appears as a viscous liquid (high viscosity), and as it cures, it hardens into a solid adhesive.

Characterization of lignin-glyoxal (LG) resin

Physicochemical characterization of the bio-adhesive encompassed 3 methodologies. Viscosity was quantified using a viscosity meter, wherein the sample's viscosity was directly measured upon placement in the device's beaker and rotor engagement. pH assessment utilized a universal pH indicator, with the bio-adhesive (1 mL) diluted in distilled water (5 mL). Homogeneity evaluation involves microscopic examination (40× magnification) of a thin adhesive film on a glass slide, focusing on the presence or absence of granules, coarse particles, or bubbles to ascertain structural uniformity. These analyses provided critical data on the bio-adhesive's rheological properties, acidity/alkalinity, and structural consistency.

The solid content determination adhered to the ASTM D4426-01 protocol. LG resin (1 g) was subjected to thermal drying at 125 °C for 105 min, followed by cooling to ambient temperature in a desiccator before re-weighing. This procedure was performed in triplicate to derive a mean solid content value, ensuring the statistical reliability of the results. Following cooling in the desiccator, the samples were weighed to determine their solid content, which was calculated using Eq. (2):

$$\% \text{ Solid Content} = \frac{\text{weight of the oven-dried resin (g)}}{\text{weight of the initial resin (g)}} \times 100\ \% \quad (2)$$

The gelation time assay measures the temporal interval necessary for an adhesive to undergo a phase transition from a liquid to a gel state [15]. A one-gram aliquot of resin was introduced into a test tube and subsequently immersed in a boiling water bath. The gelation time was recorded from the instant of immersion until the resin exhibited gel-like properties, as evidenced by its adherence to the stirring implement. A stopwatch was used to chronometrically measure the gelation time, ensuring the reliability of the time measurement. Throughout the procedure, the resin was agitated via vertical reciprocation of the stirring rod. Chronometric measurement commenced immediately upon immersion and continued until the gelation endpoint was observed. The gelation time was measured at a constant temperature of 100 ± 1 °C, maintained using a boiling water bath.

Water resistance was assessed by distributing approximately 5 mL of resin into 3 separate petri dishes. Each sample was mixed with 0.5 g of sawdust and subsequently heated in an oven at 130 °C for 1 h following cooling, the samples were submerged in a beaker containing approximately 100 mL of distilled water. Visual assessments were carried out over a period of up to seven days, with the samples maintained at ambient temperature. The observations revealed that the LG resin-sawdust samples retained their structural integrity throughout the one-week immersion in water. The resin demonstrated cohesion and effective adhesion to the sawdust particles, with no visible evidence of swelling, deformation, or leaching. These findings indicate that the LG resin possesses satisfactory water resistance properties.

Preparation of lignin-glyoxal (LG) bio-adhesive

The LG bio-adhesive was synthesized following a protocol analogous to that used for the preparation of commercial phenol resorcinol formaldehyde (PRF) [10] The procedure commenced with the homogenization using an overhead mixer of wheat flour (6.5 %, all data samples are on a weight basis) and water (18 %), followed by the gradual incorporation of alder bark modal (6.5 %) under continuous agitation. Subsequently, LG resin (66 %) and 1 M NaOH (3 %) were introduced into the mixture. The solution was then subjected to agitation for 3 - 4 min to ensure complete homogeneity of the resultant bio-adhesive.

Characterization of lignin-glyoxal (LG) bio-adhesive

Tensile strength/shear mechanical tests were conducted by ASTM D5868-01. Bio-adhesive (0.10 g) was applied to a 26 mm² area of wood veneer (26×10×1.2 mm^3). Veneers were pressed at 1400 kPa and 180 °C for 3 - 4 min, aligning with commercial PRF adhesive parameters. An Instron universal testing machine assessed tensile strength at a 13 mm/min loading rate. FT-IR spectrophotometric analysis was performed on 1 g wet samples at 4000 - 400 cm^{-1} (2 cm^{-1} resolution), with fingerprint regions analyzed at 1700 - 400 cm^{-1}. Wet shear strength evaluation followed PS 1-09 Structural Plywood standard, subjecting LG bio-adhesive bonded between 2 wood veneer samples to 4 h boiling water immersion followed by 20 h drying at 65 °C to simulate humid conditions. Subsequently, the specimens underwent another 4 h immersion in boiling

water. Immediately after this 2nd immersion, the adhesive strength of the specimens was measured using an Instron testing machine.

Results and discussion

Pretreatment and isolation of lignin from sugarcane bagasse

The lignin was produced as a solid in the form of a dark brown powder. The yield of lignin from bagasse obtained was 17.46 ± 3.61 % with 13 repetitions. This is in accordance with some literature which states that the composition of lignin in bagasse reaches 17 - 25 % [16,17]. Differences in lignin sources, isolation methods, and the specific type of biomass studied lead to variations in the percentage of lignin content. For example, lignin content varies in bagasse (17 - 25 %) and beet pulp (1 - 5.50 %). This variation shows how the type of plant material and its natural chemical makeup can affect the lignin content.

Characterization of lignin

FT-IR Spectrophotometry analysis

FT-IR spectrophotometric analysis was successfully conducted on sugarcane bagasse, lignin isolates, and commercial lignin samples, with the resultant spectra depicted in **Figure 2**. The bagasse spectrum exhibited characteristic peaks indicative of lignocellulosic composition, encompassing lignin, cellulose, and hemicellulose. Lignin presence in bagasse was evidenced by distinctive peaks at 1633, 1247, and 1051 cm^{-1}. The 1633 cm^{-1} peak corresponds to C=C stretching vibrations in phenol groups and C-H conjugation within aromatic rings [7,16]. The 1247 cm^{-1} peak is attributed to aromatic ring vibrations in lignin S units [18], while the 1051 cm^{-1} peak signifies aromatic G-type C-H plane deformation [12,14,19]. Cellulose and hemicellulose moieties were identified by characteristic peaks at 667 and 1734 cm^{-1}, respectively [9,14]. The former peak is associated with ethyl β-glycosidic bond strain in cellulose, while the latter corresponds to a carbonyl group (C=O) stretching in uronic acid derived from hemicellulose.

Other common peaks are observed in the spectra. The stretching vibrations of O-H groups, originating from intra- and intermolecular hydrogen bonds, appear at wave numbers ranging from 3404 to 3442 cm^{-1}[13]. The broadening of the peak around 3400 cm^{-1} suggests the presence of hydrogen bonding. Spectral bands observed in the region of 2916 - 2935 cm^{-1} are attributed to C-H bond stretching vibrations within methyl (CH_3) and methylene (CH_2) moieties [8]. The absorption band manifesting between 1604 - 1641 cm^{-1} is indicative of C=C stretching vibrations within the aromatic ring structures of phenolic hydroxyl groups, thereby corroborating the presence of lignin constituents [14]. A prominent absorption at 1260 cm^{-1} is characteristic of C-O stretching vibrations, suggesting the presence of ether or ester functionalities [16]. Additionally, the spectral feature at 1120 cm^{-1} is ascribed to C-O-C stretching vibrations, specifically associated with aryl ether linkages [10] . In the spectrum of lignin, the absence of peaks at 667 and 1734 cm^{-1} indicates the successful removal of cellulose and hemicellulose compounds through the alkali isolation method.

The effectiveness of this method in isolating lignin is further confirmed by the appearance of new peaks at wavenumbers 1512, 1427, 1265, 893, and 584 cm^{-1}. The new peaks that appear at isolated lignin have also appeared on commercial lignin. At commercial lignin, the peaks appear at 1510, 1417, and at 1265 cm^{-1}. The appearance of new peaks in the FT-IR spectrum of the isolated lignin that is identical to the spectrum of commercial lignin indicates the effectiveness of the alkali treatment method used for lignin extraction. These new peaks are associated with the C=C stretching vibrations within the aromatic skeleton of lignin, methoxy C-H bending and C-C stretching in the aromatic skeleton, C=O stretching in the G unit, and S=O stretching alongside aliphatic S-O and C-S bending vibrations. The presence of these lignin-specific peaks confirms that the alkali treatment successfully extracted and preserved the structural integrity of the lignin polymer. The S-O and C-S vibrations detected in the lignin spectrum are attributed to the precipitation process involving H_2SO_4 [11,19].

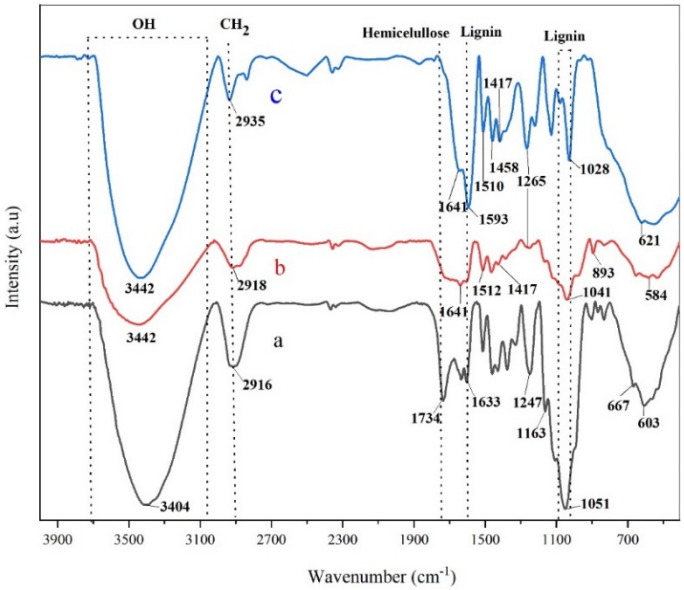

Figure 1 FT-IR spectra of sugarcane bagasse (a), lignin isolated from this study (b), and commercial lignin (c).

Gel permeation chromatography analysis

Based on the Mn and Mw results in **Table 1**, the Mn (1068 g/mol) and Mw (1196 g/mol) values are relatively close, suggesting that the molecular weight distribution is not excessively broad. This indicates that the isolation process yielded samples with consistent molecular weights. The polydispersity index (PDI) value of 1.12 further demonstrates that the lignin samples possess a relatively narrow and homogeneous molecular weight distribution. This implies that most of the lignin molecules have molecular weights close to the average value. The high homogeneity and narrow molecular weight distribution suggest that this lignin could exhibit consistent physical and chemical properties, which are crucial for applications in adhesive materials.

Based on **Table 1**, the lignin sample exhibits the lowest Mn and Mw values compared to samples from other studies. This suggests that the polymer chains in the lignin sample are relatively shorter, indicating a lower degree of polymerization (DP). The DP refers to the number of monomer units (or repeating units) that compose the polymer chain. In simpler terms, DP measures the number of monomer units linked together to form a polymer molecule. The DP is crucial as it influences the physical properties of the polymer. Generally, a higher DP results in longer polymer chains, which can enhance mechanical properties such as tensile strength and elasticity.

Table 1 The yields of lignin's Mn, Mw, and PDI values.

Sample	Mn (g/mol)	Mw (g/mol)	PDI
Lignin	1068.0	1196.0	1.12
Lignin [20]	1072	1765	1.65
Lignin [21]	2090	3760	1.80
Lignin [3]	1710	3690	2.20

Lower Mn and Mw result in shorter polymer chains, improving adhesive penetration into porous substrates like wood and enhancing bonding performance. These shorter chains also provide more reactive sites, allowing more effective cross-linking and faster polymerization. It also allows greater flexibility in adjusting formulation properties, and reduces steric hindrance, leading to stronger adhesive bonds through efficient cross-linking [22]. Variations in Mn, Mw, and PDI can be attributed to differences in lignin isolation methods, feedstock sources (e.g., type of plant and plant parts used), and reaction conditions (such as temperature, time, and catalysts) [23].

Ultraviolet Ionization Difference Spectrophotometry (Δε-IDUS) analysis

The phenolic hydroxyl moieties were quantified within lignin specimens using Δε-IDUS. This analytical technique exploits the bathochromic and hyperchromic shifts observed in the lignin absorption spectrum, which are induced by the ionization of hydroxyl functionalities under alkaline conditions. In basic media, the ionized phenolic hydroxyl groups engender a shift in absorption towards longer wavelengths and heightened intensities. The ionization difference spectrum, or Δε spectrum, is derived through the subtraction of the neutral solution's absorption spectrum from that of the alkaline solution.

Based on the spectral analysis presented in **Figure 3**, absorbance maxima are identified at wavelengths of 298 and 344 nm, which are in proximity to 300 and 350 nm, respectively. These maxima are indicative of bathochromic and hyperchromic shifts within the absorption spectrum of lignin, occurring as a result of the ionization of phenolic hydroxyl groups under alkaline conditions. Such spectral shifts serve to corroborate the existence of phenolic hydroxyl groups within the lignin structure. The total phenolic hydroxyl content quantified in the lignin sample is 0.35 ± 0.01 mmol/g, as detailed in **Table 2**. This phenolic content is comparable to that documented for hydroxylpropyl-modified kraft lignin, which is reported at 0.33 mmol/g. In contrast, it is significantly higher than the phenolic content of lignosulfonate lignin derived from softwood, measured at 0.16 mmol/g. However, it is lower than the phenolic hydroxyl content found in alkaline lignin sourced from Curaua (0.66 mmol/g), corn cob (1.23 mmol/g), and commercial organosolv lignin (2.4 mmol/g).

Table 2 Total hydroxyl phenolic (OH_{ph}) content of lignin with Δε-IDUS.

Sample	Extraction method	Measurement of OH_{ph} content	Origin	Total OH_{ph} (mmol/g)
Lignin	Alkali	Δε-IDUS	Sugarcane bagasse	0.35 ± 0.01
Hydroxylpropyl-modified Lignin [24]	Kraft	Δε-IDUS	-	0.33
Lignin [15]	Lignosulfonate	HPLC and ^{31}P NMR	softwood	0.16
Lignin [17]	Alkali		Curaua	0.66
Lignin [15]	Organosolv	HPLC and ^{31}P NMR	Corn stover	1.23
Commercial lignin [24]	Organosolv	Δε-IDUS	-	2.40

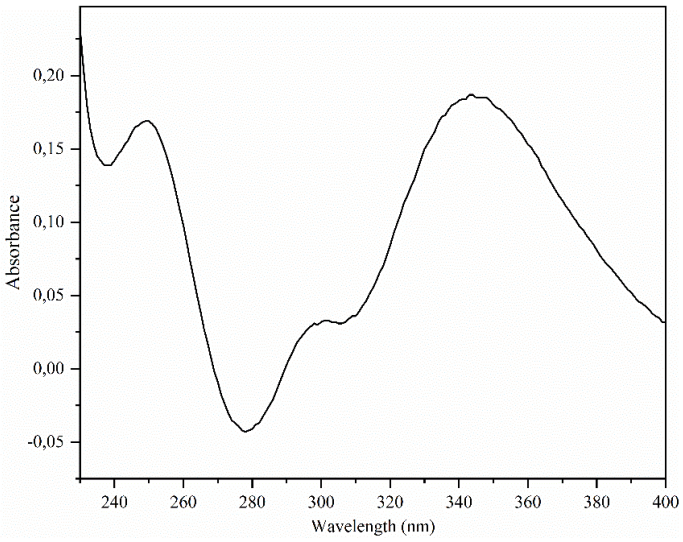

Figure 2 Ionization difference spectrum (Δε-spectrum) of lignin.

The lignin isolate exhibits lower phenolic hydroxyl content, confirmed by FT-IR analysis showing weaker O-H stretch peak intensity compared to commercial lignin. This content is crucial for the

reactivity and adhesive performance in LG bio-adhesives, as phenolic groups can react with glyoxal, enhancing cross-linking and polymerization, which improves mechanical properties like tensile strength [12]. Differences in phenolic hydroxyl content between bagasse-derived lignin and other sources relate to the lignin content in each biomass. Bagasse has a higher proportion of G units, leading to greater phenolic hydroxyl content than lignins from softwoods or hardwoods, which contain more S units. This variation affects the availability of reactive sites for cross-linking and the overall performance of lignin-based adhesives [12,13,21]. Data indicates that the lignin sample contains active sites for reacting with glyoxal compounds. Understanding the total phenolic hydroxyl content in lignin allows for determining the appropriate amount of glyoxal needed for effective resin manufacture, maintaining a mole ratio of 1:2 between phenolic hydroxyl content and glyoxal. Discrepancies in phenolic content arise from various factors, including lignin source, isolation methods, purity, and measurement techniques [17].

Characterization of lignin-glyoxal (LG) resin and bio-adhesive

Table 3 delineates the pH, viscosity, solid content, gelation time, and homogeneity of LG resins in comparison to standard resins. It is apparent that a reduction in the proportion of glyoxal results in a corresponding increase in the pH of the resin. This phenomenon can be attributed to the fact that in the 0:1 LG variant, which consists solely of glyoxal, the Cannizzaro side reaction of glyoxal under alkaline conditions generates glycolic acid, consequently leading to a decrease in the pH of the resin.

Table 3 Properties of LG resin and standard resin.

No	Lignin-glyoxal	pH	Viscosity (cps)	Solid content (%)	Gelation time (min)	Homogeneity*
1	0:1	11	57.0 ± 1.16	17.24 ± 2.12	35.0 ± 1.73	+++
2	1:2	12	292.0 ± 1.53	25.58 ± 0.13	10.0 ± 0.58	++
3	1:0	13	240.0 ± 0.58	20.24 ± 0.23	15.0 ± 1.16	-
4	PF (STD)	12	270.0 ± 0.46	23.77 ± 0.32	11.0 ± 0.58	+++

Note: * +++: This indicates excellent or very high homogeneity, ++: This signifies good or high homogeneity, +: This indicates low homogeneity, and -: This represents poor homogeneity or a lack of homogeneity.

The Cannizzaro reaction is more common at lower temperatures and occurs in aldehydes that do not have a hydrogen atom on the alpha carbon. The Cannizzaro reaction occurs when 1 molecule of formaldehyde combines with another in an alkaline medium, however, since the glyoxal compound has 2 carbonyls close together in 1 compound, an intramolecular Cannizzaro reaction can occur. The presence of 2 carbonyl groups with partial positive charges increases the susceptibility of glyoxal to this Cannizzaro reaction. As a result, glycolic acid is generated causing a decrease in the pH of the resin. If the pH of the resin is not properly regulated, the decrease in pH will interfere with the electrophilic substitution reaction between lignin and glyoxal.

When comparing the LG 1:2 and LG 1:0 variants, it is noted that the LG 1:2 variant exhibits a lower pH; however, it also demonstrates higher viscosity, solid content, and gelation time. This particular outcome is ascribed to the reduced pH, which diminishes the solubility of lignin that remains unreacted with glyoxal within the resin matrix, thereby increasing viscosity and solid content. The elevated viscosity, in turn, contributes to a more rapid gelation time [3]. The LG 1:2 resin also had a shorter gelation time (10.0 ± 0.58 min) than the LG 0:1 (35.0 ± 1.73 min) and LG 1:0 (15.0 ± 1.16 min) resins, indicating a higher reactivity between the lignin and glyoxal. The relationship between the increased viscosity and shorter gelation time in the LG 1:2 resin suggests enhanced reactivity and cross-linking, which can lead to improved adhesive properties and better

performance compared to the other formulations. This optimal combination of high viscosity and rapid gelation time likely contributed to the LG 1:2 resin's ability to achieve tensile strength properties comparable to the commercial PF adhesive standard. The higher viscosity and lower homogeneity of the 1:2 LG bio-adhesive compared to PF adhesives may hinder application, leading to uneven coverage and reduced penetration in porous substrates. Inconsistencies from lower homogeneity can weaken bonds, highlighting the need to address these issues for improved performance.

In the 0:1 LG formulation, the absence of lignin is clearly demonstrated by its markedly reduced viscosity and solid content, alongside an extended gelation period. In contrast, the LG 1:2 formulation exhibits an increased solid content, which can be attributed to the synthesis of LG compounds with higher molecular weights, in comparison to formulations devoid of glyoxal. This observation suggests a chemical interaction between lignin and glyoxal. The elevated solid content in the LG 1:2 variant contributes to enhanced adhesive coverage of the binder, thereby improving its resistance to deformation when subjected to tensile stress [14]. As indicated in **Table 3**, the LG 1:2 formulation closely corresponds with the standards set forth by Phenol Formaldehyde (PF). This conclusion aligns with the stipulations outlined in SNI 06-4567-1998 regarding the use of liquid PF in plywood adhesives.

Based on the results of the tensile strength tests (**Table 4**), the L:G 1:2 bio-adhesive variation exhibited tensile strength closest to the PF adhesive standard compared to other formulations. The tensile test results of LG 0:1 have a much smaller tensile strength, while LG 1:2 and LG 1:0 have almost the same tensile strength and are close to PF standards, this indicates that the addition of lignin into the resin greatly affects the bio-adhesive properties, with lignin causing a higher level of cross-linking between lignin and glyoxal resulting in better polymerization [17].

Table 4 Tensile test results of LG bio-adhesive.

Lignin-glyoxal (w:v)	Tensile strength (N/mm^2)
LG 0:1	0.02 ± 0.01
LG 1:2	0.45 ± 0.06
LG 1:0	0.43 ± 0.03
PF (STD)	0.58 ± 0.02

This phenomenon can be attributed to the molecular weight and PDI values of the lignin isolate obtained, which were not very high. Samples with higher molecular weight and PDI tend to exhibit lower tensile strength compared to those with lower molecular weight and PDI [14]. This is likely because higher molecular weight samples with broader PDI may experience greater steric hindrance, reducing the accessibility of reactive sites for glyoxal to react effectively.

The analysis of LG resin formulations reveals a strong correlation between resin properties and tensile strength. The LG 1:2 formulation, with its balanced pH, high viscosity, highest solid content, and shortest gelation time, achieved the best tensile strength among the bio-based options. This formulation most closely resembled the properties and performance of the PF standard. The data suggests that optimal cross-linking between lignin and glyoxal, resulting in higher molecular weight compounds, contributes to improved adhesive properties. The presence of lignin significantly enhances tensile strength, while the addition of glyoxal further improves cross-linking and overall adhesive performance. These findings highlight the potential of the LG 1:2 formulation as a promising bio-based alternative to traditional PF.

In the synthesis of LG resin, the glyoxalation process occurs under alkaline conditions, typically using NaOH, at temperatures between 45 and 70 °C for 1 - 24 h. This process involves three primary reactions: The Lederer-Manasse reaction, where glyoxal attaches to lignin's active sites (particularly the free C5 ortho sites

in G and H units); the Cannizzaro reaction; and a substitution reaction between glyoxal and lignin side chains. The glyoxalation results in hydroglyoxylated lignin, which subsequently condenses with other lignin units via methylene/glyoxylene bridges (**Figure 4**) [4].

To minimize undesirable side reactions, such as the Cannizzaro reaction producing carboxylic acids and alcohols, the pH must be maintained between 9 and 11, often requiring additional NaOH during synthesis at 65 °C [10].

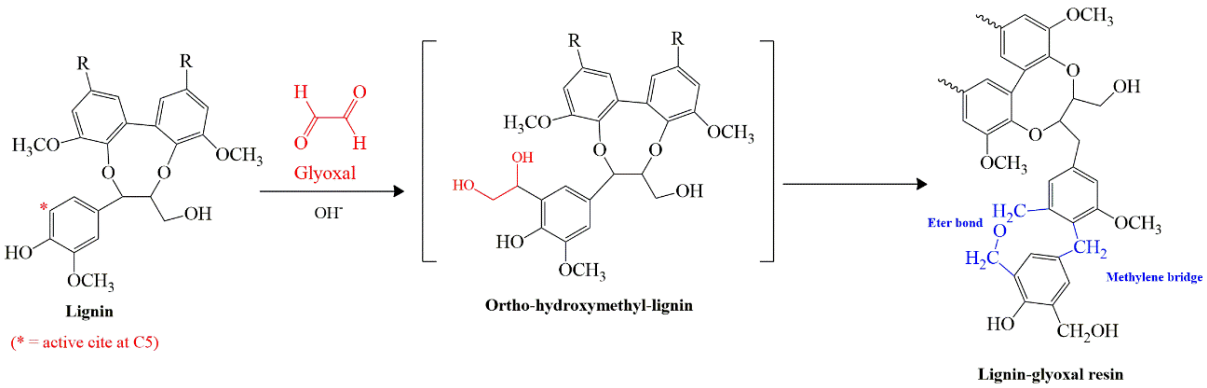

Figure 3 Suggested chemical reaction between lignin and glyoxal under alkaline conditions [17].

The evidence supporting the chemical interaction between lignin and glyoxal (**Figure 4**) is substantiated by the findings obtained from Fourier Transform Infrared (FT-IR) spectrophotometric analysis, as illustrated in **Figure 5**. **Figure 5** presents the FT-IR spectra comparing pure lignin (L) and the LG resin, highlighting key functional groups and structural changes resulting from their interaction. The peak at 3442 cm^{-1} in the lignin spectrum corresponds to O-H stretching vibrations associated with phenolic hydroxyl groups; in the LG resin, this peak shifts to 3419 cm^{-1}, indicating glyoxal's interaction with these hydroxyl groups and the formation of covalent bonds that enhance crosslinking [23]. Additionally, a peak at 2875 cm^{-1} in the LG spectrum, attributed to C-H stretching vibrations from methylene groups introduced during the reaction with glyoxal, is more pronounced, underscoring glyoxal's successful incorporation into the lignin structure [25]. Two prominent peaks were noted at 1118 and 1043 cm^{-1}, corresponding to C-O stretching of secondary alcohol and C-O stretching with deformation of primary alcohol, respectively [26]. A pronounced peak for C-C stretching vibrations appears at 1456 cm^{-1} in the LG resin, which is stronger than in the lignin spectrum, suggesting the aromatic structure is maintained while forming new bonds with glyoxal [27]. Furthermore, peaks at 1251 and 1118 cm^{-1} in the LG spectrum, associated with C-O stretching of ether bonds and primary alcohols, indicate the formation of new linkages between lignin and glyoxal, further supporting the crosslinking process [21,22]. Distinct peaks at 987 and 1043 cm^{-1} in the LG spectrum confirm the presence of glyoxal. The peak at 987 cm^{-1}, linked to out-of-plane C-H stretching, further indicates the formation of methylene bridges in the resin. Overall, the differences in peak positions and intensities between pure lignin and the LG resin highlight the chemical interactions during adhesive formulation, demonstrating the successful integration of glyoxal and the improved adhesive properties of the lignin-based resin [27].

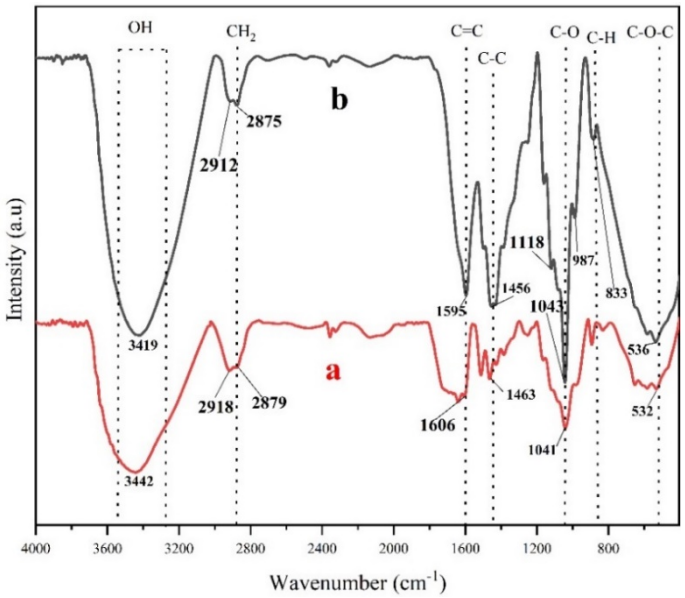

Figure 4 FT-IR spectra of lignin (a) and LG bio-adhesive (b).

In addition to the spectroscopic analysis, a water resistance evaluation was performed to determine the resin's performance under humid conditions. Following a 1-week immersion of the LG resin, combined with sawdust, in water, the resin maintained its structural integrity. It did not dissolve, thereby demonstrating its capacity to endure a humid environment (**Figure 6(a)**). Nevertheless, despite successfully passing the water resistance test under dry conditions, the LG bio-adhesive did not perform satisfactorily in the wet tensile strength assessment (boiling water test), which is designed to evaluate its efficacy in moist environments. The results shown in **Figure 6(b)** demonstrate that the LG bio-adhesive failed the wet resistance evaluation, as the wood samples bonded with it separated before the tensile test could be carried out. The wood samples submerged in boiling water exhibited separation after a duration of 2 h. Consequently, it is advisable to restrict the application of this bio-adhesive to interior wood products.

The failure of LG bio-adhesives in the wet tensile strength test may be attributed to the hydrolysis of glyoxal in boiling water, which compromises its bonding efficacy with lignin. Additionally, exposure to heat may precipitate thermal degradation of lignin, further impairing its adhesive properties. The thermal decomposition of lignin initiates at approximately 200 °C for native lignin, while isolated lignin exhibits a marginally higher onset temperature. Despite the study's use of a markedly lower temperature (100 °C), apparent degradation occurred. This suggests the presence of thermally labile impurities in the sample, exhibiting decomposition at temperatures significantly below lignin's typical degradation threshold [10].

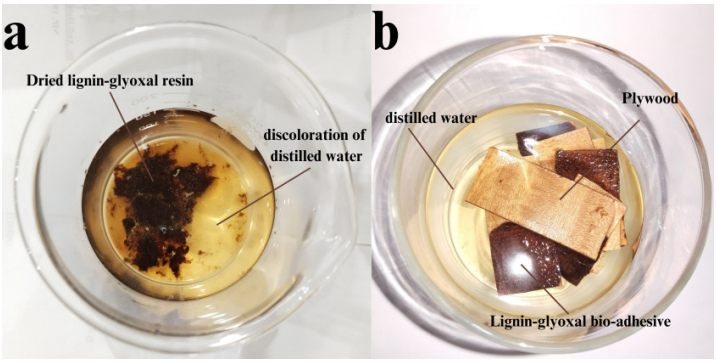

Figure 5 Dried LG resin after 1-week immersion in distilled water (water resistant test) (a) and bonded samples detached after the boiling water test (b) on LG bio-adhesive.

The dual impact of glyoxal hydrolysis and lignin degradation significantly undermines the bonding strength between lignin and wood. Moreover, the adhesive's propensity to absorb moisture in boiling water exacerbates the weakening of the bond, thereby increasing the likelihood of failure. Collectively, these factors contribute to the bio-adhesive's inability to meet the criteria for wet shear strength tests [3].

Conclusions

This study achieved its objectives with the following conclusions. Lignin isolated from bagasse using 16 % NaOH yielded 17.46 ± 3.61 %. FT-IR confirmed similar functional groups to commercial lignin, and GPC analysis showed Mn of 1068.0 g/mol, Mw of 1196.0 g/mol, and a PDI of 1.12. IDUS revealed a phenolic hydroxyl content of 0.35 ± 0.01 mmol/g. The LG 1:2 bio-adhesive exhibited a pH of 12, viscosity of 292.0 ± 1.53 mPa·s, solid content of 25.58 ± 0.13 %, and a gelation time of 10.0 ± 0.58 min, closely resembling PF adhesives. However, it failed the wet tensile test, limiting its use to interior wood products.

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