Bleached Rice Straw Lignin: Thermal-Chemical Properties and Its Application in Polyurethane-based Paper Coatings

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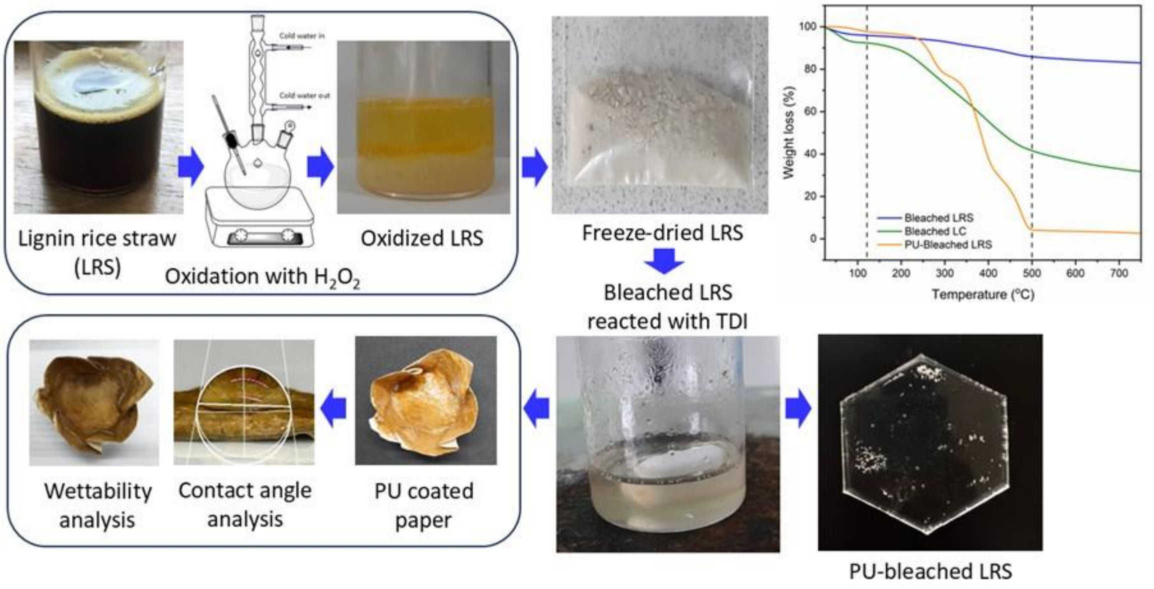
GRAPHICAL ABSTRACT



Bleached Rice Straw Lignin: Thermal-Chemical Properties and Its Application in Polyurethane-based Paper Coatings

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Rice straw lignin (LRS) tends to be dark in color, which makes it less appealing for material applications. Therefore, a bleaching process involving lignin oxidation is of interest. This study aimed to investigate the mechanical and chemical properties of bleached LRS and explore its potential application in PU-based paper coatings. LRS and commercial lignin (LC) were subjected to bleaching using 29% H_2O_2 through oxidation treatment. The bleached lignin was then used to prepare PU-based paper coatings. The effects of bleaching treatment on the functional groups, structural, and thermal properties of lignin, as well as the water resistance of the PU composites were assessed. The oxidation treatment resulted in a reduction in the phenolic hydroxyl content, methoxy content, antioxidant activity, and equivalent weight of lignin. However, LRS exhibited greater thermal resistance than did LC. The bleached LRS was successfully integrated with toluene di-isocyanate (TDI) to produce transparent polyurethane. This polyurethane was then applied as a coating for paper containers, which successfully held cold water for over 4 h without leaking, indicating its outstanding water repellency.

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Keywords: Rice straw lignin; Oxidation treatment; Polyurethane; Coating; Water resistance

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INTRODUCTION

Lignin is one of the most abundant biopolymers in nature, and its potential as a renewable resource has garnered significant interest in recent years. Lignin, which is derived from the cell walls of plants, provides structural support and contributes to resistance against biodegradation. However, despite its abundance, lignin remains underutilized, particularly in agricultural residues such as rice straw. Rice straw is known as a major byproduct of rice production. It contains substantial amounts of lignin. The staw is often disposed of as waste, including open-field burning, which causes environmental pollution, or limited low-value uses like composting and soil amendments. On the other hand, rice straw is now extensively utilized in various industrial applications, such as the production of adhesives, bioplastics, carbon fibers, and biofuels (Shi *et al.* 2024). In this context, it is important to address the missed opportunities in the use of rice straw lignin, particularly in the development of sustainable materials (Chelliah *et al.* 2023; Patel *et al.* 2023).

One of the promising applications of lignin is in the enhancement of polymer-based materials. Polyurethane (PU) is a widely used polymer known for its durability, flexibility, and resistance to chemicals and abrasion (Delavarde *et al.* 2024). Integrating lignin as a polyol source into polyurethane matrices can potentially reduce the reliance on petroleum-based materials while improving the overall properties of the polymer (Das and Mahanwar, 2020). However, the direct use of unmodified lignin in PU has the drawback of darkening the material, which diminishes its visual and aesthetic appeal (Wang *et al.* 2016; Zhang *et al.* 2020). Therefore, a bleaching process is necessary for rice straw lignin. Bleaching is commonly used for cellulose, as reported by Bakhsi *et al.* who treated kenaf pulp with 30% H_2O_2 and subsequently stored it in a water bath at 80 °C (Bakshi *et al.* 2024). A similar bleaching method with 30% H_2O_2 has also been applied to cotton fibers (Walawska *et al.* 2024). Additionally, bleaching with 0.5 to 3% NaClO has been used to oxidize celluloses from apple and kale pomaces at temperatures ranging from 60 to 80 °C (Wang and Zhao 2021). Unlike cellulose, which is a linear polymer composed of glucose units connected by β (1→4)-glycosidic bonds and exhibits high stability during oxidative treatments, lignin is a complex, amorphous polymer made of phenylpropanoid units (Douglas 1996; Wen *et al.*, 2013). This structural distinction makes lignin far more reactive to oxidative agents, as its aromatic rings and phenolic hydroxyl groups undergo significant chemical modification during oxidation (Vangeel *et al.* 2018). This oxidative bleaching of lignin not only enhances its visual appeal by removing color but also chemically modifies the lignin to make it more compatible with other materials. This modification is particularly effective for incorporating lignin into PU-based coatings.

Apart from good surface properties, paper coatings should possess excellent durability and some of them require moisture resistance. Therefore, this study examined the physical and chemical characteristics of bleached rice straw lignin and its utilization in polyurethane-based paper coatings. The objective was to assess the impact of bleaching treatment on the functional groups, structural, and thermal properties of lignin. Additionally, the performance of PU composites in water resistance tests was evaluated.

EXPERIMENTAL

Materials

The lignin used in this study was isolated from rice straw, which was extracted from black liquor, a byproduct of the alkali process. The rice straw lignin had a particle size of 60 mesh with a moisture content of approximately 5% w/w. Commercial lignin (LC) was obtained from Sigma–Aldrich (Sigma–Aldrich, USA). The LC was used as a reference to compare the properties of rice straw lignin (LRS) and evaluate its potential as an alternative material. The bleaching process for both LRS and LC was carried out using 29% H_2O_2 (Merck, Germany). Additionally, the bleaching process required a 5% w/w NaOH solution and 2 M HCl solution (Merck, Germany). The lignin product was then analyzed with DI water as the solvent, along with chemicals such as 1,4-dioxane, NaCl, absolute ethanol, 2,2-diphenyl-1-picrylhydrazyl (DPPH), tetrahydrofuran (THF), and toluene diisocyanate (TDI) for polyurethane synthesis.

Lignin Oxidation

Rice straw lignin was subjected to a bleaching process to lighten its dark color, utilizing an oxidation mechanism with H_2O_2. The oxidation process sequence has been patented in Indonesia under the patent number P00202407756 (Fatriasari *et al.* 2024). Initially, 1.25 g of lignin was dissolved in 10 mL of NaOH solution, heated to 70 °C, and stirred at 400 rpm *via* a magnetic stirrer. The H_2O_2 solution was then gradually added until the lignin solution lightened to a yellowish hue. This process was carried out for 2 h, followed by continuing the reaction at 80 °C and 400 rpm for an additional 3 h. The lignin was subsequently precipitated with HCl and allowed to settle overnight. The mixture was then centrifuged to separate the lignin, which was washed several times with DI water until the pH reached neutrality. The obtained lignin was then freeze-dried (Fig. 1(a)).

Polyurethane Synthesis and its Application to Container Paper

The bleached lignin can be utilized as a precursor for PU production (Fatriasari *et al.* 2024). In this process, 0.25 g of lignin was dissolved in 1.5 mL of tetrahydrofuran, followed by the addition of 1.5 mL of absolute ethanol. The mixture was stirred at 300 rpm for 30 min and then further stirred while heating at 45 °C for 15 min. TDI (0.3 g) was subsequently added, and the mixture was stirred at 45 °C for an additional 60 min (Fig. 1(b)). The resulting PU was directly applied manually onto the surface of the paper. Each batch of PU mixture was applied with a single coating on a surface area of 70.85 cm^2 with a thickness of 0.5 mm. The coated paper was then left to air-dry at room temperature for 12 to 24 hours. Once dried, the coating adhered to the paper, giving the surface a slightly stiff texture.

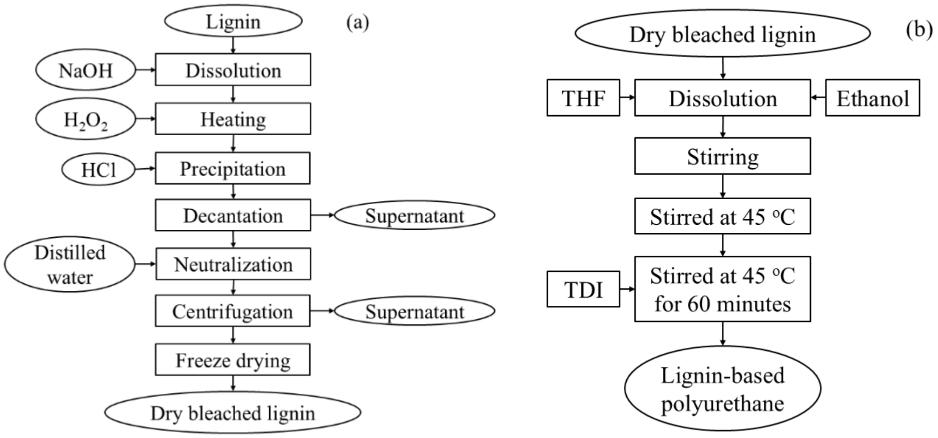


Fig. 1. Schematic diagram of the lignin oxidation process (a) and the process for producing polyurethane based on bleached lignin (b)

Methoxy Content and Phenolic Hydroxyl Content Analysis

The methoxy content of lignin was analyzed to quantify the methoxy groups in both the rice straw lignin and the bleached rice straw lignin samples. To perform this analysis, 0.101 g of lignin was dissolved in 1 mL of absolute ethanol, followed by the addition of 20 mL of a 1% w/w NaCl solution. Two drops of phenolphthalein were then added. Next, 5 mL of 0.25 N NaOH solution was added, and the mixture was allowed to stand for 30 min. Subsequently, 5 mL of 0.25 N HCl was added. The solution was then titrated with 0.1 N NaOH until a color change was observed (Hermiati *et al.* 2017). The methoxy content was calculated by Eq. 1.

$$\text{Methoxy content} = \frac{\text{concentration of NaOH in N x Volume of NaOH } in\ mL \text{ x } 3.1}{\text{sample weight in g}} \quad (1)$$

The phenolic hydroxyl content was analyzed in 20 mg samples of lignin. Each sample was treated with 10 mL of 1,4-dioxane and 10 mL of 0.2 M NaOH. The dissolution was enhanced via a vortex mixer for 60 seconds per sample. The solution was then filtered through a 0.45-µm nylon microfilter. Subsequently, 4 mL of the filtered solution was mixed with 0.2 M NaOH and analyzed for absorbance *via* a UV spectrophotometer across the range of 200 to 600 nm (Serrano *et al.* 2018).

Antioxidant Analysis

Antioxidant activity was analyzed via a DPPH radical scavenging assay (Bakshi *et al.* 2024). A 1 mg sample of lignin was dissolved in DMSO in a test tube wrapped with aluminum foil. A DPPH radical solution with a concentration of 0.1 mM in ethanol was prepared for the assay. As a control, 1 mg of BHT was separately prepared in 100 mL of ethanol. For each sample, 1 mL of the lignin solution was mixed with 2 mL of the DPPH solution and homogenized via a vortex mixer. The mixture was then covered with aluminum foil and incubated in a dark chamber for 60 min. The absorbance was measured with a UV–Vis double-beam spectrophotometer (UV-1800, Shimadzu, Japan) at a wavelength of 517 nm. Each sample was tested in duplicate, and the average value was obtained. The DPPH radical scavenging activity was calculated *via* Eq. 2.

$$\text{Radical scavenging activity} = \left[1 - \frac{\text{Abs}_{\text{sample}}}{\text{Abs}_{\text{control}}}\right] \text{x}100 \quad (2)$$

Equivalent Weight Analysis

A total of 0.5 g of lignin was added to 5 mL of absolute ethanol, followed by the addition of 1 g of NaCl powder. The mixture was then diluted with 100 mL of deionized water and allowed to stand until lignin precipitated. The pH of the solution was measured via a pH meter. The solution was subsequently titrated with 0.1 N NaOH until the pH reached 7.5 (Brauns 1952). The equivalent weight of lignin was calculated by Eq. 3.

$$\text{Lignin equivalent weight} = \frac{1000 \text{ x sample weight in g}}{\text{NaOH volume in ml x NaOH concentration in N}} \quad (3)$$

CHO/N, FTIR and Pyrolysis-GCMS Analysis

A 0.5 mg lignin sample was prepared for elemental analysis using a CHNSO analyzer (LECO CHN-2000, St. Joseph, MI, USA). Fourier transform infrared spectroscopy (FTIR) was employed to examine the lignin samples. FTIR analysis was conducted within a scanning range of 4000 to 400 cm^{-1} at 25 °C using the attenuated total reflectance method (PerkinElmer Corporation, Waltham, MA, USA). Additionally, 10 mg of lignin was used to identify the compounds present in the lignin sample *via* pyrolysis-GCMS via the QP2020 NX system (Shimadzu, Japan). The analysis was performed for 60 min with a column temperature of 50 °C and an injection temperature of 250 °C. The column pressure was maintained at 20 kPa, and the flow rate was set at 0.61 mL/min. The results from FTIR and pyrolysis-GCMS were processed with OriginPro 2024 software.

Thermogravimetric Analysis

A 6 mg sample of powdered lignin was placed in an aluminum crucible for thermal stability analysis over a temperature range of 25 to 750 °C. The heating rate was set at 10

°C/min, with nitrogen gas used as the carrier. The analysis was conducted with a Perkin Elmer TGA 4000 instrument (Perkin Elmer, Waltham, MA, USA).

Surface Wettability Analysis

Surface wettability was analyzed through optical contact angle measurements using a Dino-Lite Pro Digital Microscope (AnMo Electronics Corporation, Taiwan) and the Dino-Lite Capture application (Version 2.0) to record the surface water contact angle over a 60-minute period. The video recordings were segmented at 0, 5, 10, 15, 30, and 60 minutes, and the contact angles were subsequently calculated using ImageJ software equipped with the Drop Snake and Contact Angle plugins (Daulay *et al.*, 2024).

RESULTS AND DISCUSSION

Chemical Characteristics of Lignin Before and After Bleaching Treatment

Table 1 shows that LRS before the bleaching process had a phenolic hydroxyl content of 4.63 mmol/g, which was lower than that of LC (6.68 mmol/g). The presence of phenolic hydroxyl groups in lignin allows for the occurrence of diverse chemical reactions, including the ability to scavenge free radicals. The phenolic hydroxyl groups have the ability to donate electrons, which accounts for the high antioxidant capacity of LRS. Nevertheless, following the bleaching process, LRS was observed to lack any measurable phenolic hydroxyl groups, while still maintaining a significantly reduced antioxidant capacity. These findings suggest that the absence of phenolic hydroxyl groups significantly diminishes the ability of lignin to function as an antioxidant (Cesari *et al.* 2019; Lu *et al.* 2022). The antioxidant capacity of lignin fractions correlates with their phenolic content~~,~~ typically measured as gallic acid equivalents (GAE). Lignin fractions with high phenolic contents exhibit strong antioxidant activity. The presence of various functional groups, such as methylene (-CH_2-) and carbonyl (C=O) groups in guaiacyl and syringyl units, also influences the reactivity of lignin as an antioxidant. Similarly, ortho substitution with methoxy groups (-OCH_3) can alter the chemical properties of lignin (Lourençon *et al.* 2021).

The methoxyl content in both LRS and LC was also relatively high, at 37.39% and 24.89% (Table 1), respectively, suggesting the predominance of syringyl and guaiacyl units (Sun and Tomkinson 2002; Rosado *et al*. 2021). While methoxy groups do enhance the stability of compounds, their impact on antioxidant capacity is less direct compared to phenolic hydroxyl groups in radical reactions. Methoxy and phenolic hydroxyl groups contribute to antioxidant activity through distinct yet complementary mechanisms. Phenolic hydroxyl groups transfer an electron to scavenge radicals. The resulting unpaired electron becomes delocalized over the aromatic benzene ring through resonance, significantly reducing the reactivity of the radical. Methoxy groups further enhance this stabilization by donating electron density into the aromatic system, strengthening the delocalization effect and making the phenoxyl radical more stable. The combination of these two functional groups often results in a synergistic effect, where their combined actions lead to more effective radical scavenging compared to the presence of only one functional group (Priyadarsini *et al.* 1998; Chen *et al.* 2020; Qin *et al.* 2020). Additionally, the bleaching process impacted the equivalent weight of the lignin samples. As shown in Table 1, a significant decrease in the equivalent weight was found after the oxidation of both the bleached LC and the bleached LRS. Lignin with a high-weight equivalent typically has a greater density of reactive sites, which enables it to participate in radical reactions, such as antioxidant activity. Conversely, when phenolic hydroxyl groups are not detected, the number of active sites decreases, leading to a drastic reduction in antioxidant activity. Although this cannot be stated definitively, the oxidation of lignin appeared to reduce its structural complexity, leading to the conversion of longer lignin polymer chains into shorter chains. The reduction in structural complexity due to oxidation suggests the cleavage of ether bonds and aromatic rings, converting larger lignin macromolecules into smaller oligomers (Fernandes *et al.* 2019). These smaller fragments may retain some functional groups but lack the density of active sites necessary for significant antioxidant activity.

Table 1. Chemical Properties of LRS and the Bleached LRS

Properties	**LRS**	**Bleached LRS**	**LC**	**Bleached LC**
ph-OH (mmol/g)	4.63 ± 0.20	n. d.	6.68 ± 0.90	n. d.
Methoxy content (%)	37.39 ± 0.11	n. d.	24.89 ± 0.09	n. d.
Antioxidant content (%)	89.18 ± 0.65	0.27 ± 1.05	80.77 ± 0.70	3.15 ± 0.95
Equivalent weight (meq/g)	1380	269.85	5016	310.33
Elemental analysis:				
Carbon (%)	51.62 ± 0.66	16.01 ± 0.10		
Hidrogen (%)	6.23 ± 0.12	3.38 ± 0.19		
Nitrogen (%)	2.49 ± 0.02	0.73 ± 0.03		
Oxygen (%)	39.67 ± 0.53	79.87 ± 0.32		

*

Table 2. Py-GCMS Results of Bleached LRS and Bleached LC

Compound group	**Bleached LRS**		**Bleached LC**	
	Compound name	**Abundance (%)**	**Compound name**	**Abundance (%)**
Carboxylic acid	Dodecanoic acid	0.58	Acetic acid	0.96
	Tetradecanoic acid	1.05	Tetradecanoic acid	0.38
	n-Hexadecanoic acid	15.09	n-Hexadecanoic acid	3.34
	cis-9-Tetradecenoic acid, isobutyl ester	0.66	Oleic Acid	7.4
	Octadecanoic acid	0.42	Octadecanoic acid	1.86
	Pentadecanoic acid	0.47	δ^8(14)-Isopimaric acid	3.04
			Isopimaric acid	1.12
			1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, [1S-(1. alpha.,4a. alpha., 10a.beta)]	8.6
Sugar derivatives with hydroxyl groups and	1,6-anhydro-beta-D-glucopyranose	14.39%	Ethyl p-hydroxybenzoate	0.78%

Compound group	**Bleached LRS**		**Bleached LC**	
	Compound name	**Abundance (%)**	**Compound name**	**Abundance (%)**
ether bonds				
Aromatic compounds	Pyridine	0.31%	Toluene	0.62%
	Benzyl methyl ketone	0.53%	Phenol	1.16%
	o-Xylene	0.35%	2-Methylphenol	0.68%
	Diethyl Phthalate	2.32%	p-Cresol	1.46%
			2-methoxy-Phenol	9.89%
			2,4-dimethyl-Phenol	0.72%
			2-Methoxy-5-methylphenol	0.7%
			2-Methoxy-5-methylphenol	5.38%
			Catechol	3.38%
			3,4-Dimethoxytoluene	0.77%
			1,2-Benzenediol, 3-methoxy-	0.5%
			Phenol, 4-ethyl-2-methoxy-	2.98%
			Phenol, 2-methoxy-4-propyl-	1.23%
			2,4-Dimethoxybenzeneethanamine	1.43%
			Apocynin	1.05%
			Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	1.35%
			2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.76%
			1-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.42%
			Benzenepropanol, 4-hydroxy-3-methoxy-	1.41%
			Methyl dehydroabietate	0.44%
			Phenanthrene, 2,5-dimethyl-	0.37%
			3,4-Divanillyltetrahydrofuran	1.26%
			[1,1'-Biphenyl]-4,4'-diol, 3,3'-dimethoxy-	1.56%
			Acetic acid, 7-hydroxy-1,3,4,5,6,7-hexahydro-2H-naphthalen-4a-ylmethyl ester	0.59%
			1,1'-Biphenyl, 6-hydroxy-2',3',4'-trimethoxy-	2.05%
			Methyl dehydroabietate	1.16%
			2-(3-Isopropyl-6a,10b-dimethyl-7-methylene-dodecahydro-benzo[f]chromen-8-yl)-1-phenyl-ethanone	0.56%

Compound group	**Bleached LRS**		**Bleached LC**	
	Compound name	**Abundance (%)**	**Compound name**	**Abundance (%)**
			Dibenz[d,f]cycloheptanone, 2,3,9-trimethoxy-	0.83%
			3,4-Divanillyltetrahydrofuran	0.74%
C-H bond of alkenes	1-Decene	0.69%	2-Methoxy-4-vinylphenol	6.18%
	1-Dodecene	0.6%	Eugenol	1.46%
	1-Octadecene	0.42%	Benzene, 4-ethenyl-1,2-dimethoxy-	0.2%
	Heptadecane	0.23%	trans-Isoeugenol	1.98%
	1-Heptadecene	0.42%	Benzene, 1-(1-butenyl)-4-methoxy-, trans-	0.28%

The carbon content of LRS before bleaching was 51.6%. Treatment with H_2O_2 results in the oxidation of LRS, reducing the carbon content to 16.0%. This significant reduction indicates extensive oxidation, which likely leads to the formation of more oxygenated functional groups, such as carboxyl (-COOH) and carbonyl (C=O) groups. Oxidation is a well-established method for increasing the hydroxyl content of lignin, thereby enhancing its reactivity and versatility for various applications. Mancera *et al.* reported that the oxidation of sugarcane bagasse lignin using hydrogen peroxide in an acidic medium significantly increases the presence of carboxylic groups, as evidenced by higher C=O levels (Mancera *et al.* 2010). The oxidation process also decreases the levels of hydrogen and nitrogen while increasing the oxygen content. The rise in oxygen facilitates the binding of more oxygen within the lignin and leads to the formation of new compounds such as carboxylic acids, aromatic compounds, and sugar derivatives containing hydroxyl groups or ether linkages (Abdelaziz *et al.* 2022). According to the py-GCMS analysis, carboxylic acids are the predominant compounds in the oxidized LRS. Moreover, compared to oxidized LRS, oxidized LC contains more carboxylic acid compounds and aromatic compounds (Table 2). Although these changes significantly reduce its antioxidant activity, they enhance the chemical compatibility between oxidized lignin, which is rich in aliphatic hydroxyl groups, and the isocyanate groups (-NCO) of TDI. This reaction forms strong urethane bonds (-NHCOO-) through nucleophilic addition. Such chemical interactions increase cross-linking density, thereby improving the mechanical and thermal properties of the resulting polyurethane product.

Effects of Oxidation Treatment on the Structure and Stability of Lignin

Figure 2 shows the FTIR spectra of LRS before and after oxidation. For the untreated LRS, the peak at 1512 cm^{-1} represents aromatic C=C vibrations, which are indicative of guaiacyl and syringyl units of lignin. The peak at 1426 cm^{-1} corresponds to aromatic C–H in-plane stretching vibrations and C–H deformation in methyl groups (Karmanov and Derkacheva 2013; Ajjan *et al.* 2015). Similar peaks were observed in LC, suggesting that the basic lignin structure was consistent across both sources. The oxidation treatment introduced functional group changes in LRS. The peak at 1512 cm^{-1} became significantly weaker and nearly disappeared, whereas the peak at 1077 cm^{-1} indicated changes in ether bonds (C-O-C) from glycosidic linkages in polysaccharides (Zhang *et al.* 2022). This peak may arise from ether groups or the stretching vibrations of C-O bonds (Luo *et al.* 2010), which are also present in compounds such as 1,6-anhydro-beta-D-glucopyranose (Table 2).

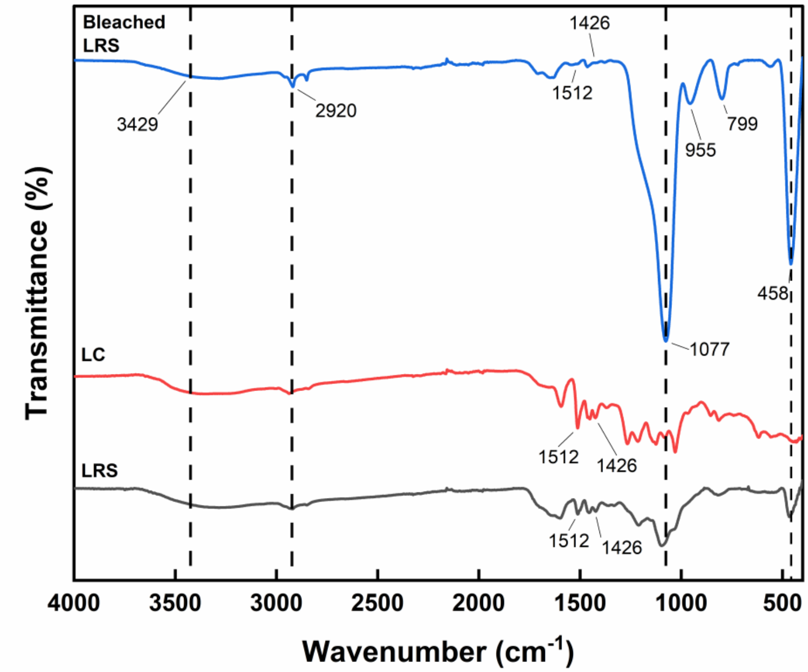


Fig. 2. The FTIR results revealed that bleached lignin rice straw, lignin rice straw and commercial lignin were present.

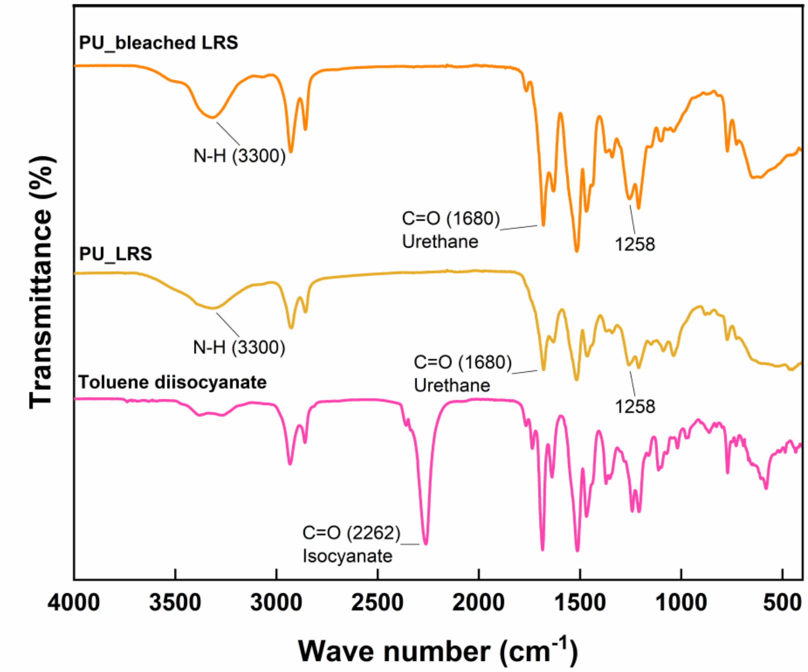


Fig. 3. FTIR results of PU from bleached lignin rice straw, lignin rice straw and toluene diisocyanate

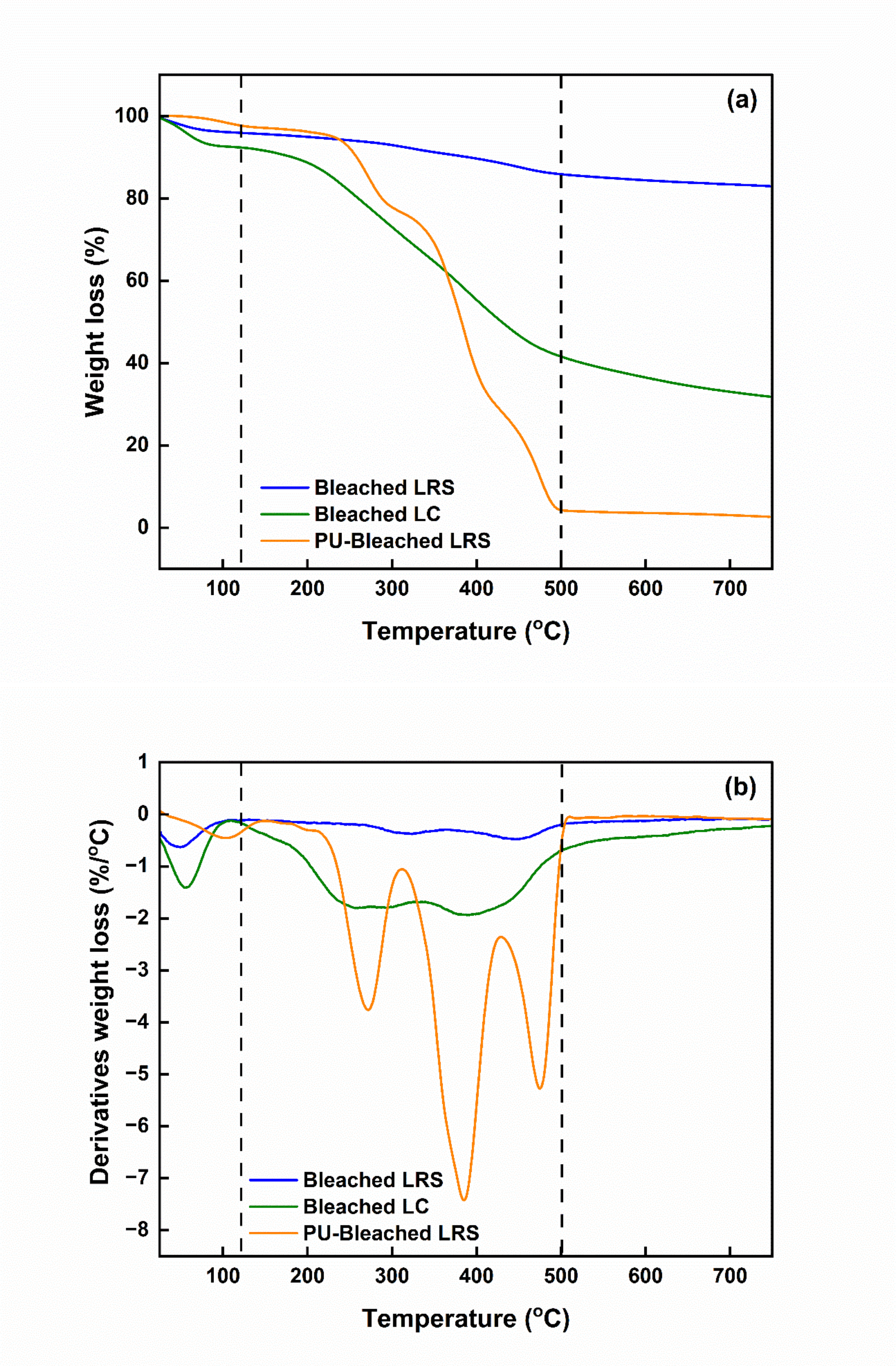


Fig. 4. TGA results of bleached LRS, bleached LC and PU with bleached LRS: (a) weight loss and (b) derivative weight loss

The peak at 955 cm^{-1} is associated with C-H out-of-plane deformation in the aromatic ring. The peak at 799 cm^{-1} is related to the vibration of SiO_2 (Nazopatul *et al.* 2018). The strong peak at 458 cm^{-1} is associated with the Si–O–Si bending region (Do *et* *al.* 2020). Table 2 shows that the main products of oxidation included carboxylic acids, sugar derivatives with hydroxyl groups and ether bonds, aromatic compounds, and the C–H bonds of alkenes.

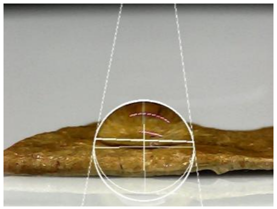
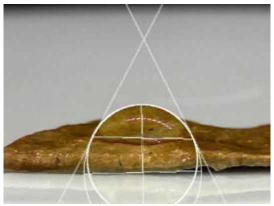
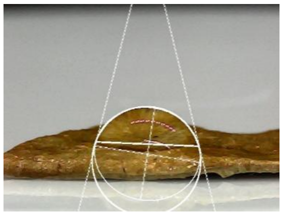
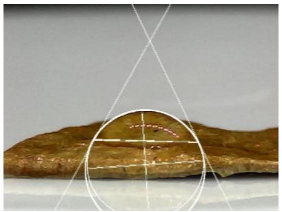
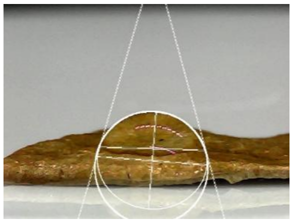
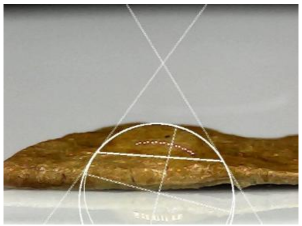
The PU was successfully synthesized *via* oxidized LRS, and a transparent PU was obtained, as shown in Fig. 5 (a). The success of the reaction was determined by the formation of CO_2 bubbles when the oxidized LRS solution was reacted with TDI (Fig. 5 (d)). Figure 3 shows the functional groups formed in TDI and PU from lignin before and after oxidation. TDI exhibited a sharp peak at 2262 cm^{-1}, corresponding to the stretching vibration of the isocyanate group (-N=C=O) (Sultan *et al.* 2012). The polyurethane derived from LRS shows a band at 1680 cm^{-1}, which is attributed to the stretching vibration of the carbonyl group (C=O) in the urethane linkage (Turan 2021). The band at 1258 cm^{-1} is associated with the stretching vibrations of the C–N bond attached to the carbonyl group (C=O) and the C–O vibrations from ester or ether groups (Bahadur *et al.* 2016). The broad band at 3300 cm^{-1} indicates the stretching vibration of the N–H bond (Asefnejad *et al.* 2011; Lubis *et al.* 2020). Additionally, the PU synthesized from oxidized LRS exhibited the same peaks as the PU prepared from non-oxidized LRS did, indicating that PU can be successfully synthesized from oxidized LRS.

On the basis of the TGA results (Fig. 4), compared with oxidized LC, oxidized LRS exhibited greater thermal stability. The data revealed that between 25 and 120 °C, oxidized LRS resulted in a mass loss of 3.87%, whereas oxidized LC resulted in a mass loss of 7.51%. In the temperature range of 120 to 500 °C, the mass loss for oxidized LRS remained lower at 10.5%, whereas it was 55.0% for oxidized LC. During the final degradation phase, the mass losses for the oxidized LRS and LC were 3.3% and 23.4%, respectively. Overall, the oxidized LRS retained 2.5 times more char than the oxidized LC did. This indicates that the oxidation of LRS led to the depolymerization of lignin, resulting in the formation of aromatic compounds, carboxylic acids, and SiO_2 minerals. These minerals contribute to the enhanced thermal resistance of the bleached LRS. Rice straw is known to have an ash content of up to 16% (Chaloupková *et al.* 2021), with silica as the dominant component. This composition may contribute to its resistance to heat (Liehr *et al.* 1987). This can be supported by the FTIR spectra of the bleached LRS, in which the peaks at 799 cm^{-1} and 458 cm^{-1} are clearly related to the presence of SiO_2 and Si-O-Si.

Surface Wettability of Polyurethane-Coated Paper

The results of the contact angle analysis are detailed in Table 3. The data indicate that at 0 min, the contact angle of the water droplet was 79.8°, and it gradually decreased to 54.7° at 60 min These results demonstrate that the polyurethane-coated paper from bleached lignin had water-resistance properties. Water droplets applied to the surface did not spread quickly, highlighting the hydrophobic nature of the paper, which can be attributed to the presence of nonpolar surface groups (Huhtamäki *et al.* 2018). Compared to non-oxidized LRS-based polyurethane, the bleached LRS-based polyurethane exhibited a higher contact angle over an equivalent duration. Nurcahyani *et al.* reported that the contact angle of non-oxidized lignin-based PU coatings decreased from 86.2° to 42.1° at 16 min (Nurcahyani *et al.* 2024). However, theoretically, a hydrophobic surface is characterized by a contact angle greater than 90° (Danish 2020), suggesting that the coating in this study falls into the category of a hydrophilic surface. This hydrophilic characteristic is attributed to the presence of free hydroxyl groups remaining after the polyurethane synthesis (Yang *et al.*, 2011).

Table 3. Contact Angle Analysis Results

Contact Angle Changes on Coated Paper	Remarks	Contact Angle Changes on Coated Paper	Remarks
	At time: 0 min Theta Left: 81.2° Theta Right: 78.5° Theta C: 79.8°		After 15 min Theta Left: 67.1° Theta Right: 65.9° Theta C: 66.3°
	After 5 min Theta Left: 71.1° Theta Right: 70.9° Theta C: 71.0°		After 30 min Theta Left: 61.8° Theta Right: 63° Theta C: 61°
	After 10 min Theta Left: 71.0° Theta Right: 70.3° Theta C: 70.7°		After 60 min Theta Left: 57.4° Theta Right: 54.8° Theta C: 54.7°

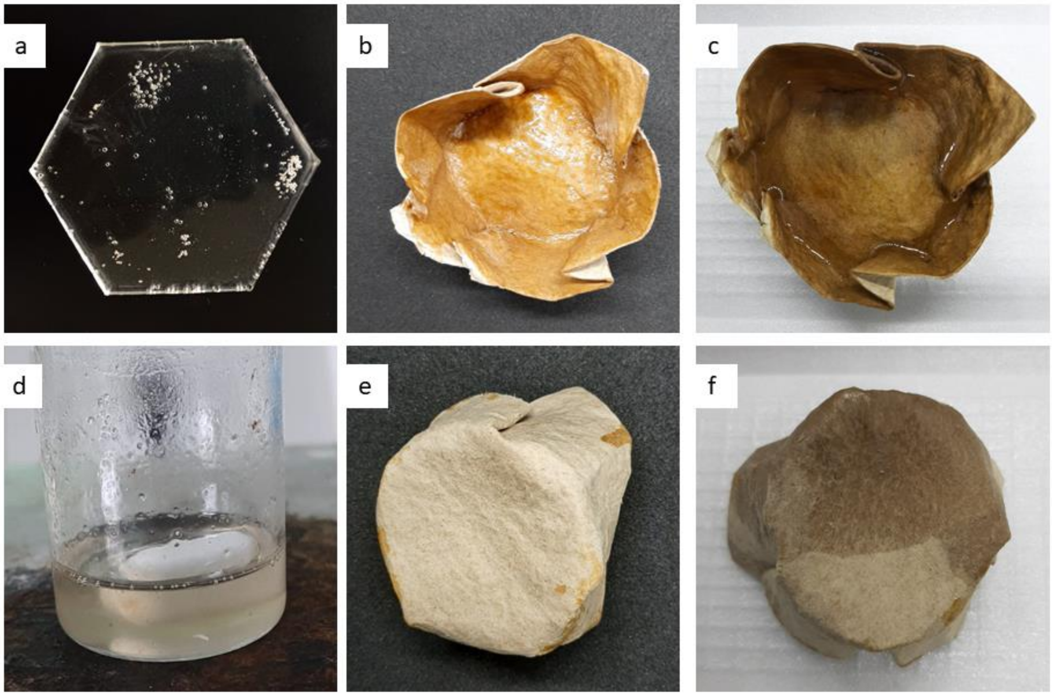


Fig. 5. (a) PU with bleached LRS, (b) paper container coated with PU, (c) water resistance measurement, (d) PU synthesis with bleached LRS, (e) back side of the container before wettability test, (f) back side of the container after 200 h

These hydroxyl groups enhance the material's affinity for water by attracting water molecules through hydrogen bonding. This interaction reduces the interfacial energy between water and the polyurethane surface, thereby accelerating the wetting process. The greater the exposure of hydroxyl groups on the surface, the higher the tendency of the polyurethane surface to absorb water, which subsequently results in a lower water contact angle. Further testing involved evaluating the water resistance of the PU-coated paper formed into a container. The results revealed that water was retained within the containers for up to 200 h, as shown in Fig. 5 (c) and (f). Meanwhile, the non-oxidizing polyurethane coating from LRS provides cold water resistance for up to 9 hours (Nurcahyani *et al.* 2024). The enhanced performance may be attributed to the bleaching process, which could influence the interaction between the hydroxyl-rich substrate and the polyurethane matrix. Unlike before water was applied, the PU-coated container still appeared dry and clean (Fig. 5 (b) and (e)). The high contact angle indicated reduced surface energy of the paper due to the polyurethane coating, thereby affecting the adhesion properties of the paper to water.

Despite these promising results, there are several limitations to consider. This study focused on a specific bleaching process and PU formulation, which may not be generalizable to all lignin types or polymer systems. Additionally, the long-term performance and environmental impact of these coatings under diverse conditions have not been examined. Further research is needed to optimize the oxidation process under different conditions and with other materials to ensure compatibility with other types of lignin.

CONCLUSIONS

1. This study has successfully demonstrated the potential of bleaching lignin from rice straw (LRS) in enhancing polyurethane (PU)-based paper coatings.
2. The oxidized LRS contained higher levels of hydroxyl groups, aromatic compounds, carboxylic acids, and silica minerals. However, some chemical-related properties, such as antioxidant and methoxy contents and equivalent weight, were pronounced after the oxidation of lignin.
3. The bleached LRS effectively integrated with toluene di-isocyanate (TDI) to form a transparent PU coating with high thermal resistance. This coating exhibited impressive water resistance, withstanding exposure for up to 200 h.

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