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Preparation of Formaldehyde-Free Bio-Based Plywood Adhesive Using Polyvinyl Alcohol and DES-Extracted Lignin Composite

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Abstract: The purpose of this paper is to develop a preparation method for a formaldehyde-free, low CO2 emission, and sustainable plywood adhesive. Previous research approached VOC emissions in formaldehyde-based adhesives via additives or VOC absorbents but failed to completely eradicate VOC emission. Lignin, as an abundant biomass feedstock, is a strong candidate for formaldehyde-free sustainable adhesive research. In this paper, three choline chloride-based (ChCl) Deep Eutectic Solvents (DES) were prepared for lignin extraction. ChCl and lactic acid showed the highest lignin solubility at 41.3% weight percentage and was used to extract lignin. The extracted lignin quality was verified using nuclear magnetic resonance. Lignin-polyvinyl alcohol adhesive was then prepared and hot-pressed to produce plywood, which were then subjected to mechanical and rheological testing. The end result was a plywood product that met GB/T 17657-2013 Chinese national standards with adhesive strength of 0.7 MPa. We hope this paper can act as reference for future works concerning formaldehyde-free adhesives.

1. Introduction

Indoor VOC pollution caused by plywood-based building materials, such as particleboards and fiberboards, has been an ever-lasting concern for household health concerns and environmental concerns[1]. Currently, formaldehyde-based resins (urea-formaldehyde (UF), phenol-formaldehyde (PF), melamine-formaldehyde (MF)) are widely used due to their low-cost and high mechanical performance. However, such adhesives cause high levels of VOC emissions[2]. Urea-formaldehyde, the most widely used adhesive for indoor applications, can pollute 7.8 million m3 of atmosphere per square meter of particleboard produced[3]. The health concerns are well-known: exposure to high formaldehyde concentrations is associated with respiratory irritation and allergies[4,5].

Previous research employing strategies such as nanoparticle reinforcement or the use of formaldehyde scavengers has demonstrated notable improvements. In particular, the incorporation of nanoparticles into formaldehyde-based adhesives has been shown to enhance thermal stability and reduce rate of decomposition. Yu et al, 2017[6] investigated nano titanium oxide-β-cyclodextrin (nano-TiO2-β-CD) microcapsules in UF, which increased degradation temperature by 90°C. Zhang et al, 2013[7] report a maximum decrease in formaldehyde emission by 13.0% below 1.5% nanocrystalline cellulose modifications. Dukarska et al, 2016[8] found surface modification with nano-SiO2 and (3-aminopropyl) triethoxysilane to aid thermal resistance of UF-composites. According to de Cademartori et al, 2019[9], 2% alumina modification can reduce formaldehyde emission by 14%. However, such solutions require substantially higher manufacturing costs, produce more pollution, and do not completely eradicate indoor formaldehyde emission.

In comparison, biopolymer-based adhesives, such as starch, cellulose, and proteins, achieved little-to-no VOC emission while having the advantage of natural raw materials providing potential environmental benefits along with prospects of high mechanical performance. Ferguson et al, 2014[10] produced M-2-grade commercial particleboards based on soy protein according to American National Standards Institute. Jiang et al, 2019[11], produced a strong wood (bonding strength: 7.77 MPa) adhesive based on cassava starch and polyvinyl alcohol. Zhu et al, 2024[12] created an adhesive with bonding strength of 2.41 MPa using animated alkali lignin and epoxy-terminated hyper-branched polyester. Islam et al, 2021[13] investigated bone-based adhesives as well.

Among the biopolymers, lignin shows exceptional potential. Lignin is the second most abundant biopolymer, existing in cell walls of plants, and as a common waste product in the paper industry as black liquor[14]. Research using lignin in lieu of phenol showed low costs and less environmental pollution[15]. Attempts on formulations of lignin-based adhesives have been carried out before. Lignin-epoxy formulations have been shown by Gutierrez et al, 2018[16] to be viable alternatives to traditional adhesives, and Siahkamari et al, 2022[17] have attempted to replace traditional PF resins entirely with lignin and glyoxal, creating a final product with impressive dry strength (3.9 MPa). Hu et al., 2025[18] attempted a similar replacement with lignin and glutaraldehyde, achieving a lower dry strength but a higher wet strength. Blending lignin with polymers is a convenient way to utilize lignin by disrupting its strong interactions. Polyvinyl Alcohol (PVA) is known to be capable of good interaction with lignin's hydroxyl groups due to PVA itself having hydroxyl groups as well[19]. PVA also has high degradability and high adhesive strength[20], making it a good candidate for sustainable adhesives. But, its hydroxyl groups mean poor moisture resistance. Hence, PVA needs modifications of a hydrophobic material or crosslinking to combat hydrolysis and other erosive effects[21,22]. Crosslinking agents are typically glutaraldehyde[23] and glyoxal[24], with glutaraldehyde offering better crosslinking efficiency[25], most notably with cellulose[26]. It is therefore feasible to use it for similar applications in lignin. A PVA-lignin composite adhesive is therefore a solution worth considering.

Deep Eutectic Solvents (DESs) are biodegradable and cheap to synthesize, and have solubility, low vapor pressure, recyclability, and a tunable range of physical properties[27], making them the ideal way to extract lignin in an environmentally-friendly and cheap manner. DES usage in lignin extraction has garnered remarkable interest due to its capacity in dissolving lignin[28-30]. More specifically, choline chloride-based DESs present high solubility and selectivity for phenolic compounds[31]. They are also found to be eco-friendly, non-toxic, and preserve bioactivity of target compounds[32]. Hence, ChCl-DESs are the main methods for lignin extraction in this paper.

Therefore, in this paper, we investigate a low-cost, industrial-standard synthesis scheme of lignin-based formaldehyde-free adhesive, from extraction using DES to a lignin-polyvinyl alcohol product.

2. Methodology

2.1 Chemicals and materials

Dried corn straw was obtained locally, then mechanically ground to size 40-60 mesh before pre-extracting with toluene/ethanol (2:1, v/v) for 6h to remove wax. Lignin alkali was purchased from Energy Chemical Anhui Senrise Technology Co, Ltd. Choline Chloride (ChCl), glycerol (Gly), and glutaraldehyde (GA) were purchased from Innochem Technology Co., Ltd. (Beijing, China). Lactic acid (LA) was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Urea was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polyvinyl alcohol 0588 low-viscosity (PVA-205) and potassium persulfate were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

2.2 DES preparation and determining lignin solubility

Three binary DESs (ChCl: LA, ChCl: Gly, ChCl: Urea) were prepared by mixing hydrogen bond acceptor (HBA) ChCl in a 1:2 molar ratio with hydrogen bond donors (HBD) LA, Gly and Urea respectively. The samples were heated and stirred at 80°C until a transparent, homogeneous liquid was formed.(Table 1)

Table 1 Ideal masses of ChCl and different HBDs in preparation of DES

Solvent	**ChCl / g**	**HBD / g**
ChCl-LA	10.000	14.190
ChCl-Gly	10.000	13.130
ChCl-Urea	10.000	8.517

For each kind of DES, a two-step method was used to determine lignin solubility in DES.

1) Rough Testing of Lignin Solubility in DES

3 samples of DES of mass 1.0g are heated to 60°C, 70°C, 80°C respectively under stirring at 400rpm. 30mg lignin is added to each sample in 2h intervals until full dissolution could not be reached between intervals. We record the rough quantity of lignin dissolved.

2) Accurate Testing of Lignin Solubility in DES

3 samples of DES of mass ~1.0g are heated to 60°C, 70°C, 80°C respectively under stirring. We record the masses of DES used as m_1. We dissolve 90% mass of lignin dissolved in 3.1. Then, after uniform temperature is reached, 5 mg of lignin is added to each sample in 2h intervals until full dissolution could not be reached between intervals. We record total mass of lignin dissolved as m_2. The solubility of lignin in weight percentage could be determined by the equation below:

$$\text{Lignin wt.\%} = \frac{m_2}{m_1 + m_2} \times 100\%$$

2.3 Lignin extraction using DES

We take the DES with the greatest solubility from 3. We prepare a 1:10 mass ratio mixture of CS and DES, with heating at 120°C and stirring at 400 rpm for 6 hours. We record the mass of CS as m0. We wash the solution with a 1:1 volume ratio of ethanol. The resulting solution was centrifuged at 10,000 rpm for 15min.

We isolate clear ethanol solution and leave in vacuum oven overnight at 60 ℃. We stir all ethanol solution remaining in 1:10 volume ratio of water for one day. We leave in fridge at 4°C overnight. We dry and weigh the remaining sample to obtain extracted lignin mass m_l. The final lignin content is calculated by equation:

$$\%\text{content} = \frac{m_l}{m_0} \times 100\%$$

2-Dimensional Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance (2D HSQC NMR) is a good method to distinguish proton-carbon relationships and has been widely recognized as one of the most reliable methods in characterizing lignin structure. 2D HSQC Nuclear magnetic resonance (NMR) spectra of the final sample of lignin were performed on a Bruker Avance 400 MHz spectrometer, with ^{1}H NMR spectra on the F2 axis and ^{13}C NMR spectra on the F1 axis.

2.4 Preparing lignin-PVA composite formaldehyde-free adhesive

Two samples of lignin-PVA composites are prepared using the same method and in accordance with the parameters shown below in Table 2.

Table 2 Parameters for preparation of adhesive sample 1 and 2

Sample	**Mass of PVA-205 / g**	**Oxidation temperature/ ℃**	**Oxidation time / minutes**	**Mass of lignin /g**
1	25	50	60	13
2	20	60	70	5

We dissolve the corresponding mass of PVA-205 in 100 ml of water. After stirring, we heat to 90°C until the PVA-205 is completely dissolved and cool to oxidation temperature. We add potassium persulfate of 2.5% the mass of PVA-205 used and oxidize for the corresponding oxidation time.

We dissolve the corresponding mass of lignin in 30 ml of 6% mass percent sodium hydroxide solution, and remove foam-like impurities. We add it to sample 1. We add glutaraldehyde of 5% mass of lignin used as a cross-linking agent, then react at 70°C and 400 rpm for 60 minutes. We cool to room temperature after the reaction completes.

2.5 Characterizing mechanical performance of adhesives

(1) Fabrication: We use two samples of lignin-based formaldehyde-free adhesive to fabricate three-layered poplar plywood boards. We apply 250 g/m^2 per surface. We hot press after leaving to settle for 30min.

Hot-pressing process: hot-pressing at temperature of 135°C and pressure of 1.0 MPa for 15min. Hot-pressed plywood was first left in a ventilated environment at 25°C for 24h, then subjected to adhesion strength tests.

(2) Adhesion strength testing: We adhere to plywood tests defined by article 4.15-I of Chinese Standard GB/T 17657-2013 “Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels”. Each set plywood sample has 12 test samples with length of (100 ±1) mm, width of (25 ±1) mm.

(3) Dry strength test: samples were clamped on a Universal Testing Machine (UTM) (AGS-X, Shimadzu) to conduct dry strength test.

(4) Rheology curve testing utilizes rheometers. Samples are subjected to controlled external forces and simultaneously measured for deformation.

Range for shear rate is 0.1-1000 s^{-1}, with rapid scanning and even progression to ensure sample responds predictably and stably to shear rate.

3. Results and discussion

3.1 Solubility of Lignin

The solubility of lignin in ChCl-Gly, ChCl-LA, and ChCl-Urea is shown in table 3. ChCl-LA, ChCl-Gly, and ChCl-Urea are chosen for a wide range of pH in the HBA, with LA having a pH of about 3, glycerol with slight acidity of about 6.7, and urea being slightly basic with pH of slightly above 7.

From figure 1, at reaction temperatures of 60°C, 70°C, and 80°C, ChCl-LA consistently exhibited the best lignin solubility at weight percentages of 39.8%, 41.3% and 41.5% respectively, with ChCl-Gly following at 35.9%, 37.5%, and 37.9%. This implies that ChCl-LA and ChCl-Gly are both stable DESs and can disrupt polymerized lignin's hydrogen bonds in a wide temperature range. ChCl-Urea showed the worst lignin solubility at 60℃ at around 150mg of lignin added.

Table 3 Determining solubility in DES at 60℃, 70℃, and 80℃.

Temperature / ℃	**DES**	**DES mass / g**	**Lignin dissolved / mg**	**Lignin solubility / %**
60	ChCl-LA	1.000	660	39.8
60	ChCl-Gly	1.000	560	35.9
60	ChCl-Urea	1.000	150	13.0
70	ChCl-LA	1.000	705	41.3
70	ChCl-Gly	1.000	600	37.5
70	ChCl-Urea	1.000	580	36.7
80	ChCl-LA	1.000	710	41.5
80	ChCl-Gly	1.000	610	37.9
80	ChCl-Urea	1.000	590	37.1

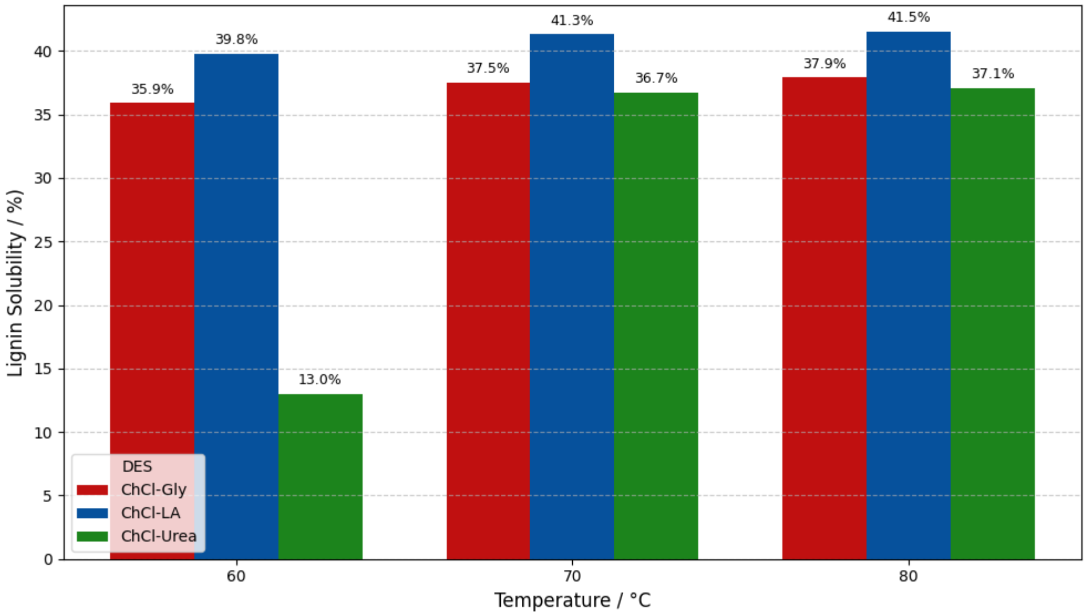

Figure 1 Lignin Solubility in Different DES at Various Temperatures

Solubility of lignin steadily increased with increasing temperature, a justifiable trend possibly due to lignin bonds thermally breaking at high temperatures[33]. Another proposed possibility is the increased contact between lignin and DES brought by lower viscosity[34]. As ChCl-LA had the highest lignin solubility among the three DESs, it is chosen for lignin extraction and pretreatment.

The apparently high solubility of all three solvents deserves attention. The methodology in this paper has difficulties with precisely pinpointing degree of solubility in solution. Hladnik et al, 2021[35] attempted in-situ Fourier Transform Infrared Spectroscopy (FTIR) to precisely examine solubility, but the limitations in temperature control did not fit the needs of this paper. Chen et al, 2023[36] utilized a similar formula for solubility calculations in weight percentage, but first dissolved lignin in excess, then centrifuged and washed to calculate mass dissolved and thus, weight percentage. The obtained results are drastically lower at below 10% weight percentage. However, Chen et al, 2023 found the same relative results, with ChCl-LA showing better performance than ChCl-Urea and ChCl-Gly.

The general trend can be easily explained by intermolecular interactions. Hong et al, 2020[37] suggests that hydroxyl groups, like those in glycerol, and amide groups as in urea, have the potential to form excess hydrogen bonding networks with Choline Chloride. This occupies hydrogen bonding sites of lignin and reduces lignin solubility in DES. Hence, ChCl-Urea and ChCl-Gly have weaker interactions with lignin. The correlation between hydrogen bonding (HB) capability of the DES is further shown through observations of HB number and lifetime by Pan et al, 2024[38], where longer HB number and lifetime showed correlation with higher solubility of lignin.

However, the especially low solubility of lignin in ChCl-Urea is intriguing due to accompanying precipitation. The sample was synthesized at 80 ℃. At 60 ℃, pure ChCl-Urea DES still appeared to be a colorless uniform liquid. However, the melting point of ChCl-Urea is at roughly 65 ℃[39]. Such a phenomenon is explainable by the inclusion of water in DES solution. Choline chloride is known to be very hygroscopic. During preparation of DES, it is possible choline chloride had pulled moisture from the surroundings. Water in DES gives increased hydrophilic interaction and hydrogen bonding in the DES sample[40,41] which can potentially lower melting point of ChCl-Urea (and other DES samples) and also increase solubility[42]. As the amount of lignin increased, the number of HB sites formed is no longer enough to keep eutecticity, so some urea precipitates out of the solvent.

3.2 Lignin extraction

A total of 1.241 grams of CS was mixed with 12.41 grams of ChCl-LA at 120 ℃ for 6 hours. The resulting mixture is washed with ethanol, centrifuged, then washed with water and left at 4 ℃. The final dry mass of lignin obtained was about 0.074 grams, giving a total lignin content in CS of 5.9%.

In comparison, the expected CS lignin content is about 27.39% overall[43,44]. The low extraction could be due to several reasons. Lignin loss could have occurred during pretreatment with toluene/ethanol, storage conditions and microorganisms, and washing of extracted lignin using ethanol and water.

The extracted lignin sample was subjected to 2D HSQC NMR spectroscopy. Figure 2 provides the specific NMR peaks and main lignin substructures. All main substructures had corresponding NMR readings.

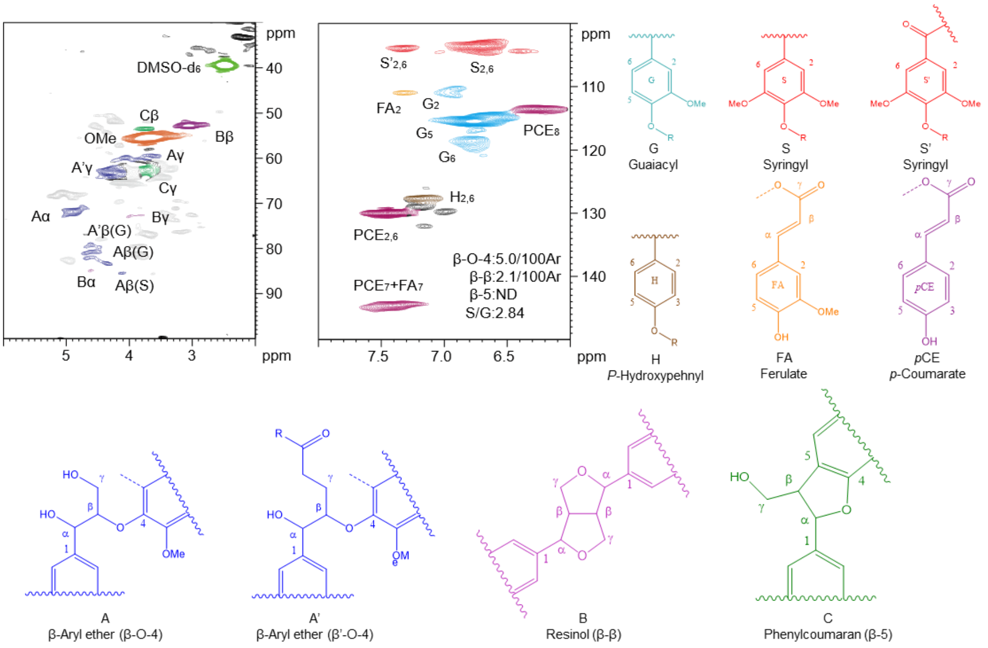

Figure 2 2D HSQC NMR results in comparison to lignin substructures

The aliphatic spectrum shows different bonding structures (Figure 2 left), including β-O-4, β-5, β-β etc. On the left side of figure 2 concerning lignin side-chains, we can observe strong signals at 55.3/3.69 ppm, which can be attributed to methoxyl groups. Signals at 68.5/4.91 ppm, 83.4/4.38 ppm and 59.9/3.35-3.80 ppm represent respectively C-H correlation of β-O-4 bonding at α, β, and γ positions of (A). The signal at 63.0/4.36 ppm represent esterification at the γ position of (A') due to β-O-4 bonding. Semi-quantitative analysis further reveals that β-O-4 has a relative abundance of 5.0/100 Ar. Resinol (B) has a relative abundance of 2.1/100 Ar, as shown by signals in lignin of B_α (52.7/3.08 ppm), B_β (53.5/3.07 ppm), and B_γ (71.2/3.82-4.18 ppm). Signals at 63.3/3.65 ppm (C_γ - H_γ) and 53.1/3.46 ppm (C_β-H_β) prove the presence of Coumaran (C) structures in lignin. From the right side of figure X in the aromatic spectrum, we can note the relatively clear observation of guaiacyl units at 111.8/6.68 ppm (G_2), 114.9/6.65 ppm (G_5) and 119.2/6.65 ppm (G_6). Observations of Syringyl and Hydroxyphenyl signals at 103.4/6.68 ppm ($S_{2,\ 6}$) and 127.8/7.03 ppm ($H_{2,\ 6}$) show in semi-quantitative analysis of an S/G ratio of 2.84. Furthermore, 2D HSQC NMR spectroscopy also proved the presence of *p*-Coumarate (*p*CE) and Ferulate (FA) in lignin as minor constituents.

The detailed 2D HSQC NMR spectroscopy proved that the lignin extracted using DES is sufficient for further use in fabricating adhesives.

3.3 Lignin-based adhesive mechanical performance

(1) Dry testing

The two samples of lignin-based formaldehyde-free adhesive were spread in approximately 250 g/m^2 per surface on three-layered plywood and settled for 30 minutes before hot-pressing, as shown in figures 3 and 4.

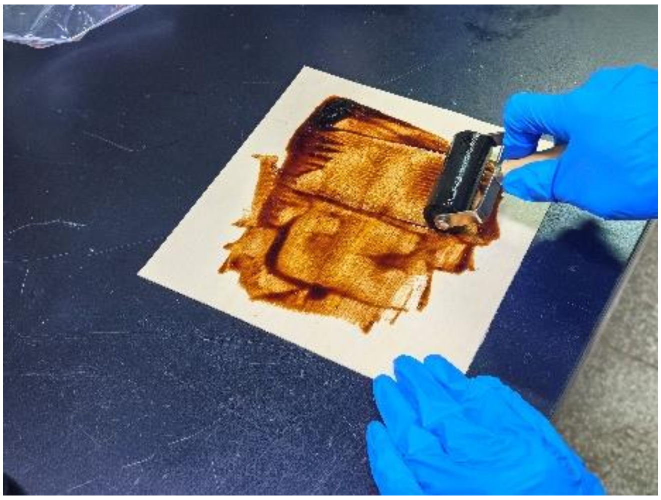

Figure 3 Adhesive Application

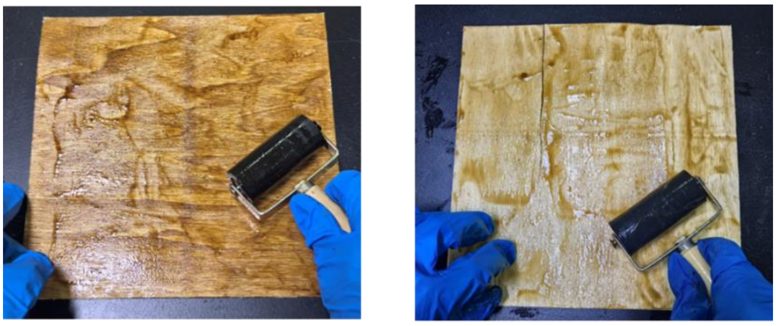

Figure 4 Samples 1 (left) and 2 (right) after adhesive application

The plywood samples were hot-pressed at temperature of 135℃ and pressure of 1.0 MPa for 15min and ventilated at 25℃ for 24h. The results are shown below in figure 5. 12 test samples with length of $(100 \pm 1)\text{mm}$, width of $(25 \pm 1)\text{mm}$ were spliced from each plywood sample, as shown in figure 6.

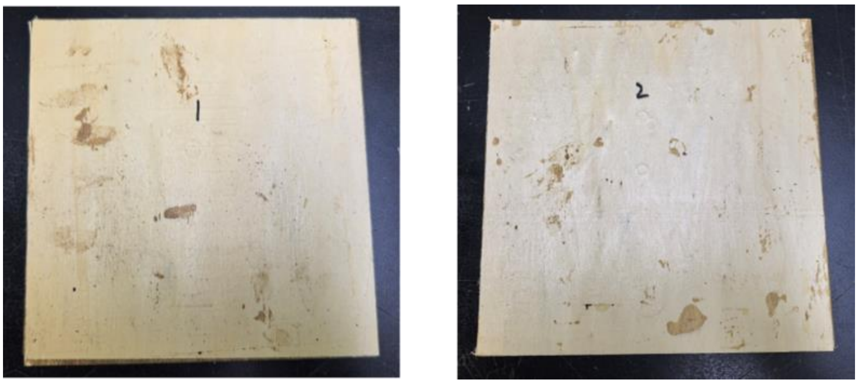

Figure 5 Hot-pressed plywood samples 1 (left) and 2 (right)

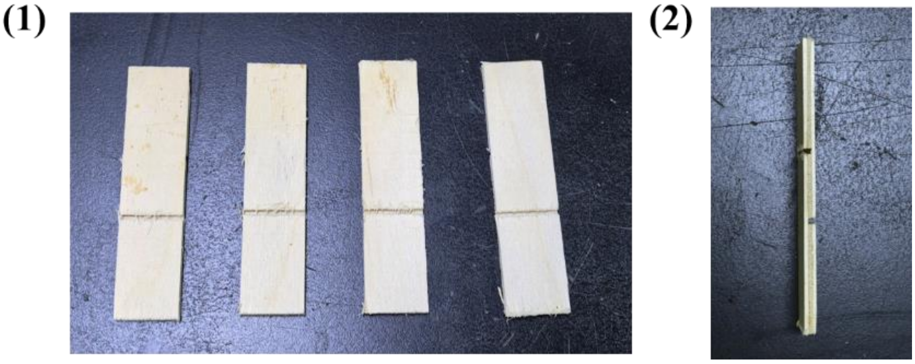

Figure 6 (1) front-view of spliced plywood samples; (2) side-view of spliced plywood samples

As shown in figure 7, the samples were clamped to the Universal Testing Machine according to **GBT 17657-2013**. Adhesion strength tests and rheology tests were carried out subsequently.

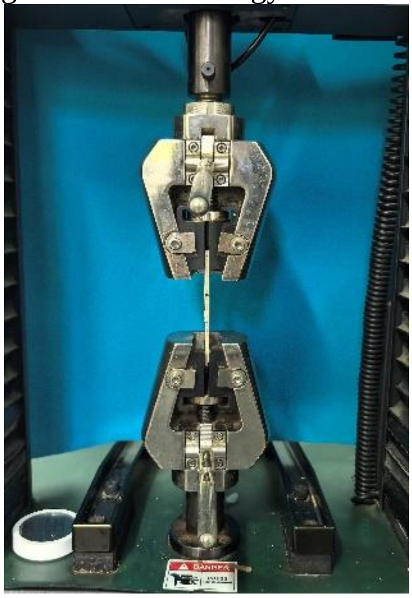

Figure 7 Testing process of dry adhesion strength on Universal Testing Machine.

Under the same reaction conditions, sample 1 of three-layered poplar plywood hot-pressed with lignin-based formaldehyde-free adhesive showed the highest adhesion strength, with all trials yielding maximum shear stress above 0.7 MPa, fitting the type I plywood manufacturing requirements determined by the Chinese Standard **GB/T 17657-2013** "Test methods of evaluating the properties of wood-based panels and surface decorated wood-based panels", indicating potential for industrial use.(Table 4)

Table 4 Mechanical performance of sample 1 determined by universal testing machine

Sample	**1**	**2**
Trial sample cross-sectional area / mm^2	543.76±60	501.78±6
Maximum shear stress / MPa	0.8012±0.04	0.3995±0.02
Maximum force / N	414.56±20	200.42±10

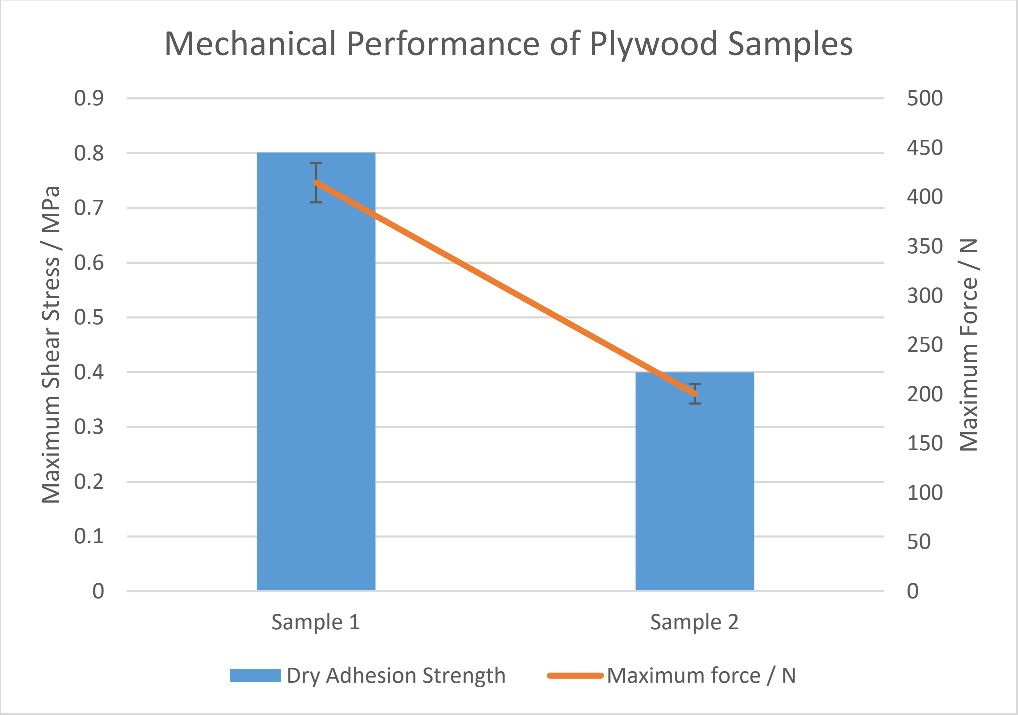

Figure 8 Dry adhesion strength and maximum strength of plywood samples one and two

From figure 8, it can be observed that sample 2 consistently shows a maximum shear stress of around 0.3 MPa to 0.4 MPa, about half of the corresponding values in sample 1. Referring to methodology, sample 2 used about 38.5% lignin used in sample 1, suggesting a potential relationship in mechanical performance and amount of lignin used. This suggests a close-to-linear positive correlation with amount of lignin included in the PVA-lignin adhesive. A similar correlation was found by Lubis et al, 2022[45], who demonstrated a similar relationship in tensile shear stress, although only tested up to 20% lignin content. Further research has to be done on the relationship between lignin content and adhesion properties to determine a specific trend.

(2) Rheology curve

Table 5 shows the scanned shear rate curve at 20°C, with shear rate on the x-axis in units of s^{-1} with range 0.1-1000, and viscosity on the y-axis in units of Pa s. The curve shows the pattern of change of viscosity under different shear rates. First, the viscosity of the two samples reduce significantly with increasing shear rate, forming a pseudo-plastic liquid. At low shear rates and high shear rates, the moderate viscosity shown implies that even application could be favored in the adhesive application process by increasing shear forces to lower viscosity.

Table 5 Adhesive sample 1 viscosity after hot-pressing to plywood various shear rates

Data point	Shear rate [1/s]	Shear stress [Pa]	Viscosity [mPa s]	Temperature [℃]	Torque [mN m]
1	0.00999	0.35721	35752.00	19.98	0.001647
2	0.0178	0.72715	40903.00	19.99	0.003353
3	0.0316	1.35400	42828.00	19.99	0.006244
4	0.0562	2.44280	43441.00	19.99	0.011265
5	0.100	3.55430	35544.00	19.99	0.016391
6	0.178	4.45170	25033.00	19.99	0.020529
7	0.316	5.46970	17297.00	20.00	0.025224
8	0.562	6.86180	12202.00	20.00	0.031644
9	1.00	8.61870	8618.30	20.00	0.039746
10	1.78	10.59600	5958.30	20.00	0.048865
11	3.16	12.94700	4093.80	20.00	0.059706
12	5.62	16.27800	2894.30	20.00	0.075065
13	10.0	20.65100	2064.80	20.00	0.095232
14	17.8	27.06300	1521.70	20.00	0.124800
15	31.6	36.79000	1163.20	20.00	0.169660
16	56.2	52.04600	925.38	20.00	0.240010
17	100	75.84100	758.28	20.00	0.349750
18	178	113.74000	639.49	20.00	0.524530
19	316	170.91000	540.40	20.00	0.788170
20	562	260.87000	463.81	20.00	1.203000
21	1000	411.37000	411.29	20.02	1.897000

Table 6 Adhesive sample 2 viscosity after hot-pressing to plywood various shear rates

Data point	Shear rate [1/s]	Shear stress [Pa]	Viscosity [mPa s]	Temperature [℃]	Torque [mN m]
1	0.00999	1.06360	106000.00	19.98	0.004905
2	0.0178	2.24180	126000.00	19.99	0.010338
3	0.0316	3.95870	125000.00	19.99	0.018256
4	0.0562	6.41100	114000.00	19.99	0.029565
5	0.100	9.53840	95389.00	19.99	0.043987
6	0.178	12.68700	71349.00	19.99	0.058508
7	0.316	16.55600	52355.00	19.99	0.076348
8	0.562	20.13700	35810.00	19.99	0.092864
9	1.00	22.61900	22619.00	20.00	0.104310
10	1.78	26.61000	14964.00	20.00	0.122710
11	3.16	29.81700	9428.50	20.00	0.137500
12	5.62	33.81800	6013.30	20.00	0.155950
13	10.0	39.96400	3996.00	20.00	0.184290
14	17.8	50.24000	2824.90	20.00	0.231680
15	31.6	67.16100	2123.60	20.00	0.309720
16	56.2	93.62100	1664.60	20.00	0.431740
17	100	134.28000	1342.60	20.00	0.619250
18	178	195.58000	1099.60	20.00	0.901910
19	316	298.43000	943.55	20.00	1.376200
20	562	470.04000	835.71	20.01	2.167600
21	1000	739.27000	739.01	20.03	3.409200

Among the two samples, sample 2 showed significantly higher viscosity measurements throughout all shear rates, implying a higher cohesion strength in the adhesive. However, sample 2's highest shear rate was measured at a shear rate of around 0.0178 s^{-1}, while sample 1's highest viscosity was measured at a shear rate of around 0.0562 s^{-1}, indicating earlier structural failure in sample 2. Similarly, sample 1's viscosity showed considerable decrease from 35.75 Pa s at 0.1s^{-1} to 0.45 Pa s at 1000s^{-1}, but at a lower rate of change of viscosity than sample 2, meaning predictable storage stability and no significant structural defects or performance decline.(Table 6, figure 9)

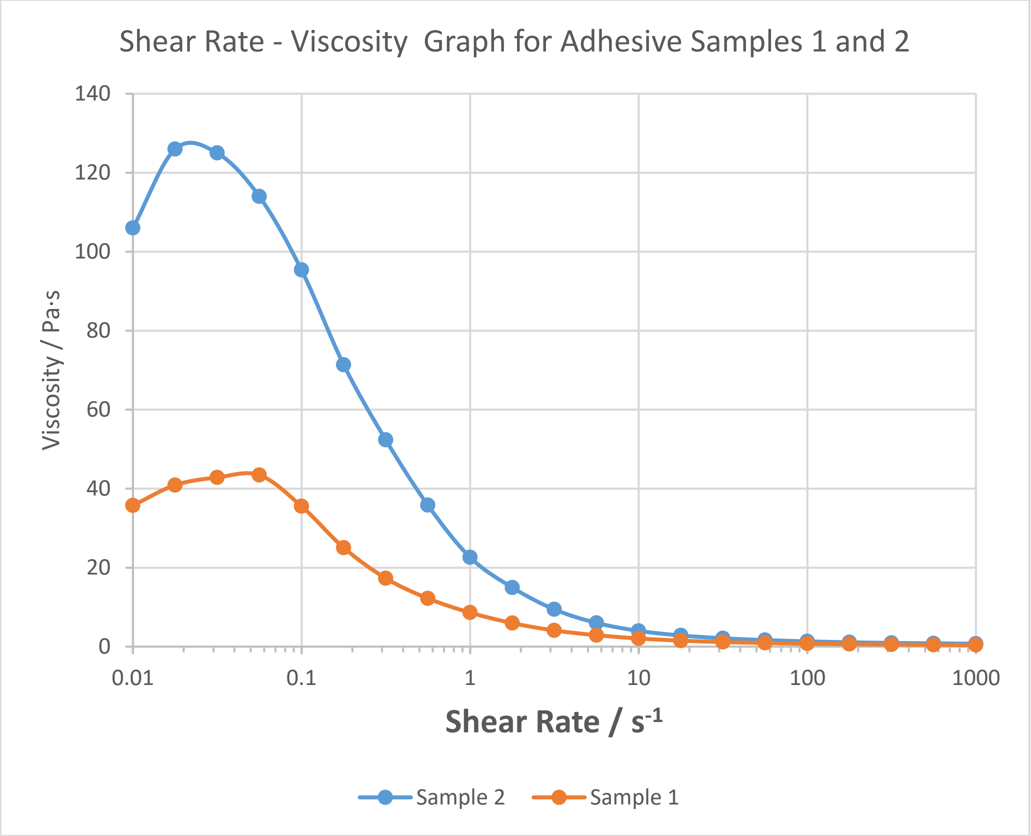

Figure 9 Rheology curve of plywood samples 1 and 2

This result echoes that of Lubis et al, 2022[42] as well, who found steadily lower viscosity figures with increasing lignin structure. The higher cohesion strength proposed symbolizes a greater force of attraction between compounds in the lignin-PVA adhesive. This corresponds to previous research, which found that the crystallinity of lignin-PVA composites are negatively correlated to lignin content[46]. Lower crystallinity means less order in PVA with a more amorphous structure and therefore lower strength. Combined with the previous higher mechanical shear strength trend, we can conclude that the lignin-PVA adhesive is highly tunable. The lignin content can be modified to fit manufacturing or practical needs, hence showing potential as a versatile industry candidate.

4. Conclusion

In short, we successfully formulated an efficient, low-cost, environmentally-friendly synthesis scheme for a green bio-based adhesive that has potential for industry usage by leveraging DES as a green and efficient lignin pre-treatment strategy. We discovered that lignin-PVA composite adhesive has tunable properties that can be adapted to suit production requirements or practical applications. Although the conditions for pre-extraction, types of DES, and ratios of adhesive content could be expanded to investigate relationships between compounds, the results still demonstrated to a great extent the potential of lignin and its value-added chemicals in low-cost, environmentally friendly, and efficient adhesive applications.

References

[1] Wiglusz R, Jarnuszkiewicz I, Sitko E, Wolska L. Hygienic aspects of the use of pressed-wood products in residential buildings. Part II. The effect of environmental conditions (temperature and relative humidity) on formaldehyde emission from particleboards. Bull Inst Marit Trop Med Gdynia. 1990;41(1-4):79-87. PMID: 2135931.

[2] International Agency for Research on Cancer, 2007. Press release no. 153. 15 June 2004. URL http://www. iarc.fr/en/Media-Centre/IARC-Press-Releases/Archives-2006-2004/2004/IARC-classifies-formaldehyde-as-carcinogenic-to-humans Accessed, 6.

[3] Dos Santos, M.F.N., Rosane Ap G, B., Bezerra, B.S. and Varum, H.S., 2014. Comparative study of the life cycle assessment of particleboards made of residues from sugarcane bagasse (Saccharum spp.) and pine wood shavings (Pinus elliottii). Journal of Cleaner Production, 64, pp.345-355.

[4] Thetkathuek A., Yingratanasuk T., Ekburanawat W. Respiratory symptoms due to occupational exposure to formaldehyde and MDF dust in a MDF furniture factory in Eastern Thailand. Adv. Prev. Med. 2016:11. doi: 10.1155/2016/3705824.

[5] Mathur N., Rastogi S.K. Respiratory effects due to occupational exposure to formaldehyde: Systematic review with meta-analysis. Indian J. Occup. Env. Med. 2007;11:26–31. doi: 10.4103/0019-5278.32461

[6] Yu, X., Qi, H., Huang, Z., Zhang, B. and Liu, S., 2017. Preparation and characterization of spherical β-cyclodextrin/urea–formaldehyde microcapsules modified by nano-titanium oxide. RSC advances, 7(13), pp.7857-7863.

[7] Zhang, H., She, Y., Song, S., Lang, Q. and Pu, J., 2013. Particulate reinforcement and formaldehyde adsorption of modified nanocrystalline cellulose in urea-formaldehyde resin adhesive. Journal of adhesion science and technology, 27(9), pp.1023-1031.

[8] Dukarska, D. and Bartkowiak, M., 2016. The effect of organofunctional nanosilica on the cross-linking process and thermal resistance of UF resin. Journal of Polymer Research, 23(8), p.166.

[9] de Cademartori, P.H.G., Artner, M.A., de Freitas, R.A. and Magalhães, W.L.E., 2019. Alumina nanoparticles as formaldehyde scavenger for urea-formaldehyde resin: Rheological and in-situ cure performance. Composites Part B: Engineering, 176, p.107281.

[10] Ferguson, R.C., Mendon, S.K., Rawlins, J.W. and Thames, S.F., 2014. Formaldehyde-free wood composites from soybean protein adhesive. Journal of Renewable Materials, 2(3), pp.166-172.

[11] Jiang, Y., Chen, Q., Tan, H., Gu, J. and Zhang, Y., 2019. A low-cost, formaldehyde-free, and high-performance starch-based wood adhesive. BioResources, 14(1), pp.1405-1418.

[12] Zhu, Y., Zhang, F., Bian, R., Zeng, G., Li, J., Lyu, Y. and Li, J., 2024. Formaldehyde-free biomass adhesive based on industrial alkali lignin with high strength and toughness. Industrial Crops and Products, 222, p.119525.

[13] Islam, M.N., Liza, A.A., Khatun, M.L., Faruk, M.O., Das, A.K., Dey, M. and Akanda, M.J.H., 2021. Formulation and characterization of formaldehyde-free chemically modified bone-based adhesive for lignocellulosic composite products. Global Challenges, 5(9), p.2100002.

[14] Lebo Jr, S.E., Gargulak, J.D. and McNally, T.J., 2002. Encyclopedia of polymer science and technology, 3.

[15] Yang, W., Jiao, L., Wang, X., Wu, W., Lian, H. and Dai, H., 2021. Formaldehyde-free self-polymerization of lignin-derived monomers for synthesis of renewable phenolic resin. International Journal of Biological Macromolecules, 166, pp.1312-1319.

[16] Li, R.J., Gutierrez, J., Chung, Y.L., Frank, C.W., Billington, S.L. and Sattely, E.S., 2018. A lignin-epoxy resin derived from biomass as an alternative to formaldehyde-based wood adhesives. Green chemistry, 20(7), pp.1459-1466.

[17] Siahkamari, M., Emmanuel, S., Hodge, D.B. and Nejad, M., 2022. Lignin-glyoxal: a fully biobased formaldehyde-free wood adhesive for interior engineered wood products. ACS Sustainable Chemistry & Engineering, 10(11), pp.3430-3441.

[18] Hu, S., Chen, X., Ni, S., Wang, Z., Fu, Y., Qin, M. and Zhang, Y., 2025. Formaldehyde-Free, High-Bonding Performance, Fully Lignin-Based Adhesive Cross-Linked by Glutaraldehyde. ACS Applied Polymer Materials, 7(2), pp.859-867.

[19] Kadla, J.F. and Kubo, S., 2004. Lignin-based polymer blends: analysis of intermolecular interactions in lignin–synthetic polymer blends. Composites Part A: Applied Science and Manufacturing, 35(3), pp.395-400.

[20] Schellekens, R. and Bastiaansen, C.W.M.J., 1991. The drawing behavior of polyvinylalcohol fibers. Journal of applied polymer science, 43(12), pp.2311-2315.

[21] Vineeth, S.K. and Gadhave, R.V., 2024. Corn starch blended polyvinyl alcohol adhesive chemically modified by crosslinking and its applicability as polyvinyl acetate wood adhesive. Polymer Bulletin, 81(1), pp.811-825.

[22] Arndt, K.F., Richter, A., Ludwig, S., Zimmermann, J., Kressler, J., Kuckling, D. and Adler, H.J., 1999. Poly (vinyl alcohol)/poly (acrylic acid) hydrogels: FT-IR spectroscopic characterization of crosslinking reaction and work at transition point. Acta Polymerica, 50(11-12), pp.383-390.

[23] Gallo, S., Artuso, E., Brambilla, M.G., Gambarini, G., Lenardi, C., Monti, A.F., Torresin, A., Pignoli, E. and Veronese, I., 2019. Characterization of radiochromic poly (vinyl-alcohol)–glutaraldehyde Fricke gels for dosimetry in

external x-ray radiation therapy. Journal of Physics D: Applied Physics, 52(22), p.225601.

[24] Zhang, Y., Zhu, P.C. and Edgren, D., 2010. Crosslinking reaction of poly (vinyl alcohol) with glyoxal. Journal of Polymer Research, 17(5), pp.725-730.

[25] Sainik, S.K., Panda, P.K. and Sreekumar, T.V., 2025. Fast and energy efficient crosslinking of PVA to make water resistant coating using glutaraldehyde. International Journal of Polymer Analysis and Characterization, pp.1-17.

[26] Choi, H.M., Kim, J.H. and Shin, S., 1999. Characterization of cotton fabrics treated with glyoxal and glutaraldehyde. Journal of Applied Polymer Science, 73(13), pp.2691-2699.

[27] Alonso, D.A., Baeza, A., Chinchilla, R., Guillena, G., Pastor, I.M. and Ramón, D.J., 2016. Deep eutectic solvents: the organic reaction medium of the century. European Journal of Organic Chemistry, 2016(4), pp.612-632.

[28] Alvarez-Vasco, C., Ma, R., Quintero, M., Guo, M., Geleynse, S., Ramasamy, K.K., Wolcott, M. and Zhang, X., 2016. Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): a source of lignin for valorization. Green chemistry, 18(19), pp.5133-5141.

[29] Shen, X.J., Wen, J.L., Mei, Q.Q., Chen, X., Sun, D., Yuan, T.Q. and Sun, R.C., 2019. Facile fractionation of lignocelluloses by biomass-derived deep eutectic solvent (DES) pretreatment for cellulose enzymatic hydrolysis and lignin valorization. Green chemistry, 21(2), pp.275-283.

[30] Chen, Z. and Wan, C., 2018. Ultrafast fractionation of lignocellulosic biomass by microwave-assisted deep eutectic solvent pretreatment. Bioresource technology, 250, pp.532-537.

[31] Koutsoukos, S., Tsiaka, T., Tzani, A., Zoumpoulakis, P. and Detsi, A., 2019. Choline chloride and tartaric acid, a Natural Deep Eutectic Solvent for the efficient extraction of phenolic and carotenoid compounds. Journal of Cleaner Production, 241, p.118384.

[32] Choi, Y.H. and Verpoorte, R., 2019. Green solvents for the extraction of bioactive compounds from natural products using ionic liquids and deep eutectic solvents. Current Opinion in Food Science, 26, pp.87-93.

[33] Hong, S., Shen, X.J., Pang, B., Xue, Z., Cao, X.F., Wen, J.L., Sun, Z.H., Lam, S.S., Yuan, T.Q. and Sun, R.C., 2020. In-depth interpretation of the structural changes of lignin and formation of diketones during acidic deep eutectic solvent pretreatment. Green chemistry, 22(6), pp.1851-1858.

[34] Al-Dawsari, J.N., Bessadok-Jemai, A., Wazeer, I., Mokraoui, S., AlMansour, M.A. and Hadj-Kali, M.K., 2020. Fitting of experimental viscosity to temperature data for deep eutectic solvents. Journal of molecular liquids, 310, p.113127.

[35] Hladnik, L., Vicente, F.A., Novak, U., Grilc, M. and Likozar, B., 2021. Solubility assessment of lignin monomeric compounds and organosolv lignin in deep eutectic solvents using in situ Fourier-transform infrared spectroscopy. Industrial Crops and Products, 164, p.113359.

[36] Chen, H., Wang, A., Yan, C., Liu, S., Li, L., Wu, Q., Liu, Y., Liu, Y., Nie, G., Nie, S. and Yao, S., 2023. Study on the solubility of industrial lignin in choline chloride-based deep eutectic solvents. Sustainability, 15(9), p.7118.

[37] Hong, S., Shen, X.J., Xue, Z., Sun, Z. and Yuan, T.Q., 2020. Structure–function relationships of deep eutectic solvents for lignin extraction and chemical transformation. Green Chemistry, 22(21), pp.7219-7232.

[38] Pan, X., Liu, Y., Ma, Z., Qin, Y., Lu, X., Feng, X., Shao, Q. and Zhu, Y., 2024. Molecular insight into the mechanism of lignin dissolution in acid choline chloride–based deep eutectic solvents. Journal of Molecular Liquids, 406, p.125123.

[39] Zhang, H., Lang, J., Lan, P., Yang, H., Lu, J. and Wang, Z., 2020. Study on the dissolution mechanism of cellulose by ChCl-based deep eutectic solvents. Materials, 13(2), p.278.

[40] Soares, B., Tavares, D.J., Amaral, J.L., Silvestre, A.J., Freire, C.S. and Coutinho, J.A., 2017. Enhanced solubility of lignin monomeric model compounds and technical lignins in aqueous solutions of deep eutectic solvents. ACS Sustainable Chemistry & Engineering, 5(5), pp.4056-4065.

[41] Sumer, Z. and Van Lehn, R.C., 2022. Data-centric development of lignin structure–solubility relationships in deep eutectic solvents using molecular simulations. ACS Sustainable Chemistry & Engineering, 10(31), pp.10144-10156.

[42] Xie, Y., Dong, H., Zhang, S., Lu, X. and Ji, X., 2014. Effect of water on the density, viscosity, and CO2 solubility in choline chloride/urea. Journal of Chemical & Engineering Data, 59(11), pp.3344-3352.

[43] Liu, S., Wu, S., Pang, C., Li, W. and Dong, R., 2014. Microbial pretreatment of corn stovers by solid-state cultivation of Phanerochaete chrysosporium for biogas production. Applied biochemistry and biotechnology, 172(3), pp.1365-1376.

[44] Wang, H.W., Ying, W., Ma, B.L. and Xue, Q.L., 2013. The research progress of comprehensive utilization of crop straw. Advanced Materials Research, 807, pp.1211-1218.

[45] Lubis, M.A.R., Labib, A., Sudarmanto, Akbar, F., Nuryawan, A., Antov, P., Kristak, L., Papadopoulos, A.N. and Pizzi, A., 2022. Influence of lignin content and pressing time on plywood properties bonded with cold-setting adhesive based on poly (vinyl alcohol), lignin, and hexamine. Polymers, 14(10), p.2111.

[46] Kubo, S. and Kadla, J.F., 2003. The formation of strong intermolecular interactions in immiscible blends of poly (vinyl alcohol)(PVA) and lignin. Biomacromolecules, 4(3), pp.561-567.