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ARTICLE

Phenolic Wood Adhesives by Amino Acid-Derived Deep Eutectic Solvents-Treated Lignin for Complete Phenol Replacement

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ABSTRACT: In this study, Lysine-based Amino Acid-derived Deep Eutectic Solvents (Lys-AADESs) were employed as reactive media for lignin modification, followed by substitution of 80%, 90%, and 100% of phenol in phenol-formaldehyde (PF) resin formulations. Lignin properties were investigated, and adhesive performance was evaluated via plywood manufacturing tests. Fourier-transform infrared spectroscopy (FTIR) analysis revealed substantial structural and functional-group changes in lignin following Lys-AADES treatment, particularly involving ether/C–O-containing functionalities and hydroxyl-related groups. Reactive amino ($–NH_2$) groups promoted chemical interactions with formaldehyde during resin synthesis. Differential Scanning Calorimetry (DSC) showed a reduction in the glass transition temperature of lignin from 92°C to 79°C after modification. The resin containing 100% AADES-modified lignin exhibited lower curing peak temperature, molecular weight, and polydispersity than resins prepared using lower substitution ratios, ChCl–$ZnCl_2$-modified lignin, or pristine lignin. AADES modification increased resin solid content and viscosity while shortening gelation time. Plywood panels bonded with modified lignin adhesives demonstrated enhanced dry and wet shear strength, reduced formaldehyde emission, and improved dimensional stability. The lignin-substituted adhesive showed performance comparable to conventional PF resin, demonstrating feasibility of complete phenol replacement. This work demonstrates reactive-solvent lignin modification enabling complete phenol substitution in phenol–formaldehyde resins adhesives.

KEYWORDS: AADES; lignin; phenol-formaldehyde; lignin-formaldehyde; lignin-phenol-formaldehyde; plywood; wood adhesive

1 Introduction

Phenol–formaldehyde (PF) adhesives are extensively used in the wood industry owing to their excellent performance, including high bonding strength, excellent water resistance, heat resistance, and chemical stability. However, the global consumption of PF adhesives is lower than that of urea-formaldehyde (UF) adhesives. The main reason for the low consumption of PF adhesives is that their cost and toxicity are much higher than those of UF adhesives. For this reason, the replacement of phenol by phenolic biopolymers such as lignin has attracted increasing attention due to the anticipated reduction in cost and toxicity, as well as the declining reserves of world fossil resources. The phenolic nature of lignin biopolymers, especially those extracted from the black liquor of the pulp and paper industry is very attractive to the wood industry owing to their low cost and high availability. It is for this reason that so far extensive research activities have been focused on the replacement of phenol by lignin in the production of lignin-phenol-formaldehyde (LPF) resins [1,2]. Kalami et al. [3] showed that there was no significant difference between the shear

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strengths of plywood samples bonded with a 100% corn stover lignin-based adhesive and those bonded with a commercial PF resin. It was also shown that other types of lignin cannot be used completely instead of phenol in phenol-formaldehyde adhesives. The major challenge in substituting lignin for phenol is that lignin has fewer reactive sites for the reaction with formaldehyde in the synthesis of LPF resins. Therefore, several methods have been proposed for lignin modification, such as phenolation and glyoxalation. One of the newest methods proposed for lignin modification is the use of deep eutectic solvents (DESs). DESs are a class of mixtures prepared from hydrogen bond donors (HBD) and acceptors (HBA). Younesi-Kordkheili and Pizzi indicated that ChCl-$ZnCl_2$ (as DES)-modified lignin exhibited the best results among all modification methods for wood adhesive preparation [4]. However, previous studies have indicated that the type of DES can influence the lignin modification process [5,6]. For example, the strong charge effects of ionic DESs may disrupt the structural integrity of lignin, which could negatively impact subsequent lignin modification and utilization [7].

Conversely, amino acid-derived DESs (AADESs), as a reactive type of DES, offer several advantages, such as lower toxicity, better biodegradability, versatility, and renewability. As non-ionic DESs, AADESs can also modulate the hydrogen-bonding network through the selection of different amino acids, thereby reducing the generation of degradation by-products during lignin processing [7]. Conversely, Li et al. indicated that side chain structures can also affect the performance of AADES, as the reactivity of AADESs is notably influenced by the nucleophilicity of the side chains of the amino acids [7]. The lysine (Lys)-based system is one of the most stable systems owing to its strong nucleophilicity. Unlike choline chloride-based DES, the strong nucleophilicity of Lys could induce nanocrystallization and targeted modification of α-OHs to attach phenolic hydroxyls in lignin. For this reason, in the present work, for the first time, Lys-based AADES was selected for lignin modification before its use as a substitute for part or all of the phenol in a PF resin. In this regard, Younesi-Kordkheili and Pizzi indicated that modification of lignin by AADES can significantly decrease the formaldehyde emissions of plywood panels bonded with a UF resin [8].

Extensive studies have been conducted on the substitution of phenol with lignin to prepare LPF resins [9,10]. There is also information in the literature regarding the influence of different methods of lignin modification on LPF resin properties [11,12]. In the work presented here, for the first time, lignin was modified by lysine-based amino acid-derived deep eutectic solvents (Lys-AADESs) and substituted phenol to prepare wood adhesives. Finally, the properties of the prepared resins and bonded plywood panels were evaluated according to relevant standard methods.

2 Materials and Methods

2.1 Materials

Bagasse Soda black liquor with pH = 13 and 40% solid content as a source of lignin was prepared by the Pars Company (Haft Tepe, Iran). For this purpose, soda lignin was extracted from the black liquor using the sulfuric acid method. The initial black liquor had a total solids content of approximately 45%. Lignin was precipitated by the slow addition of concentrated sulfuric acid (36 N) to the black liquor until the pH reached 2. The resulting precipitate was subsequently washed with distilled water until the pH of the rinsing water approached 6. The recovered lignin was then dried at 60°C for 24 h. Under these conditions, the overall lignin separation yield was 93%. The chemicals used in this study, such as formalin, methanol, lysine, and ChCl–$ZnCl_2$ were purchased from Sigma Aldrich (Burlington, USA).

2.2 Methods

2.2.1 Preparation of AADES

Lys-based AADES were prepared according to the method reported by Li et al. [7]. Briefly, lysine (HBA) and formic acid (HBD) were combined at a molar ratio of 1:4 in a round-bottom flask and heated in an

oil bath at 85°C under constant stirring until a homogeneous and clear liquid was obtained. The resulting AADES was sealed and stored in a desiccator to minimize moisture absorption until further use.

2.2.2 AADES Modification of Lignin

Modification of lignin using AADES was performed in a round-bottom flask according to Li et al. (2025). Dry lignin was combined with AADES at a solid–liquid ratio of 1:8 and stirred in an oil bath at 120°C for 5 h. After cooling the sample to room temperature, it was transferred to a dialysis bag with a molecular weight cut-off of 1500 Da. The sample was dialyzed against deionized water, replacing the water every 6 h for 2 d. Subsequently, the samples were freeze-dried using a freeze dryer (Dena Vacuum Industry Co., Ltd., Tehran, Iran). The dried modified lignins were stored in a sealed desiccator for subsequent analyses. The yield of regenerated lignin was approximately 96% by weight.

2.2.3 DES Modification of Lignin

Modification of lignin using ChCl–$ZnCl_2$ as a control was performed according to the method reported by Hong et al. [13]. Briefly, dried choline chloride and zinc chloride were mixed at a molar ratio of 1:2 in an Erlenmeyer flask and heated in a water bath at 90°C under magnetic stirring until a transparent and homogeneous mixture was obtained. Subsequently, 1 g of lignin was mixed with 15 mL of the ChCl–$ZnCl_2$ DES, corresponding to a solid-to-liquid ratio of 1:15 (g/mL). After modification, water was added to precipitate and regenerate the lignin. The regenerated lignin was separated by centrifugation at 200 rpm for 4 min at room temperature and washed repeatedly with distilled water until the conductivity of the washing water approached that of distilled water. The recovered samples were dried at 45°C and subsequently dried under vacuum at 50°C for 24 h. The yield of regenerated lignin was approximately 66% (w/w).

2.2.4 Preparation of Lignin-Phenol-Formaldehyde (LPF) and Lignin-Formaldehyde (LF) Resin

LPF and ALF resins were prepared in a four-neck round-bottom flask equipped with a stirrer, thermometer, condenser, and dropping funnel. In the case of LPF resin, 80% and 90% AADES-modified lignin as a substitute for the phenol, phenol, formaldehyde (formalin 37%), ethanol, and water were mixed in a flask. The prepared resins were named LPF80 and LPF90. To prepare the VLF resin, all of (100%) pristine lignin, DES-modified lignin, and AADES-modified lignin were used instead of phenol, and the prepared resins were named VLF, DLF, and ALF, respectively. Under stirring, the flask was heated in a water bath preheated at 80°C, and NaOH was added dropwise. After 4 h resinification, the flask was cooled to room temperature to stop the reaction. The ethanol in the flask was removed by rotary evaporation at 60°C under reduced pressure to produce a dark brown and viscous aqueous resin solution. The molar ratio of formaldehyde/phenol (F/P) was 2.2:1.

2.2.5 Preparation of Phenol-Formaldehyde Resin

Phenol-formaldehyde (PF) resin was prepared as a control sample, similar to the LPF resin method. Sufficient molten phenol, formaldehyde solution (formalin 37%) and each, distilled water, and ethanol were added to the reaction flask. The mixture was heated to 80°C, NaOH was added, and the reaction was continued for 4 h at 80°C. The molar ratio of formaldehyde to phenol used was 2.2:1.

2.2.6 Physicochemical Properties of Synthesized Resin

Gel time, viscosity, solid content, pH and density of the synthesized resins were measured according to standard methods. The non-volatile content (solid content) of the resins was determined in accordance with

ASTM D4426–01(2006) standard [14] (by oven drying at 125°C for 2 h). For gel time measurements, 5 g of the adhesives were weighed in a 16 mm × 180 mm test tube, and then a thin wire spring was placed in the tube. The test tube was placed in a constant-temperature oil bath, and the thin wire spring was moved gently up and down by hand until gelation. A stopwatch was used to record the gel time, and the gelation tests were performed at 140°C. Each value of the physical test was the average of the three test results. The viscosity of the resins was measured at 25°C using a Ford Cup and recalculated to mPa·s. The pH was measured using a Hanna pH meter (Brasov, Romania). The density of the prepared resins was measured using a hydrometer.

2.2.7 Fourier Transform Infrared Spectrometry

Changes in the chemical structure of lignin after modification were analyzed by Fourier transform infrared spectrometry (FTIR) (Shimadzu FTIR 8400S, Japan). FTIR spectra were obtained from KBr pellets with 1 wt% of powdered resin at wave numbers in the 400 and 4000 cm^{-1} range. The spectra were then normalized to a constant peak.

2.2.8 Differential Scanning Calorimetry (DSC) Analysis

The changes in the glass transition temperature (T_g) of oven-dried lignin before and after modification were determined by DSC using a NETZSCH DSC 200 F3 instrument. The DSC scans were recorded at a heating rate of 10°C/min under nitrogen atmosphere at a flow rate of 60 mL/min. In addition, the changes in the curing temperature of the adhesive containing modified lignin compared to the resin with unmodified lignin were determined using a NETZSCH DSC 200 F3 Model thermal analyzer (Nerzsch, Selb, Germany). To determine the curing temperature of the resins, approximately 5 mg of freeze-dried sample was added to an aluminum pan. The samples were then heated from ambient temperature (25°C) to 250°C under a nitrogen atmosphere. The DSC scans were recorded at a heating rate of 10°C/min under a nitrogen atmosphere at a flow rate of 60 mL/min.

2.2.9 Gel Permeation Chromatography

The molecular weight and polydispersity of lignin samples before and after modification were determined using gel permeation chromatography (GPC) (LC-20A, Shimadzu, Kyoto, Japan). Lignin acetylation was performed prior to molecular weight testing. The concentration of lignin in tetrahydrofuran (THF) was approximately 5 mg/mL. The column temperature was 40°C, THF was the eluent, and the flow rate was 1 mL/min. The average molecular weights of the pristine and modified lignin were measured using an external standard method, in which monodisperse polystyrene was used as the standard compound.

2.2.10 Plywood Panel Preparation

The plywood panels were manufactured according to what was reported by Younesi-Kordkheili and Pizzi [15]. Standard single-layer sheets (Beech) with dimensions of 400 mm × 400 mm × 2 mm were dried to less than 6 wt% moisture content, coated with 310 $g{\cdot}m^2$ adhesive to prepare 3 layer plywood, and then hot-pressed. The hot press temperature was 190°C, the maximum pressure was 6 MPa, and the hot-pressing time was 9 min. The plywood samples were kept indoors for 24 h and then sawed to test the shear strength. Three samples of each adhesive were randomly selected and tested for their strength.

2.2.11 Panel Testing

Shear specimens were prepared from each board to evaluate the wet and dry shear strengths according to EN 314 [16]. The specimens were prepared according to the dimensions specified in ASTM D906-98, with

dimensions of 82.6 × 25.4 × 5 mm and a shear area of 25.4 × 25.4 mm. For the wet shear test, the specimens were immersed in water at 20 ± 3°C for 24 h prior to testing. Water absorption and thickness swelling were determined according to ASTM D1037 [17] after immersion in water at 25°C for 24 h. Before testing, the specimens were conditioned at 23 ± 2°C and 60 ± 5% relative humidity for two weeks. Five specimens were randomly selected for each treatment group. The shear strength was measured using an Instron Model 1186 universal testing machine (Instron, High Wycombe, UK). Formaldehyde emission from the plywood panels was determined using the flask method according to EN 717-3.

2.2.12 Statistical Analysis

The effects of pristine and modified lignin content in LPF resin on the panel properties were evaluated using two-way analysis of variance (ANOVA) at a 95% confidence level. Statistical analyses were performed using IBM SPSS Statistics (Version 26.0), and Duncan's multiple range test was used for mean comparisons at a significance level of $p < 0.05$.

3 Results and Discussion

3.1 FTIR Analysis

Fig. 1 presents the FTIR spectra of pristine lignin, DES-treated lignin, and AADES-modified lignin, while a schematic representation of the proposed lignin modification by DES and AADES is shown in Fig. 2. The FTIR spectra indicate noticeable changes in the chemical environment of lignin following DES and AADES treatments. Compared with pristine lignin, the DES-treated lignin exhibited changes in the absorption bands associated with oxygen-containing functional groups, particularly in the region around 1208 cm^{-1}. This region is commonly associated with C–O stretching vibrations in lignin and other oxygen-containing structures. The observed spectral changes suggest modifications in ether- and C–O-containing functionalities during DES treatment. However, because these FTIR bands may arise from multiple overlapping lignin structures, the FTIR results alone do not provide direct evidence for the cleavage of specific interunit linkages such as β–O–4. Previous studies using structure-specific techniques, particularly 2D ^{13}C–^{1}H HSQC NMR, have demonstrated that DES treatment can promote the cleavage or transformation of β–O–4 linkages in lignin under appropriate reaction conditions [18]. Therefore, β–O–4 cleavage may contribute to the structural modification observed in the present study; however, this possibility cannot be directly confirmed from the FTIR results obtained herein.

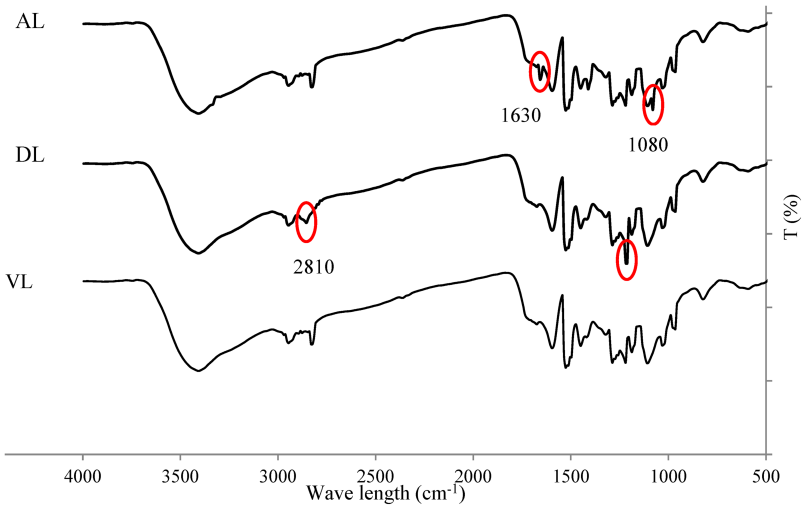
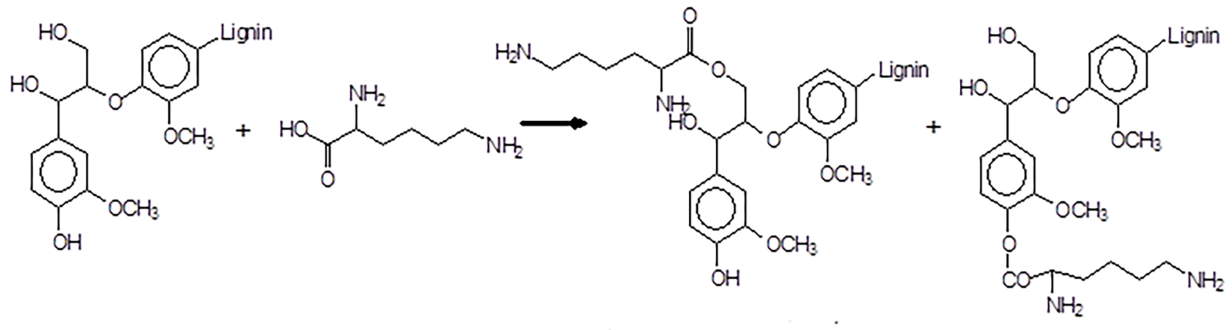
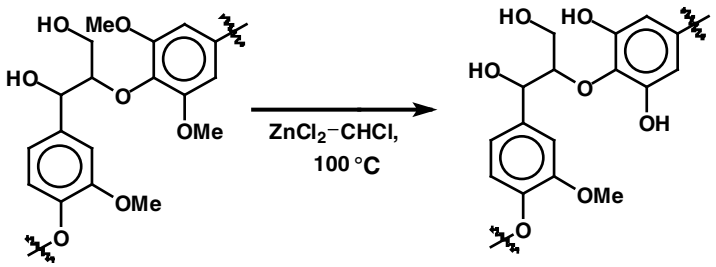


Figure 1: FTIR of the pristine lignin (VL), DES-treated lignin (DL) and AADES-modified lignin (AL).



(**a**) Lys-AADES: proposed lignin modification pathway



(**b**) Zncl2-ChCl: possible lignin modification pathway

Figure 2: proposed lignin modification pathway induced by Lys-AADES (**a**) and $Zncl_2$-ChCl DES (**b**). The schematic represents the proposed mechanism and is not direct evidence of specific ether bonds or β–O–4 cleavage.

Fig. 1 also shows changes in the absorption region associated with methoxy- and other oxygen-containing functionalities after DES treatment. The reduced relative intensity of methoxy-associated bands suggests a lower relative abundance of methoxy groups after DES treatment. However, this observation should be considered qualitative because FTIR spectroscopy does not provide a direct quantitative measurement of methoxy-group content. The observed changes in the relative intensities of oxygen-containing functional-group bands suggest modification of the chemical environment of lignin, which may contribute to changes in its chemical reactivity. Similar structural and chemical changes in lignin following DES treatment have been reported in previous studies [15,18]. Compared with pristine and DES-treated lignin, the AADES-modified lignin exhibited additional changes in the FTIR spectrum, including a distinct absorption band around 1080 cm^{-1}. This band may be associated with C–N and/or C–O stretching vibrations; therefore, its assignment solely to C–N stretching should be made with caution. The observed spectral changes are consistent with the possible introduction of nitrogen-containing functionalities into the lignin structure following treatment with the amino-acid-based AADES. A change in the absorption region around 1630 cm^{-1} was also observed for AADES-treated lignin. Because this region can be associated with several overlapping lignin functionalities, including aromatic skeletal and carbonyl-related vibrations, the observed change was interpreted as evidence of modification of the chemical environment of the lignin structure rather than as definitive evidence of N–H stretching or formation of a specific chemical bond. The AADES-treated lignin also exhibited changes in the absorption bands associated with oxygen-containing functional groups compared with pristine and DES-treated lignin. These spectral changes suggest modification of the chemical environment and functional groups of lignin and may be associated with changes in its chemical reactivity. Amino-acid-derived DESs have previously been reported to promote lignin depolymerization and modification of lignin interunit linkages under appropriate reaction conditions [7]. However, the specific cleavage of C–C linkages in the Lys-AADES-treated lignin investigated in the present study was not directly

determined. In particular, conventional FTIR spectroscopy cannot identify specific lignin C–C interunit linkages or provide direct evidence of their cleavage. Therefore, no specific C–C linkage is assigned as being cleaved in the present study, and the FTIR results should not be interpreted as evidence of C–C bond cleavage. Identification of specific C–C linkages and their cleavage products would require complementary structure-specific analyses, such as 2D ^{13}C–^{1}H HSQC NMR, quantitative ^{13}C NMR, and/or detailed analysis of lignin degradation products using chromatographic and mass-spectrometric techniques. Accordingly, any C–C bond cleavage is considered only a possible mechanistic pathway reported for some lignin depolymerization systems and is not claimed as a demonstrated reaction in the present study. Previous studies have suggested that DES treatment can promote the transformation of lignin ether linkages [19,20], which provides a plausible mechanistic explanation for some of the structural changes observed in the present work. However, these literature findings cannot be considered direct evidence of β–O–4 cleavage in the lignin samples examined here. Direct assessment of changes in β–O–4 abundance would require a structure-specific technique such as 2D ^{13}C–^{1}H HSQC NMR. Accordingly, the absence of direct β–O–4 characterization represents a limitation of the present study. Overall, the FTIR results indicate that both DES and Lys-AADES treatments modified the chemical environment and functional groups of lignin. The spectral changes observed after AADES treatment are also consistent with the possible introduction of nitrogen-containing functionalities. These structural modifications may contribute to changes in the chemical reactivity of the modified lignin.

3.2 DSC Analysis

Fig. 3 shows the changes in the glass transition temperature (T_g) of pristine, DES-modified, and AADES-modified lignin. As shown in the DSC analysis, AADES-modified lignin had a lower Tg (79°C) compared to DES-modified lignin (86°C) and pristine lignin (92°C), respectively (Fig. 3). As shown by FTIR analysis, the majority of linkages within lignin can be cleaved by AADES treatment. Thus, it seems that the size of the molecular network and molecular weight of lignin decreased. To confirm this, the molecular weights of pristine lignin, DES-modified lignin, and AADES-modified lignin were examined by Gel Permeation Chromatography (GPC) and the results are shown in Table 1. Table 1 lists the values of the weight-average molecular weights (M_w), number average molecular weights (M_n), and polydispersity index (PDI) (M_w/M_n) of the three lignins.

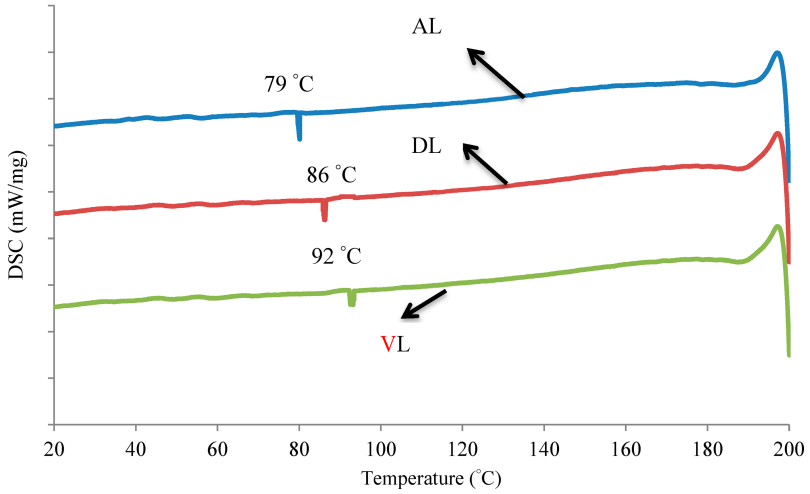


Figure 3: DSC analysis of pristine lignin (VL), DES-modified lignin (DL) and AADES-modified lignin (AL).

Table 1: Molecular weight and polydispersity of lignin and modified lignin.

Type	M_w	M_n	M_w/M_n
lignin	7323	2435	3.0
DES-modified lignin	1989	1244	1.6
AADES-modified lignin	1870	1242	1.5

This shows that both the molecular weight indices of lignin were decreased more by the AADES pretreatment than by the DES modification. The polydispersity index (PDI) of AADES-modified lignin (1.5) was also significantly lower than that of DES-modified lignin (1.6) and pristine lignin (3.0). This implies that the homogeneity of lignin was improved by DES and AADES pretreatments. However, AADES treatment appears to decrease both the molecular weight and polydispersity of lignin compared to DES treatment. The heterogeneity of lignin has always presented key challenges that limit its use as a partial substitute for phenol in phenol-formaldehyde (PF) wood adhesives. The research presented here appears to indicate that AADES treatment significantly decreases this limitation. The AADES-modified lignin has a lower T_g and lower molecular weight, which implies that it may also have a higher segmental mobility, thus reacting faster than DES-treated lignin and pristine lignin in LPF resin synthesis.

DSC thermographs of the VLF, DLF, and ALF resins are shown in Fig. 4. The graphs indicate that in all cases, the curing was completed by two exothermic curves. The VLF resin showed two overlapping exotherms with peaks at 140°C and 188°C. The first peak is due to chain-building condensation reactions, and the second peak is attributed to self-condensation reactions. Similar to the VLF resin, the DLF resin also showed two overlapping curves with peak temperatures of 135°C and 167°C. These curves can also be attributed to self-condensation reactions of the DLF resin. Fig. 4 indicates that, compared to the VLF resin, the peaks of the DLF resin started to appear at lower temperatures. The high rate of curing of the DLF resin showed that the incorporation of DES-modified lignin accelerated the curing of the resin. It can also be seen that the ALF resin had a lower peak temperature than those prepared from DES-modified lignin and pristine lignin. This can be attributed to the faster condensation of the ALF resin because of its higher phenolic hydroxyl content and lower methoxyl content than those of the DLF and VLF resins. This result is consistent with that of the gel time analysis in this study.

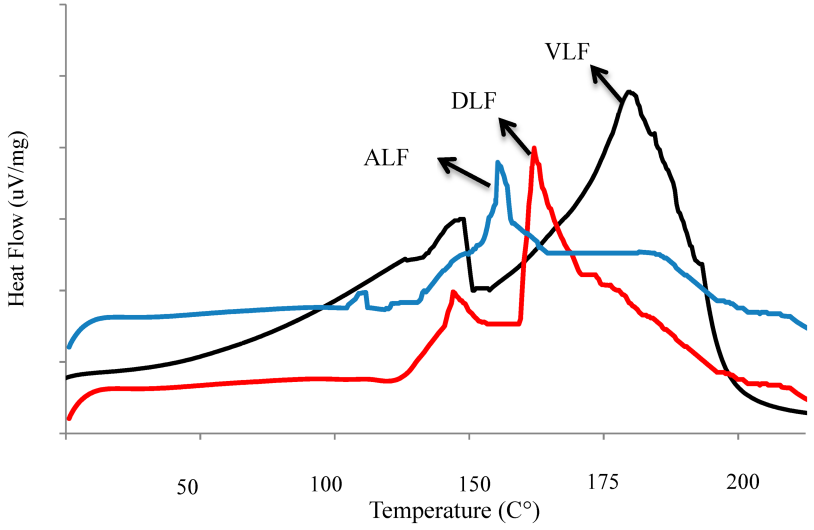


Figure 4: DSC thermographs of the pristine lignin-formaldehyde (VLF), DES-modified lignin-formaldehyde (DLF) and AADES-modified lignin-formaldehyde (ALF) resins.

3.3 Physicochemical Properties of the Resins Prepared

The viscosity, density, solid content, and gel time of the prepared adhesives were determined and are presented in Table 2. It can be seen that the ALF resin containing 100% AADES-modified lignin has higher viscosity, solid content, density and faster gel time than those of both the DLF resin with DES-modified lignin and the VLF resin with pristine lignin. The faster gel time of the ALF resin shows that the AADES-modified lignin and formaldehyde can cross-link faster than the other two types of lignin when preparing a lignin-based resin.

Table 2: Physicochemical properties of prepared resins.

Resin	Density (g/mL)	Viscosity (mPa·s)	Solid Contents (%)	Gel Time (s)
PF	1.24	672	59	335
VLF	0.9	336	23	375
DLF	1.01	425	28	355
LPF80	1.09	481	33	346
LPF90	1.12	523	36	340
ALF	1.16	555	43	338

Conversely, the viscosity of the resin depends on different parameters. The percentage solid content and proportion of crosslinks between the elements of the resin are the main factors that significantly affect the viscosity of the resin [21]. Hence, the higher viscosity of the ALF adhesive containing AADES-modified lignin is probably due to the higher proportion of crosslinks and its higher solids content than those of resins from DES-modified lignin and pristine lignin. Both FTIR spectroscopy and DSC analysis showed that AADES-modified lignin has a higher proportion of amine and phenolic hydroxyls and a lower proportion of methoxy groups (these groups influence the reactivity of lignin) as well as a lower molecular weight than DES-modified lignin. Hence, from a chemical perspective, the higher viscosity of ALF resins containing AADES-modified lignin can be attributed to the difference in the relative proportions of these groups. Table 2 also shows that the density of the VLF resin was 0.9 kg/L which is the lowest one measured while the ALF resin had the highest density (1.16 kg/L). However, it must be noted that there were no statistically significant differences between the density values of the prepared resins.

Table 2 also shows that the density, viscosity, and solid content of the synthesized resins have increased and the gel time has decreased by increasing the content of AADES-modified lignin from 80% to 100%. The ALF resin made from 100% lignin has a faster gel time as well as a higher density, viscosity, and solids content than the LPF90 and LPF80, respectively. Based on the physicochemical test results, the properties of the ALF resin were rather close to those of the control PF resin. This can be attributed to the good performance of lysine-based AADES used to modify the lignin structure.

3.4 Mechanical Properties of the Panels Prepared

Table 3 shows the wet and dry shear strengths and wood failure percentages of the plywood panels bonded with the resins made from AADES-modified lignin, DES-modified lignin, and pristine lignin. The shear strengths of the plywood panels bonded with PF resin as a control sample are also listed in Table 3. The panels bonded with the DLF resin with DES-modified lignin had a significantly higher shear strength and wood failure percentage than those bonded with the VLF resin using pristine lignin. Younesi-Kordkheili and Pizzi showed that the modification of lignin by deep eutectic solvents can significantly improve the mechanical strength of wood panels bonded with lignin-based resins [22].

Table 3: Properties of manufactured plywood panels.

Resin	Dry		Wet		Formaldehyde Emission (mg/100 g)
	Shear Strength (MPa)	Wood Failure Percentage (%)	Shear Strength (MPa)	Wood Failure Percentage (%)	
PF	1.8 (0.07)	100	1.4 (0.05)	100	4.3
VLF	0.7 (0.08)	65	0.55 (0.06)	40	4.5
DLF	0.9 (0.07)	90	0.63 (0.04)	65	4.0
LPF80	1.2 (0.05)	100	1.1 (0.06)	100	4.0
LPF90	1.4 (0.07)	100	1.22 (0.05)	100	3.8
ALF	1.7 (0.06)	100	1.32 (0.03)	100	3.6

Note: The numbers in the parenthesis are standard deviation.

Conversely, ALF and both LPF resins have higher shear strength and wood failure percentages than DLF resin. The higher shear strength and wood failure percentages of the panels bonded with resins prepared from lys-based AADES-modified lignin compared to those bonded with DES-modified lignin resins can be ascribed to their differences in chemical reactivity. The reactivity of lignin is influenced by the number of phenolic hydroxyl groups, methoxy groups, and molecular weight. Enhancement of lignin chemical reactivity is achieved by increasing the proportion of phenolic hydroxyl groups and simultaneously reducing methoxy group content and molecular weight through AADES treatment, which in turn promotes a higher level of cross-linking between the modified lignin and formaldehyde. Increasing the level of crosslinking leads to an increase in the cohesive strength of the resin and, finally, the shear strength and wood failure percentage of the bonded plywood panels. The amino groups of Lys preferentially interact with the phenolic hydroxyl groups of lignin through hydrogen bonding, π-π stacking, or other aromatic interactions [23]. Alternatively, the α-carbon of lignin is susceptible to protonation or ether bond hydrolysis, leading to the generation of carbocations. Due to the high reactivity of the α-carbocation, it acts as a strong electrophilic site and can react at the C5 or C6 nucleophilic sites of the lignin aromatic rings or with amphiphilic amino acids in an electrophilic substitution reaction. This results in the formation of α-5′ or α-6′ linkages [7]. The amino groups can also form hydrogen bonds with the hydroxyl and phenolic hydroxyl groups of lignin, thereby increasing intermolecular interactions.

Conversely, Table 3 also shows that greater mechanical strength can be obtained when AADES-modified lignin increases from 80% to 100%, as the panels bonded with ALF resin had 30% and 45% dry shear strength compared to LPF90 and LPF80, respectively. However, the shear strengths of all plywood panels bonded with the LPF and ALF resins were lower than those bonded with the control PF resin. This can be attributed to the higher chemical reactivity of phenol than that of the pristine and modified lignins. However, it can be seen that the shear strength of the plywood panels bonded with ALF is very close to those bonded with the PF resin. This indicates the good performance of the Lys-based AADES modifying lignin before its use in resin synthesis to obtain plywood panels with acceptable shear strength.

3.5 Water Absorption and Thickness Swelling

Figs. 5 and 6 show the short-term (24 h) water absorption and thickness swelling of plywood panels bonded with lignin-based resins, respectively. Based on the water absorption results, the panels bonded with ALF resins exhibited lower water absorption and thickness swelling than those bonded with DLF and VLF resins. One of the main reasons for the lower water absorption and thickness swelling of the ALF resin-bonded plywood is probably the higher level of cross-linking between AADES-modified lignin and

formaldehyde. This is probably due to the higher proportion of free reactive sites in AADES-modified lignin. Previous work has indicated that cleaving the β–O–4 and β–β linkages within the AADES-treated lignin increased the phenolic hydroxyl content of the lignin by up to ~50% [7]. This also confirms that the $–NH_2$ of amino acids can further increase the proportion of reactive sites of lignin and thus facilitate further chemical reactions. The AADES-modified lignin, enriched with active functional groups such as amine, hydroxyl, and phenolic hydroxyl groups, likely induced strong intermolecular interactions through hydrogen bonds, van der Waals forces, and π-π stacking.

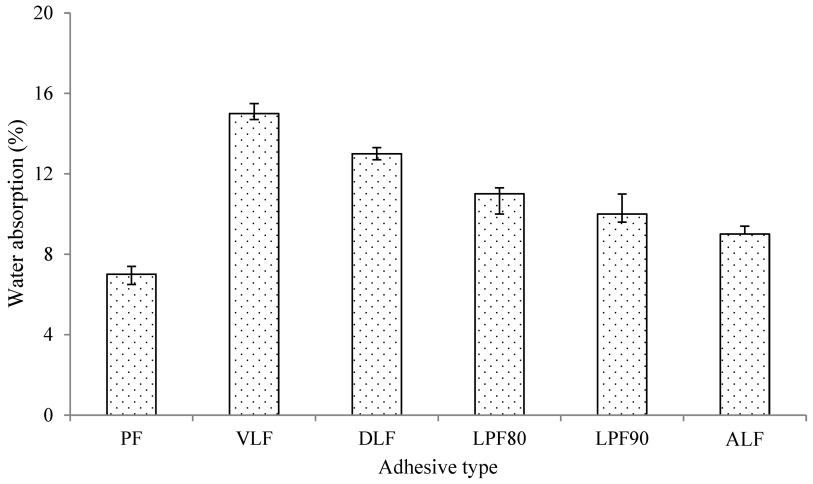


Figure 5: Water absorption of the plywood panels prepared.

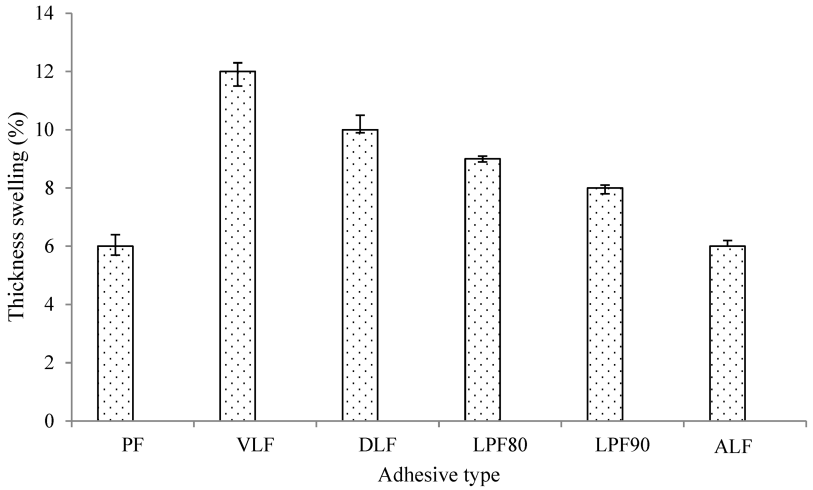


Figure 6: Thickness swelling of the plywood panels prepared.

Conversely, it can be seen that the plywood panels bonded with the control PF resins had a higher dimensional stability than those bonded with the lignin-based resins. This can be attributed to the different bridge types between lignin and formaldehyde in lignin-based resins compared to those between phenol and formaldehyde in PF resins. The covalent cross-linked structure of PF resins contributes to the dimensional stability of the resulting plywood panels. The comparatively lower free formaldehyde content of the ALF resin than that of the PF resin (Table 3) may also contribute to differences in the curing behavior and, consequently,

the dimensional stability of the plywood panels. However, the specific contribution of C–C bond formation or cleavage to the dimensional stability of the panels was not directly determined in the present study. In fact, AADES-modified lignin can act as a formaldehyde scavenger in resins. The positive effect of a decrease in free formaldehyde in the resin on the mechanical strength of the panels has been confirmed by several researchers [22,24,25]. The strong bonds formed in the lys-based AADES between the lignin structure and formaldehyde in the ALF resin can create a network with high resistance to deformation. It is for this reason, the panels bonded with the ALF resin with 100% AADES-modified lignin presented a higher dimensional stability than the LPF90 and LPF80 resins, respectively.

3.6 Formaldehyde Emissions of the Panels Prepared

Formaldehyde poses significant risks to human health and the environment. Hence, reduction of formaldehyde emissions from wood-based panels bonded with formaldehyde-based resin is very important. The formaldehyde emissions from the panels prepared are reported in Table 3, showing that addition of AADES-modified lignin from 80% to 100% can decrease the subsequent formaldehyde emissions from the panels when compared to those using DES-modified lignin and especially pristine lignin. Thus, the panels bonded with the ALF resin with 100% AADES-modified lignin showed the lowest formaldehyde emission (3.6 mg/100 g), while panels bonded with VLF resin showed the highest formaldehyde emission (4.5 mg/100 g). Unlike choline chloride-based DES, the strong nucleophilicity of lysine could induce nanocrystallization and targeted modification of lignin α-OHs to attach phenolic hydroxyl groups in lignin [7]. The different proportions of bridges in the hardened ALF and LPF adhesive networks when AADES is used for lignin modification rather than the DLF or VLF resins are most likely the cause of its lower formaldehyde emission. The amine groups available in the structure of lysine-based AADES can also participate in various chemical reactions, resulting in a decrease in formaldehyde emissions. Most of the formaldehyde emission by hardened PF resins during the panel service time is due to the presence of free formaldehyde within the resin structure. When lys-based AADES-modified lignin is used as a substitute for phenol, it can also act as a scavenger and react with the available free formaldehyde in the resin. Finally, it should be noted that the results obtained show that the present work is beneficial for the preparation of lignin-based wood adhesives and opens new avenues for the utilization of larger amounts of lignin in PF resins. The contribution of amino-functional groups to formaldehyde capture has been demonstrated in various functionalized adsorbent systems, where accessible amino groups can provide active sites for formaldehyde adsorption through hydrogen-bonding and nucleophilic interactions, particularly under low-concentration conditions [26–29]. Finally, it should be noted that the results obtained show that the present work is beneficial for the preparation of lignin-based wood adhesives and opens new avenues for the utilization of high amounts of lignin in PF resins.

4 Conclusions

In the current study, for the first time, lysine-based amino acid-derived deep eutectic solvents (Lys-AADESs) for modifying lignin were used as substitutes for part and all of the phenol in PF resins. Finally, the performance of the resulting wood adhesive was evaluated by manufacturing plywood panels. The following conclusions were drawn from the results:

- FTIR analysis indicated that Lys-AADES treatment induced substantial structural and functional-group changes in lignin, particularly involving ether/C–O-containing functionalities and hydroxyl-related groups, with the introduction of $–NH_2$ groups from the amino acid component.

- DSC analysis showed that the glass transition temperature (T_g) of pristine lignin dramatically decreased from 92°C to 79°C after AADES treatment. The ALF resin also had a lower peak temperature and molecular weight than the other two types of lignin-based resins.
- The ALF and LPF resins with AADES-modified lignin had a higher viscosity and faster gelation time than those with ChCl-$ZnCl_2$-modified lignin and pristine lignin, respectively.
- The plywood panels made from ALF and LPF resins containing AADES-modified lignin presented a higher dry and wet shear strength, as well as lower formaldehyde emission and thickness swelling than those with DES-modified lignin and pristine lignin, respectively.
- Greater mechanical strength and dimensional stability, as well as lower formaldehyde emission, can be obtained by increasing the amount of AADES-modified lignin from 80% to 100%, thus even totally substituting phenol in PF resins.
- These findings emphasize the effectiveness of AADES-modified lignin, which offers significant potential for wood adhesive preparation. Moreover, replacing all phenols with AADES-modified lignin in phenol-formaldehyde resin would improve the percentage of renewable raw materials and worker health.

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Availability of Data and Materials: All data are contained in the publication.

Ethics Approval: Not applicable.

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