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Improving the properties of urea-lignin-glyoxal resin as a wood adhesive by small addition of epoxy

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ABSTRACT

The aim of this work was to improve the properties of plywood panels bonded with urea-lignin-glyoxal (ULG) resin by small addition of epoxy resin. For this reason, various contents (1, 3 and 5% on resin solids) of an epoxy resin were added to the prepared ULG resin. The structural, thermal and physicochemical properties of the resins prepared as well as the water absorption and wet and dry shear strength of the plywood panels bonded with them were measured according to standard methods. The results showed that the addition of an epoxy resin significantly accelerated the gel time and increased the ULG resin viscosity, density and solids content. The cross-linking structure in the cured ULG resin with the epoxy resin was confirmed by FTIR analysis. The curing temperature of the ULG resin also decreases by addition of the epoxy resin as shown by differential scanning calorimetry (DSC). As a consequence, the plywood panels bonded with ULG resins containing any amount of the epoxy resin presented a better dimensional stability than those bonded with the control resin. The dry and wet tensile shear strength of plywood panels bonded with ULG resins indicate that they could be significantly improved by increasing the percentage of the epoxy resin added.

1. Introduction

Formaldehyde-based wood adhesives such as urea-formaldehyde (UF), melamine-formaldehyde (MF) and phenol-formaldehyde (PF) resins are currently the most commonly-used resins for wood-based panels. Although the results of previous studies have indicated that increasing the molar ratio of formaldehyde can improve the properties of resins, its high toxicity has nonetheless created much environmental concern for panels bonded with formaldehyde-based resins [1–7]. Thus, up to now several research groups have tried to find a new approach to solve such a problem in wood adhesives. One relatively new approach in the reduction of formaldehyde emission is the use of natural resins such as lignin (L) in the synthetic resin structures as well as substitution formaldehyde with glyoxal (G) to obtain a nontoxic wood adhesive. Younesi-Kordkheili [8] have shown that, although the panels made from urea-lignin-glyoxal (ULG) resins are mainly "green", their mechanical strength, thermal properties and some physical properties are worse than those of commercial resins. The lower mechanical strength and thermal properties of the ULG resin bonded panels, lower than those bonded with formaldehyde such as UF, is due to the lower chemical reactivity of glyoxal and lignin compared to formaldehyde and urea. For this reason, it is necessary for example to add an additive or mechanical enhancer before using ULG resins in wood-based panels.

Conversely, previous works have shown that one of the best methods for improving the properties of thermoset resins is mixing them with an epoxy resin [9]. [9] Indicated that incorporating 5 wt% epoxy improved the water resistance of the adhesive by 236.7% and the wet shear strength of the resulting plywood to 1.12 MPa, which met interior use requirements. Adding epoxy also increased the adhesive solid content and decreased the adhesive viscosity, which would be beneficial to soybean meal-based adhesive industrial applications. Due to their many useful properties such as their outstanding mechanical performance, good chemical resistance and superior dimensional stability, the use of epoxy-resins is growing [10]. Epoxide resins have also received special attention as wood adhesives because epoxy groups readily react with various functional groups such as carboxyls, hydroxyls, and primary amines. Previous research has shown that epoxy resins give significantly improved gluability, water resistance, solid content, viscosity, and thermal stability to soy-based adhesives [9,11]. For example [11], indicated that epoxy resin could effectively improve the performance of enzyme-treated soy-based adhesives, which might provide a new option for the preparation of soy-based adhesives with high gluability and

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water resistance. Thus, the aim of this work is to improve the properties of ULG resins by small additions of an epoxy resin.

So far the effect of epoxy resins on several types of wood adhesive has been studied by several researchers [12–14]. There is also some research work on the influence of some additives on ULG resins [8]. However, there is no information in the literature on the effect of epoxies on the properties of urea-lignin- glyoxal resins for plywood panels. Thus, the aim of the research work presented here was to investigate the influence of small additions of an epoxy resin on some properties of plywood panels made with ULG resins.

2. Materials and design

2.1. Lignin

Bagasse Soda black liquor with pH = 13 and 40% solid content as source of lignin was prepared by Pars Company (Haft Tepe, Iran).

2.2. Preparation of ULG resin

The ULG resin was prepared according to the method of Younesi-Kordkheili [8]. The details of the resin synthesis are described there.

2.3. Epoxy resin

Commercial diglycidyl ether of bisphenol-A (DGEBA) epoxy resin (E−51, with Epoxide number 0.50–0.54) was purchased from Sanmu Group (Wuxi, China).

2.4. Blending of ULG resin with epoxy

Various mass fractions of epoxy resin (0%, 1%, 3% and 5% of the ULG mass) were added to the slurry and stirred continuously for 10 min to obtain the ULG + epoxy resin adhesives.

2.5. Physicochemical tests

The solids content of the adhesives was determined according to American Society for Testing and Materials (ASTM) D 4426–93. The viscosity and density of the resins was measured at 25 °C using a Ford Cup and hydrometer, respectively. In order to determine the gel time, 5 g of the resin were introduced into a dry glass beaker. The beaker was then immersed into boiling water and the time until hardening was measured. The beaker used for the gelation time test had a 16 mm diameter. Three replicates for each sample were made.

2.6. Fourier transform infrared spectrometry (FTIR)

The changes in the structure of resins before and after modification with epoxy were analyzed by FTIR spectrophotometer (Shimadzu FTIR 8400S, Japan). The resins prepared were oven-dried and then reduced to powder by milling before testing by FTIR. The FTIR spectra were obtained in transmittance from KBr pellets with 1 mass% of the powdered resins at wave numbers between 400 and 4000 cm^{-1}. The spectra were obtained by 32 scans with a resolution of 4 cm^{-1}.

2.7. DSC analysis

The resins were tested by DSC with a NETZSCH DSC 200 F3 Model thermal analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere with a flow rate of 60 ml/min 10 mg of the liquid resin was used for the DSC test. The temperature range was calibrated from 20 °C to 150 °C. Two replicate tests per resin were used for the DSC analysis. Closed DSC standard cups were used.

2.8. Panel manufacturing

Plywood panels were manufactured according to Younesi-Kordkheili and Pizzi [4]. The resins obtained above were used to prepare plywood panels. Standard single layer veneers (Beech) of dimensions 400 mm × 400 mm × 2 mm were dried to lower than 6 wt% moisture content, coated with 310 gm^{-2} glue mix to prepare 3 layer plywood, then hot pressed. The hot press temperature was 180 °C, the maximum pressure was 6 MPa, and the hot-pressing time was 5 min. The plywood samples were kept indoors for 24 h, and then sawn to test the shear strength. Three samples of each adhesive type were selected randomly and tested for dry and wet strength.

2.9. Panel testing

Shear specimens were prepared from each board to examine wet and dry shear strength according to ASTM D 906-98. Water absorption tests (24 h) were performed according to ASTM D4442 – 07. Before testing, the samples were conditioned at a temperature of 23 °C ± 2 °C and a relative humidity of 60% ± 5% for two weeks.

2.10. Statistical analysis

Data for each test were statistically analyzed by SPSS software. The effects of epoxy content on the panels' properties were evaluated by two-way analysis of variance (Two-way ANOVA) at 95% confidence level.

3. Results and discussion

3.1. Physical properties of prepared resins

Some physical properties of the ULG resins prepared are reported in Table 1. It can be seen that the incorporation of an epoxy resin into the ULG resin increases the resin's solids content and accelerates its gel time. The results showed that the ULG resin without an epoxy resin exhibited the lowest solids content (50%) and the longest gel time (88 S) while the ULG resin containing 5% epoxy had the highest solids content (55%) and the fastest gel time (55 s) among all the resins synthesized. The resin solids content is important for a wood adhesive, since it determines adhesive behavior during the hot pressing process. Gao et al. [15] indicated that a lower adhesive solids content indicates that more volatiles need to be removed during the hot pressing process, which can damage the bond performance of the resulting plywood. The solids content of the ULG adhesive increased with addition of epoxies with solids content increasing from 50% to 55%. Conversely, the decrease in gel time as a function of the increase in the proportion of epoxy shows that cross-linking is noticeably faster, resulting in a greater level of cross-linking between urea, lignin and glyoxal to form ULG condensates. The gel time decreases further when passing from 1% to 5% epoxy content in the resin. Reduction of gel time is of considerable interest for the wood panels industry due to the decrease in energy used and increase in production capacity. The physical test results also indicated

Table 1
Physical properties of the prepared resins.

	Solid content (%)	Viscosity (mPa.s)	Gelation Time (s)	Density (kg/l)
ULG	50(1.4)	230(11)	88(4)	1.220(0.09)
ULG +1% epoxy	53(1.1)	243(13)	66(2)	1.223(0.1)
ULG +3% epoxy	54(1.2)	253(16)	61(3)	1.224(0.11)
ULG +5% epoxy	55(1.5)	266(10)	55(2)	1.226(0.1)

The numbers in parenthesis are standard deviations.

that with the progressive addition of higher proportions of epoxies the viscosity of the resins increases. The change in viscosity can be explained by the increased solid content and/or molecular weight of ULG adhesives. Luo et al. [9] showed that the incorporation of epoxies in resins increases their solids content and viscosity. Table 1 also indicates that by incorporating epoxies into a ULG resin, the density of the resin continuously increases. The ULG resin with 5% epoxy exhibits the highest density (1.226) while the control resin had the lowest density value (1.220) among the synthesized resins.

3.2. FTIR analysis

Fig. 1 shows the infrared spectra of the control ULG resin and the ULG resin with 5% epoxy resin. A comparison between the two FTIR spectra shows that a few main peaks varied or occurred when incorporating 5% epoxy into a ULG resin. Compared to the ULG resin, the 1030 cm^{-1} band related to C–N bonds in methylene linkages (N–CH_2–N) and the 1389 cm^{-1} band related to C–N in CH_2–N decreased markedly in the ULG resin with the epoxy. The reduction of the C–N band intensity in ULG resins with the epoxy is probably due to the decreasing content of urea and free glyoxal in the modified ULG resin. According to the FTIR spectra, the 1389 cm^{-1} band related to ethylene-ether linkages in the ULG resin containing epoxy resins is smaller than for the neat ULG resin, implying that the amount of hydrophilic groups in the adhesive decreased upon epoxy addition. Previous research confirmed that in the epoxy resin structure, the absorption peak at 910 cm^{-1} was assigned to the epoxy skeleton vibration [16]. After incorporation of the epoxy, there would be a strong absorption peak at 910 cm^{-1}. Fig. 1 also shows a peak (910 cm^{-1}) in the spectrum of the ULG/epoxy adhesive formulation, indicating that the epoxy groups could react with the active hydrogen on the –OH and –CHO groups during the curing process through a ring-opening reaction [17]. Furthermore, the ULG resin with the epoxy showed a smaller peak at 3500 cm^{-1} (the hydroxyl group) than was found with the neat ULG resin control, and which also showed a slight intensity increase with a peak at 1740 cm^{-1} which can be attributed to the existence of carbonyl groups resulting from cross-linking reactions. These results indicate that the chemical reaction between these groups was the key reaction in the curing process of the epoxy resin-modified adhesives. The decrease in hydrophilic groups (e.g.,–OH, etc.) and increased cross-linking for the cured epoxy resin-modified ULG resin will more likely improve its water resistance. The possible reactions between ULG resin and epoxy resin are shown in Fig. 2.

3.3. DSC analysis

Fig. 3 shows the exothermic DSC curves of the pure ULG resin and the ULG resin containing 5% by weight of epoxy. Similarly to other thermoset resins, the curves of ULG resins, reacted with and without epoxies, indicate exothermic behavior. Fig. 3 also indicates that the addition of an epoxy resin had a marked influence on the curing behavior of the ULG resin. A ULG resin blended with an epoxy resin shows lower onset temperatures as well as peak curing temperatures when compared to the control ULG resin. For the ULG resin, the exothermic peaks (the gel onset peak and the highest peak) can be probably attributed to the heat released from the formation of the CH_2–O – CH_2 and –CH_2- bridges by reaction of the aromatic sites in lignin with either glyoxal and/or some of the primary hydroxymethyl groups in the ULG resin. Due to the low potential reactivity of lignin and glyoxal, the curing process of the ULG resin needs high temperature (105 °C) and time. Addition of a high reactivity epoxy resin increases crosslinking between functional epoxy groups with other components resulting in potential for a lower curing temperature (89 °C). The shifting to lower temperatures of the onset and peak temperatures of the ULG resin containing an epoxy also indicates that the epoxy accelerates hardening of the ULG resin. This can be attributed to a higher proportion of cross-links within the resin after addition of the epoxy. Gel time measurements (section 3:1) of the resins prepared were confirmed by DSC analysis. Fig. 3 also indicates that the enthalpy of the cure reaction (ΔH) decreased from 137 J/g to 114 J/g following the addition of epoxy to the ULG. This means that the control ULG resin requires higher energy to reach complete curing than the ULG resin with the epoxy. Decreasing the curing temperature and increasing the enthalpy of reaction of wood adhesives with epoxies has been reported by several researchers for different adhesives [9,11].

3.4. Shear strength

The dry shear strength and corresponding wood failure percentages of the panels prepared are shown in Table 2. It can be seen that the use of the epoxy resin had a significant effect on the dry shear strength of the prepared panels. By increasing epoxy content from 1 to 5 wt% the dry strength of the adhesives increased by 1.7 MPa. Table 2 also shows that the wood failure percentages of the plywood panels increased by increasing the proportion of epoxy. The resin containing 5% epoxy

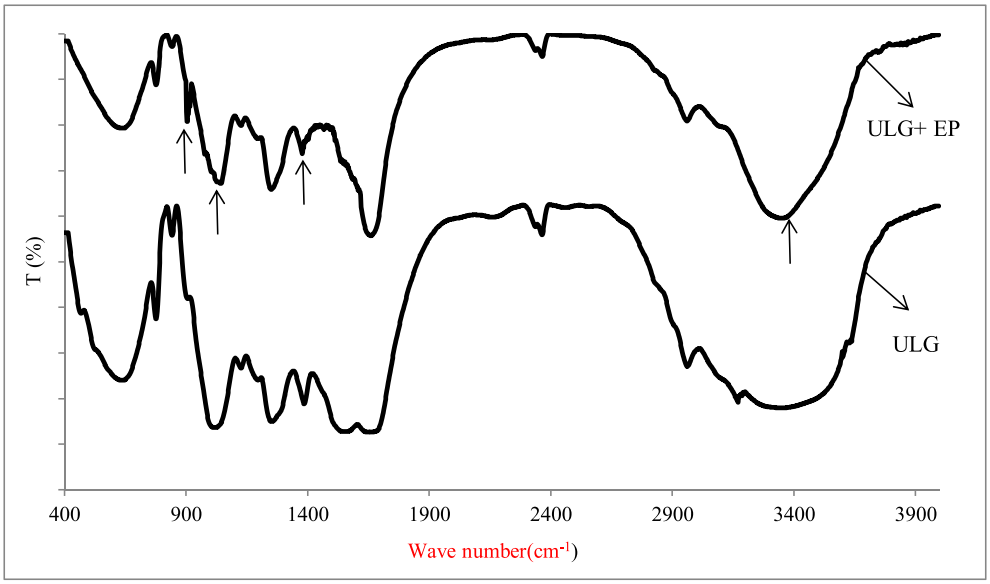

Fig. 1. FTIR analysis of ULG resin and ULG resin with epoxy.

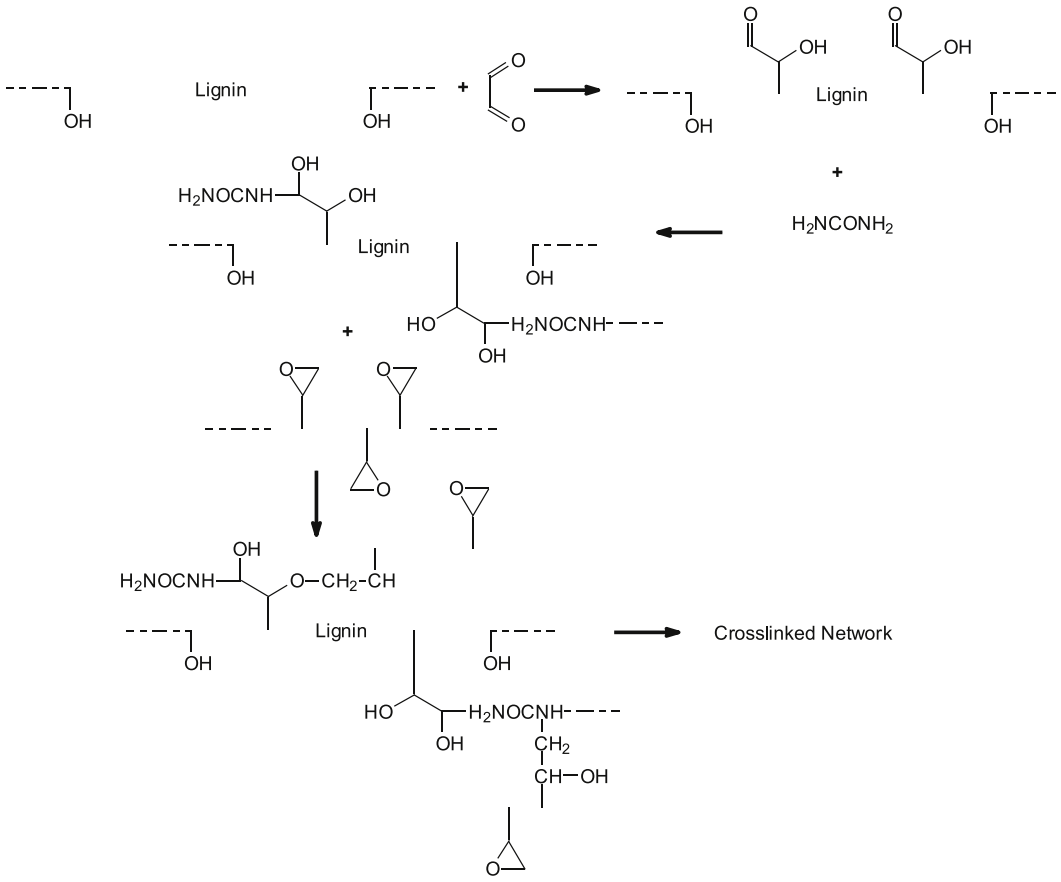

Fig. 2. Possible reactions between ULG and epoxy resins.

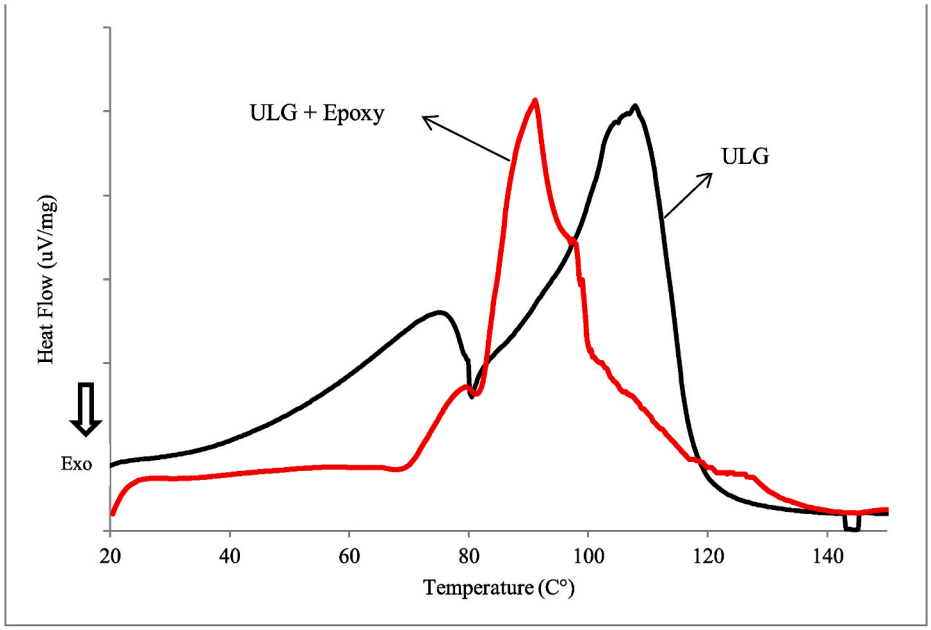

Fig. 3. DSC analysis of neat ULG resin and ULG resin with epoxy.

exhibited the highest panel dry shear strength (1.7 MPa at 100% wood failure percentage) while the panels bonded with the ULG control resin had the weakest shear strength (0.43 MPa at 50% wood failure percentage) among all the synthesized resins. Younesi-Kordkheili and Pizzi [4] indicated that shear strength and wood failure percentage are directly related to the quality of the resin and of bonding. This could be ascribed to formation of more cross-linked structures in cured adhesives as a consequence of the ready reaction of the epoxy group with all other ULG functional groups during the curing process. Previous research has also indicated that the glue line strength and spreading of a resin on the

Table 2
Physical and mechanical properties of the manufactured panels.

Resin	Dry shear strength (MPa)	Wood failure percentage (%)	Wet shear strength (MPa)	Wood failure percentage (%)	Water absorption (%)
ULG	0.43 (0.15)	50	0.2 (0.04)	20	15
ULG+1% Epoxy	0.84 (0.11)	70	0.75 (0.02)	30	11
ULG+3% Epoxy	1.20 (0.14)	100	1.05 (0.05)	70	8
ULG+5% Epoxy	1.7 (0.11)	100	1.29 (0.06)	80	6

• The numbers in the parenthesis are standard division.

wood surface is one of the main parameters to obtain good adhesion [18]. All the physical characteristics of the ULG resin were improved by addition of an epoxy resin according to the results obtained. The FTIR peak at 910 cm^{-1} also inferred good dispersibility of the hydrophobic epoxy resin in the water soluble ULG adhesive. Thus, the high strength of the panels bonded with ULG + epoxy adhesives can be related to the high quality of the resins. Increasing wood failure percentages by the addition of epoxies from 1 to 5 wt% is also due to the cohesive bond strength and was improved by an increasing percentage of epoxy. The higher reactivity of the epoxy compared to urea and lignin probably increases the level of cross-linking between the different components (urea, lignin, glyoxal and epoxy) and cohesive strength.

The wet shear strength and associated wood failure percentages of the panels prepared are shown in Table 2. The results obtained show that similar to the dry panels strength, the panels wet strength increases with increasing amount of epoxy as the panels bonded with the control ULG resin yielded the lowest strength value (0.2 MPa at 20% wood failure percentage). Increasing wet strength of the panels by addition of epoxies can be related to the epoxy groups which can link to urea and glyoxal by reacting with both the hydroxyl groups and amide groups to form a stiffer three dimensional cross-linked network. The hydrophilic nature of epoxy resins can also contribute to an increase in the wet shear strength of the synthesized resins. Luo et al. [9] indicated that the use of a commercial epoxy resin effectively improves the wet shear strength of a soybean meal-based plywood adhesive.

3.5. Water absorption

The water absorption content of the plywood panels made from ULG resins is shown in Table 2. The small additions of an epoxy to ULG resins significantly decreases the water absorption of the manufactured panels (Table 2). The lowest water absorption (6%) was observed for the panels bonded with the ULG resin with 5 wt% epoxy, while the highest absorption (15%) value belongs to those bonded without any epoxy. This result can be explained by the higher cross-linking in the ULG resin containing epoxy compared to the control resin. Moreover, from the FTIR spectra, the proportion of weak bonds affected by hydrolysis in water decreased or disappeared completely in LUG resins to which an epoxy was added. All of these together with the hydrophilic nature of the epoxy resin are the main factors responsible for the water absorption reduction in plywood panels bonded with ULG resin with an epoxy. Lei et al. [19] indicated that addition of epoxy to wood adhesives makes it possible to manufacture plywood of high dimensional stability.

Conversely, previous research has indicated that the water absorption of panels bonded with ULG resins was dramatically higher than those bonded with LUF resins [8,20]. Based on that found in the present work, such a problem can be solved by the addition of small proportions of an epoxy resin to the ULG resin. The different reasons for the poor resistance of ULG to moisture have been described elsewhere by Younesi- Kordkheili [8]. Watts et al. [21] showed that addition of an epoxy to UF resins yielded a significantly improved resistance of the glue line to water.

4. Conclusions

The aim of the work presented here was to investigate the influence of small additions of epoxy resins on the properties of plywood panels bonded with urea-lignin- glyoxal (ULG) resins. The following conclusions can be drawn from the results obtained:

- Commercial epoxy resins could be used to modify ULG adhesives due to their high reactivity potential.
- Epoxy resin-modified ULG adhesives had significantly improved solids content, density, viscosity, and gel time.
- The curing temperature of the ULG resin containing an epoxy is lower than that of a ULG resin without any epoxy according to the DSC analysis results.
- Based on the FTIR analysis, chemical reactions clearly occurred between epoxy groups and the active groups on the ULG resin during the curing process.
- Compared to an unmodified adhesive, the addition of an epoxy resin significantly increased the shear strength and dimensional stability of plywood samples.
- Dry and wet shear strength of plywood samples was improved as the amount of epoxy resin was increased whereas their water absorption was decreased.

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