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ORIGINAL

Improving physical and mechanical properties of new lignin-urea-glyoxal resin by nanoclay

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Abstract To eliminate toxic formaldehyde from wood based panels, glyoxal, a low volatility and nontoxic aldehyde, was used to react with urea and lignin to prepare a glyoxalated lignin- urea-glyoxal (LUG) wood adhesive resin. Moreover, another objective of this research work was to improve the physical and mechanical properties of the new LUG resins by nanoclay addition. For the preparation of LUG resin, glyoxalated lignin (15 mass%) was added instead of second urea to the urea-glyoxal resin synthesis under acid conditions. The LUG resin so prepared was mixed with 1, 2 and 3 mass% nanoclay by mechanically stirring for 5 min at room temperature. Then, the physicochemical and structural properties of the prepared resins as well as the water absorption and the mechanical properties of the plywood panels bonded with it were measured according to standard methods. The physicochemical test results indicated that the gel time of the LUG resin was markedly slower than that of the UF resin. Plywood panels prepared with the LUG resin also presented lower water absorption as well as weaker shear strength than those prepared with the UF resin. Addition of nanoclay changed the physicochemical properties of the resins as the gelation time of the LUG resin was shorter when adding sodium montmorillonite (NaMMT). Higher shear strength values and lower water absorption were achieved by continuously increasing nanoclay proportion from 1 to 3 mass%. Furthermore, addition of nanoclay had more influence on panels bending strength than their flexural modulus. X-ray diffraction (XRD) analysis also indicated that NaMMT exfoliated completely when mixed with LUG resin.

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1 Introduction

Formaldehyde is emitted from wood based panels bonded by amino and phenolic resins during manufacturing and while in use. The amount of formaldehyde released from the wood based panels is affected by exogenous factors, such as air humidity, air exchange and temperature and production conditions and also endogenous factors, such as raw material species and types of resin (Boran et al. 2012). There are several reports about the negative impacts of formaldehyde on human health (Tang et al. 2009; Vosoughi et al. 2012; Norliana et al. 2009). For this reason, researchers have focused on this problem to try to solve or minimize it. So far different methods have been proposed to reduce formaldehyde emission from wood panels (Tohmura et al. 2001; Woo-Kim et al. 2006). One relatively new approach in the reduction of formaldehyde emission is the use of natural resins such as lignin, tannin and soy flour as substitutes for a part of urea and phenol in urea formaldehyde (UF) and phenol formaldehyde (PF) resins synthesis, respectively (El Mansouri et al. 2006; Nair 2004; Younesi-Kordkheili et al. 2016b). Chemically, some natural resins can produce stronger bonds with formaldehyde in the resin rather than urea. Thus, it results in a reduced formaldehyde emission from wood based panels. Today the use of natural resins as wood based composite adhesives is growing due to environmental issues. Among various natural resins, because of their low cost and their abundance, lignin is of particular interest. A previous study indicated that the formaldehyde emission of plywood panels could be dramatically decreased by addition of glyoxalated lignin to UF resin (Younesi-Kordkheili et al. 2015a). Further, El Mansouri et al. (2006) and Tejado et al. (2007) indicated that the mechanical strength increased and the formaldehyde emission from the wood based panels significantly decreased when glyoxalated lignin was used instead of part of the phenol in PF resin synthesis.

However, previous studies indicated that the use of lignin as a modifier in synthetic resins could reduce the formaldehyde emission from the wood based panels, but not all of them (Younesi-Kordkheili et al. 2015a, 2016a). The general purpose of the research work presented here was to prepare a new lignin based resin of high quality and without any formaldehyde emission. The previous studies showed that lignin based resins alone due to low mechanical strength cannot be used as a wood adhesive, thus in this research work lignin is combined with a highly reactive material, namely urea. To obtain a nontoxic resin it was necessary to find an alternative aldehyde for formaldehyde. Among the various aldehydes possible, such as dimethoxyethanal, propionaldehyde, succinaldehyde, glutaraldhyde and isobutyraldehyde, having advantages such as mature production technology, being nontoxic, of low cost, nonvolatile and easily biodegradable, glyoxal exhibited the best results (Deng et al. 2014). Thus, glyoxal was selected as the new nontoxic aldehyde of preference for the current research and reacted with lignin and urea to prepare a zero formaldehyde lignin-urea-glyoxal (LUG) resin. Conversely, previous research indicated that in spite of the various advantages of applying glyoxal in wood adhesives, the chemical reactivity of glyoxal is lower than that of formaldehyde (Younesi-Kordkheili et al. 2016a; El Mansouri et al. 2011). For this reason, the weaker mechanical strength of glyoxal-based resins compared to those based on formaldehyde has been reported by several researchers (Younesi-Kordkheili and Pizzi 2016; El Mansouri et al. 2011). Deng et al. (2014) indicated that plywood bonded with urea-glyoxal resins had no formaldehyde emission, but the dry shear strength of the given specimens could only meet the type III grade plywood requirements of China national standard GB/T 9846.3-2004.

So far, to improve the mechanical properties of the wood adhesives, several methods have been proposed (Han et al. 1998, 1999). The most acceptable procedure is the use of nanofillers such as nanoclays in the resin synthesis. Younesi-Kordkheili et al. (2015b) indicated that the addition of a small percentage of sodium- montmorillonite (NaMMT) as filler could improve the mechanical strength of wood based panels. In the present research work, the effect of NaMMT on physical and mechanical strengths of nontoxic LUG resin was investigated for the first time.

Nowadays extensive works have been conducted on using glyoxal instead of formaldehyde in resin synthesis (Tohmura et al. 2001; Raval et al. 2005; Sensogut et al. 2009). There is also some work reporting on the effect of nanoclays on UF, PF and epoxy resin properties (Mu et al. 2009; El-Mansouri et al. 2011). However, there is no information about adhesives based on lignin, urea and glyoxal (LUG resin) and about the influence of nanoclays on properties of the LUG resin prepared. Hence, the aim of this research was to synthesis new zero formaldehyde emission lignin-urea-glyoxal (LUG) resins and to improve the physical and mechanical properties of the prepared resin by nanoclays.

2 Experimental

2.1 Synthesis of LUG resin

Bagasse Soda black liquor with pH 13 and 40% solid content as source of lignin was prepared by Pars Company (Haft Tepe, Iran). Black liquor was acidified to pH 7–7.5 by 1 mol/l hydrochloric acid (HCl) in order to achieve a pH of the lignin comparable with urea-glyoxal (UG) resins. Then, lignin glyoxalation was performed according to a method reported by Navarrete et al. (2011) and Younesi-Kordkheili et al. (2015a). For synthesis of LUG resins, a 500 ml flat bottom flask equipped with a condenser, thermometer and a magnetic stirrer bar was charged with glyoxal (40%). The pH was adjusted to the range 5–6 by adding a few drops of sodium hydroxide (30% concentration). Subsequently, the first urea (85 mass% total urea) was added to the reactor. Then, after stirring for 30 min at 40 °C, the mixture was heated to 75 °C for 2 h. Then, 15 mass% glyoxalated lignin was added and the reaction mixture was made by adding few drops of formic acid and reducing the pH to 4–4.5 for 1 h at 75 °C. Finally, after reaching the intended viscosity, the solution was neutralized by sodium hydroxide (30%). Distillation of the mixture was performed using a laboratory vacuum pump and equipment at 50 °C for 1 h. The resins used for this study were prepared at G/U molar ratio of 1.3:1. In addition, commercial UF resin was prepared from Northern Pars Company, Amol, Iran, with a molar ratio F: U = 1.3 to 1. The prepared LUG resin was mixed with the 1, 2 and 3% Na^+-Montmorillonite (NaMMT) (Southern Clay Products, USA) by mechanically stirring for 5 min at room temperature and then the mixture was used. The properties of the used nanoclay are listed in Table 1.

Table 1 The physical properties of the nanoclay

Properties	Values
Specific gravity (g/ml)	2.86
Bulk density (g/ml)	0.3356
Particle size (µm)	≥ 2.00

2.2 Physicochemical tests

The solid content of the adhesives was determined according to ASTM D 4426 (2001). 5 g (W_2) of the synthesized resins was selected and oven- dried at 120 °C for 2 h. Then, the weight of the samples after drying was measured (W_1). Solid content was determined as follows:

$$W_2 - W_1/W_2 \times 100 \quad (1)$$

The density of the liquid resin was obtained by density hydrometer. The viscosity of the resins was measured at 25 °C using a Ford Cup and recalculated to mPas. In order to determine the gel time, 5 g of the resin were introduced into a dry glass beaker. Then, 0.5 g of a 20% aqueous NH_4Cl solution was added to the resin. The beaker was then immersed in boiling water and the time until gelling was measured by a chronometer. Three replicates for each sample were made. For measuring water solubility, 10 g of resin (W_2) was weighed into a conical flask and then distilled water was added slowly stepwise into the flask. The flask was shaken until sediment formation occurred. The mass of distilled water was recorded when a first sediment was observed (W_1). The water solubility of the resin is then expressed as the ratio W_1/W_2 at 25 °C.

2.3 Panel manufacturing

Beech (*Fagus orientalis*) layers with dimensions of 240×200×2 mm^3 were prepared and dried to a moisture content of less than 6 mass% for manufacturing three-layer plywood. For this purpose, both faces of the veneer in the middle layer were coated with 300 g/m² resin. The three layers were assembled and hot-pressed at 120 °C and the maximum pressure of 1 MPa for 5 min. Four types of panel were prepared from LUG resins containing 0, 1, 2 and 3 mass% NaMMT. Preparation of the samples for mechanical tests and water absorption measurement was started 24 h after pressing.

2.4 Panel testing

The manufactured plywood was conditioned at 25 °C+/−2 °C and 65 ± 5% relative humidity in a climate room for one week prior to testing. All physical and mechanical tests of the manufactured particle boards were carried out according to the appropriate standard methods. The tests performed on the specimens were shear strength, bending strength (flexural modulus and flexural strength) and short term water absorption. Shear specimens were prepared from each board to examine shear strength according to ASTM D 906 (1998). Bending strength test was performed according to EN-310 (1993). The shear and bending samples were conditioned at a temperature of 23 °C+/−2 °C and a relative humidity of 60 ± 5% for two weeks. Five specimens were selected randomly from each treatment. Shear and bending strengths were measured with an Instron Model 1186 universal testing machine (Instron, High Wycombe, UK). The shape and dimension of the shear test samples are presented in Fig. 1.

Water absorption was measured according to ASTM D 1037 (2012). Dimensions of the samples were 5×5×0.3 cm^3. For water absorption test, five specimens for each resin were taken from the panels and dried in an oven for 24 h at a temperature of 100 °C+/−3 °C. The mass of the dried specimens (W_o) was determined with an accuracy of 0.001 g. The specimens were then immersed in distilled water for 24 h at a temperature of 23 ± 2 °C and mass was again measured (W_{24}). The values of the water absorption (WA_{24}) in percentage were calculated using the following equation:

$$WA_{24} = \frac{W_{24} - W_0}{W_0} \times 100 \quad (2)$$

2.5 Dispersion of NaMMT in LUG resin

Wide angle X-ray analysis (XRD) was carried out in order to investigate distribution type of nanoclay in the synthesized resins. XRD samples of LUG resins containing 3 mass% nanoclay and neat LUG resins were hardened by addition of ammonium chloride at 100 °C in an oven and then powdered by milling and mounted on a Philips X pert MPD diffractometer (Eindhoven, Netherlands) with Co radiation for analysis. The condition of XRD analysis has been described elsewhere by Younesi-Kordkheili et al. (2016b).

3 Results and discussion

3.1 Physicochemical properties of the prepared resins

Table 2 shows the physicochemical properties of the LUG resin containing 0, 1, 2 and 3 mass% nanoclays. Among the physicochemical properties, the resin gel time is one of the

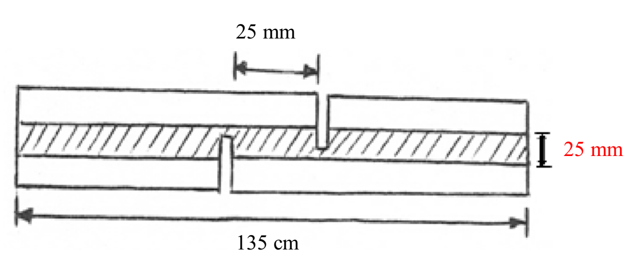

Fig. 1 Shape and dimension of each shear test sample

Table 2 Physicochemical properties of the prepared resins

	Solid content (%)	Viscosity (mPas)	Gelation time (s)	Density (kg/l)
UF	63	278	55	1.238
LUG	51	232	85	1.221
LUG + 1%NaMMT	52	235	79	1.224
LUG + 2%NaMMT	53	240	77	1.227
LUG + 3%NaMMT	55	246	71	1.231

main factors which influence the hot pressing time as well as the production yield in panel manufacturing. It is clearly seen in Table 2, that the LUG resins both with or without addition of NaMMT have slower gel times compared to the control UF resin. This is probably because of the lower reactivity of glyoxal compared to formaldehyde. Younesi-Kordkheili et al. (2015a) have reported that the resins based on glyoxal presented slower gel times than those based on formaldehyde.

The results also indicated that the physicochemical properties of the LUG resin were affected by the proportion of NaMMT used. The incorporation of nanoclays into the LUG resin dramatically increases the solid contents as well as reducing the gel times. These are both important factors affecting resin properties. The LUG resin containing 3 mass% nanoclay exhibited the highest solid content (55%) and the shortest gel time (71 s) among all the resins synthesized. The addition of NaMMT significantly increased the rate of cross-linking as well as consequently decreasing the LUG resins gel time. Younesi-Kordkheili et al. (2015b) and Lei et al. (2008) indicated that addition of nanoclay has an accelerating effect on the curing of the wood adhesives.

Table 2 also shows that higher density and viscosity in LUG resins can be achieved by increasing the proportion of NaMMT from 1 to 3 mass%. The lowest density (1.221 g/ml) and viscosity (232 mPas) is related to the neat LUG resin whereas LUG resin with 3 percent NaMMT exhibits the highest density (1.231 g/ml) and viscosity (246 mPas) values. Increasing the viscosity of the LUG resin by addition of NaMMT is mainly related to a physical effect such as the increase in resin solids content. However, chemical reasons such as reduction of free glyoxal content by addition of nanoclay can also influence the decrease in viscosity of the LUG resin.

3.2 The properties of manufactured plywood

The properties of the plywood panels prepared with the LUG resins are presented in Table 3. The shear strengths and wood failure percentage for the panels manufactured using LUG resins were lower than those made from UF resin. There is a significant difference between the shear strength of the panels prepared from a LUG resin containing 1 mass% NaMMT and the control UF resin probably due to their different physicochemical properties. Furthermore, the shear strength of the panels made with LUG resins increased with increasing amount of NaMMT from 0 to 3 mass%. According to the results obtained, the highest shear strength and wood failure values are obtained with the LUG resin containing 3 mass% NaMMT (0.58 MPa at 35% wood failure percentage), whereas the LUG resin without NaMMT exhibited the weakest shear strength (0.49 MPa at 10% wood failure percentage). This is supported by the differences in physicochemical properties of the synthesized resins (Table 3). Gelation time and viscosity of the synthesized resin are related to their chemical properties such as the amount of cross-linking. The shear strength of the panels completely depends on the quality of the resin, especially on its extent of crosslinking. Generally, the higher percentage of wood failure is attributed to the higher quality resin (Younesi-Kordkheili et al. 2015a). Conversely, Doosthoseni and Zarea-hoseinabadi (2011) indicated that the high percentage of wood failure in the plywood panels means that the resins mixes are stronger than the wood.

Table 3 also presents the bending properties (bending modulus and bending strength) of the plywood panels. Increasing nanoclay content from 0 to 3 mass% in the panels containing LUG resin significantly improved their bending properties; as the highest flexural modulus

Table 3 Physical and mechanical properties of the manufactured panels

Properties	UF	LUG	LUG + 1% NaMMT	LUG + 2% NaMMT	LUG + 3% NaMMT
Density (g/cm^3)	689 ± 12	701 ± 13	706 ± 10	707 ± 11	710 ± 15
Shear Strength (MPa)	1.93 ± 0.12	0.49 ± 0.01	0.55 ± 0.01	0.57 ± 0.02	0.58 ± 0.03
Wood Failure (%)	80 ± 5	10 ± 2	25 ± 2	35 ± 3	35 ± 4
Flexural Modulus (MPa)	2100 ± 49	1412 ± 34	1456 ± 28	1481 ± 44	1502 ± 56
Flexural Strength (MPa)	17 ± 1.30	10.4 ± 0.30	11.8 ± 0.09	12.4 ± 0.13	12.9 ± 0.24
Water absorption (%)	48 ± 2.30	14 ± 1.40	13 ± 0.21	13 ± 0.32	11 ± 0.05

The presented values related to mean ± std

(1502 MPa) as well as flexural strength (12.9 MPa) values were related to the LUG resin with 3 mass% nanoclay. The bending properties of the plywood panels depend on several factors. Previous studies indicated that glue line strength is one of the main factors having significant influence on bending properties (Li et al. 2015). Because of nanoclay size, aspect ratio (length to diameter ratio) and intrinsic mechanical properties, NaMMT can improve glue line strength. The high surface area of nanoclay particles increases the contact surface area with the adhesive resulting in strong adhesion between matrix and nanoclay. The flexural properties also depend on the modulus of individual components. Thus, the good mechanical properties of nanoclay improve the stiffness of resin. Based on the results obtained, there is no significant difference between bending properties of the panels based on the LUG resin containing 3 mass% NaMMT compared to the control resin samples. Conversely, a comparison between bending modulus and bending strength of the panels bonded with the LUG resin shows that addition of nanoclay has more influence on bending strength rather than bending modulus. This is probably because the bending strength is positively affected by the panel internal bond strength, whereas the bending modulus is mainly affected by panel stiffness (Kazemi Njafai and Younesi Kordkheili 2011).

The water absorption values of the panels are also reported in Table 3. The improvement observed is engendered by the addition of small percentages of NaMMT as regards water resistance of the plywood bonded with the LUG resins (Table 3). The plywood bonded with LUG resins showed lower water absorption values than those bonded with UF resins. Such a decrease can be related to the phenolic structure of lignin which is a relatively hydrophobic material (Bhattacharya et al. 2009). The results also showed that among lignin based resins the panels with 3 mass% NaMMT had the lowest water absorption percentage (11%), while the LUG resin without nanoparticles exhibited the highest percentage of water absorption (14%). This is probably due to the increased crosslinking in LUG resins due to the addition of NaMMT. This is an interesting result as even a slight improvement in dimensional stability of panels is much appreciated by the wood panel industries. Reduction of water absorption in wood based panels by addition of nanoclays has been reported by several researchers (Younesi-Kordkheili et al. 2015b; Lei et al. 2008).

Traditionally, wheat flour is used as UF resin filler in plywood manufacturing. The use of wheat flour in such resins has several advantages such as improving mechanical strength, limiting loss of effectiveness by limiting adhesive over penetration into the veneer as well as decreasing the cost of the resin, but unfortunately they also worsen the resin water resistance (Anisuzzaman et al. 2014). The result of this research indicates that the use of nanoclay not only improves the mechanical strength but also decreases the water absorption of the wood based panels.

3.3 XRD analysis

Figure 2 shows the XRD pattern of the NaMMT, neat LUG and LUG resin containing 3 mass% NaMMT. In the case of the NaMMT, the strong 2θ peak at 7.03° corresponds to a d-spacing of 1.26 nm according to the Bragg equation. For the LUG/NaMMT resin the peak shifts to 2θ = 9–11°. Younesi-Kordkheili et al. (2015b) indicated that the increase in the value of the 2θ angle is due to the increase in the distance between the platelet of nanoclay. According to Fig. 2, NaMMT was exfoliated (full separation of platelets into the resin) to the LUG resin. The NaMMT platelet separation in the resin is affected by several factors. The similarity of the structure between the resin (–NH_2) and alkyl ammonium salt will possibly be helpful to obtain good separation.

4 Conclusion

This research focused on finding a new way to eliminate formaldehyde emission from wood based panels such as plywood without significant reduction in mechanical strength. For this purpose the low volatile and nontoxic aldehyde glyoxal was chosen to react with urea and lignin to prepare the new wood adhesive lignin-urea-glyoxal (LUG) resin. Further, improvement of the physical and mechanical properties of LUG resins by nanoclays was also investigated. The following conclusions can be drawn from the results:

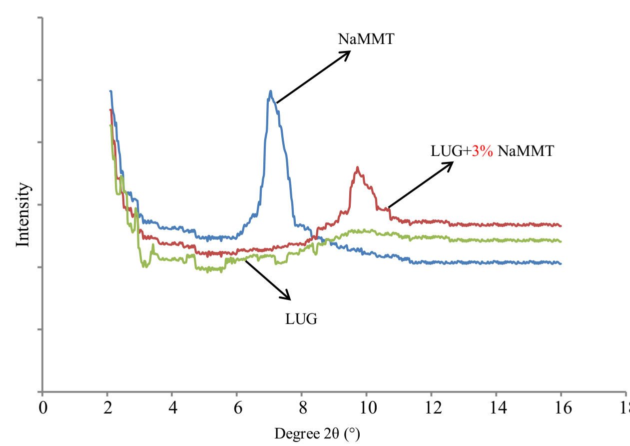

Fig. 2 X-ray diffractograms of cured LUG resins and LUG resins containing 3% NaMMT

- Glyoxal as a nontoxic aldehyde can be used instead of formaldehyde as reactant material for the preparation of wood adhesives.
- It is possible to produce an adhesive for wood panels such as plywood based on lignin, glyoxal and urea with good mechanical strength and low water absorption.
- The gel time of LUG resins was remarkably slower than that of the control UF resin. Plywood panels bonded with LUG resins presented higher dimensional stability and lower shear strength (including lower wood failure) than those bonded with UF resins.
- Nanoclay addition up to 3 mass% increased the viscosity, solid content and density of the LUG resin. In addition, the physicochemical test indicated that gel time of the LUG resin gets accelerated by addition of NaMMT. Increasing the viscosity and density of the LUG resin by addition of NaMMT is mainly related to physical and chemical effects.
- Increasing nanoclay amount from 1 to 3 mass% enhanced mechanical strength of the plywood panels made from LUG resins and reduced their water absorption. This is probably due to the increased crosslinking in LUG resins due to the addition of NaMMT.
- The addition of nanoclay has more influence on bending strength than on bending modulus in plywood panels bonded with the LUG resin.
- XRD characterization indicated that nanoclay can exfoliate (which is a state where all layers of the nanoclay are separated from all tactoids of clay) well when mixed with the LUG resin.

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