

STUDY OF CHEMICAL MODIFICATION OF ALKALINE LIGNIN BY THE GLYOXALATION REACTION

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In this study, glyoxalated alkaline lignins with a non-volatile and non-toxic aldehyde, which can be obtained from several natural resources, namely glyoxal, were prepared and characterized for its use in wood adhesives. The preparation method consisted of the reaction of lignin with glyoxal under an alkaline medium. The influence of reaction conditions such as the molar ratio of sodium hydroxide-to-lignin and reaction time were studied relative to the properties of the prepared adducts. The analytical techniques used were FTIR and ¹H-NMR spectroscopies, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Results from both the FTIR and ¹H-NMR spectroscopies showed that the amount of introduced aliphatic hydroxyl groups onto the lignin molecule increased with increasing reaction time and reached a maximum value at 10 h, and after they began to decrease. The molecular weights remained unchanged until 10 h of reaction time, and then started to increase, possibly due to the repolymerization reactions. DSC analysis showed that the glass transition temperature (T_g) decreased with the introduction of glyoxal onto the lignin molecule due to the increase in free volume of the lignin molecules. TGA analysis showed that the thermal stability of glyoxalated lignin is not influenced and remained suitable for wood adhesives. Compared to the original lignin, the improved lignin is reactive and a suitable raw material for adhesive formulation.

Keywords: Glyoxalation; Hydroxymethylation; Alkaline lignin; Glyoxal; Wood adhesives

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INTRODUCTION

With the exception of cellulose, no other renewable natural polymer is more abundant on earth than lignin. Lignin can be defined as an amorphous polymeric material, arising from the copolymerization of three monomers: coniferyl, sinapyl, and p-coumaryl alcohols. These structures are linked by a multitude of interunit bonds, which include several types of ether (α -O-4, β -O-4, and 4-O-5) and carbon-carbon linkages as well as different functional groups. The reactivity of lignin is mainly determined by both its particular structure with specific functional groups and by its structural modifications, including the use of various separation methods for different raw materials (Malutan et al. 2008). For example, the presence of the phenolic and aliphatic hydroxyl groups in lignin

has enabled its utilization as a partial substitute for phenol in the synthesis of products with a lot of applications (Popa et al. 2003; Malutan et al. 2008).

The partial substitution of phenol by a natural polymer such as lignin, the main byproduct of the pulp and paper making industry and recently also from bioethanol processes, has been presented as an attractive alternative for use in wood adhesives (Nimz 1983; Pizzi 1994; Pizzi and Mittal 2003; Lei et al. 2008; Martínez et al. 2010). In the early studies on this subject, lignin recovered directly from the pulping liquors was incorporated into wood adhesives; however, it is necessary to proceed to their modifications in order to achieve an acceptable amount of substitution and improve the properties of the final applications. These modifications can be achieved by different chemical methods: methylolation, phenolation, and depolymerisation in an alkaline medium to produce lignin with low molecular weight, demethylation, and fractionation (Alonso et al. 2001; Alonso et al. 2005; El Mansouri et al. 2006a; Hu et al. 2011; Mancera et al. 2011). Phenolation and methylolation are the most investigated and interesting modifications of lignin for use in wood adhesives.

Methylolated lignin is widely known and used for wood adhesives (Nimz 1983; Pizzi 1994; Alonso et al. 2001; Pizzi and Mittal 2003). During methylolation, also called hydroxymethylation, formaldehyde reacts with lignin in an alkaline medium to introduce hydroxymethyl (-CH₂OH) groups onto the lignin molecule. The obtained adduct is structurally modified lignin and used for wood adhesives. The formaldehyde is obtained on a large scale from non-renewable resources; therefore, the substitution of this reagent by equivalently obtained from non-fossil sources is an interesting alternative from both the economical and environmental perspectives (Razera and Frollini 2004; Hoareau et al. 2006; De Paiva and Frollini 2006; Ramires et al. 2010). Moreover, substituting formaldehyde with other aldehydes obtained from renewable sources could also eliminate the potential emission of formaldehyde during the use of formaldehyde-based adhesives and other natural adhesives based on methylolated lignins with formaldehyde (Oliveira et al. 2008; El Mansouri et al. 2007a,b).

Glyoxal is a nontoxic dialdehyde (LD_{50} rat > 2960 mg/kg; LD_{50} mouse > 1280 mg/kg) (NIOSH 2000), non-volatile (NTIS 2005), but less reactive than formaldehyde (LD_{50} rat > 100 mg/kg; LD_{50} mouse > 42 mg/kg) (NTIS 2005). It can be obtained from several natural sources, such as the oxidation of lipids or as a by-product of biological processes (Ramires et al. 2010). Glyoxal was previously used as a substitute of formaldehyde for modifying lignosulfonate incorporated in wood adhesives (El Mansouri et al. 2007a,b) and tannin adhesives (Ballerini et al. 2005) and other adhesives (Amaral-Labat et al. 2008) for application to wood panels such as particleboard.

In continuation of the research on lignin as a component of wood adhesives, the present research deals with the total substitution in the lignin methylolation step of a toxic, avowedly carcinogenic material, formaldehyde, with a non-volatile and non-toxic aldehyde, glyoxal. The preparation method is referred to as glyoxalation of lignin. The research also investigated the effects of reaction conditions, such as the molar ratio of sodium hydroxide-to-lignin and reaction time, on the properties of the prepared glyoxalated lignins.

EXPERIMENTAL

Materials

The alkaline lignin (AL) used as the starting material for the glyoxalation reactions was supplied by South China University of Technology, Guangzhou, China. This lignin was produced by ShangDong QuanMing Paper Making Co. Ltd by the alkaline process using sodium hydroxide and Na_2CO_3 from rice straw. It was used in the form of a fine dry powder.

The glyoxal (G, 40%, aqueous solution) and sodium hydroxide used in this research work were purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purification.

Glyoxalation of Lignin

The glyoxalation reactions were carried out in a round flask with four necks provided with a stirrer, a reflux condenser, a thermometer, and an additional funnel. The alkaline lignin was dissolved in the sodium hydroxide solution at room temperature. After 30 minutes of stirring, the obtained solution was heated to a reaction temperature of 45°C and then the 40% (w/w) glyoxal solution was added slowly. The G/L=2.0 molar ratio and the reaction temperature were kept constant for all experiments. The variables and ranges studied were: reaction time from 0 h to 24 h, and sodium hydroxide-to-lignin molar ratio (S/L) of 0.5 and 1.0, which correspond to a pH of 9 and 12, respectively. After the glyoxalation reaction, the obtained solutions were acidified with HCl (1N) until a pH of 2, filtered, and washed with deionized water several times until the pH of the water became neutral. The samples obtained were dried in an oven and ground into fine powders that were stored for analysis.

Fourier Transformation Infrared Spectroscopy

The FTIR spectra of the unmodified and modified lignin samples were recorded with a Nicolet 5700 instrument, using the potassium bromide pellet method. The pellets were prepared from a mixture of 300 mg of potassium bromide and 5 mg of lignin the samples. The acquisition conditions were: spectral width of 4000 to 400 cm^{-1} , 32 accumulations, and 4- cm^{-1} resolution.

$^1\text{H-NMR}$ Spectroscopy for Acetylated Lignins

Acetylation of the lignin samples was performed using the method of Thring et al. (1991). Briefly, 30 mL of 1:1 (v/v) mixture of pyridine and acetic anhydride was added to 2 g of lignin in a 100 mL conical flask, and, after stirring for 48 h at room temperature, the mixture was treated with 10 volumes of 1% HCl at 0 °C. The resulting precipitate was filtered, washed with deionized water to a neutral pH, and dried at room temperature.

$^1\text{H-NMR}$ spectra of the 10 mg acetylated lignin samples dissolved in 0.5 mL of CDCl_3 were recorded on a Bruker AVANCE at 500 MHz device using tetramethylsilane as an internal standard. Proton signals were integrated from the baseline and represented the integrated signal of methoxyl protons for proton quantification.

Molecular Weights Determination (M_w , M_n , and M_w/M_n)

The molecular weights of the acetylated lignin samples were determined by gel permeation chromatography (GPC) equipped with three Waters Styragel Columns HR345 for THF, which were packed with high performance, fully porous, highly crosslinked styrene–divinylbenzene copolymer gel of 7.6mm x 300mm from Waters Co. The effluent was monitored with a Waters RI2414 RI-detector. The testing temperature was 35°C and the amount of injection volume was 100 µL. The columns were calibrated using polystyrene standards in the 92 to 4.000.000 g/mol range. The flux of THF was 1 mL/min and the samples were dissolved in THF at a concentration of 1 mg/mL and stored for 24 h at 5°C to avoid variations in molecular weight (Glasser et al. 1993). The signal detected was digitized at a frequency of 2 Hz and the MWD was calculated from the recorded signal using normal GPC calculation procedures (Yau et al. 1979).

Dynamic Scanning Calorimetry

Glass transition temperatures (T_g) of the samples were determined using a thermal analyzer TA MDSC2910 module. The DSC scans were recorded at a heating rate of 10 °C/min under a nitrogen atmosphere with a flow rate of 60 cm³/min. About 6±2 mg of the sample was used in each test after they were dried for one day at 60 °C under vacuum to eliminate the presence of water. The glass transition temperature was defined as the midpoint of the temperature range at which the change in heat capacity occurs.

Thermal Gravimetric Analysis

The thermal stabilities of the unmodified and modified lignin samples were measured using a NETZSCH STA 409 PC/PG instrument operating from 25 °C to 800 °C at 10 °C/min under a nitrogen atmosphere. TGA analysis measures the weight change of the samples as a function of temperature or time under a nitrogen atmosphere. The first derivative of the TG curve, which corresponds to the rate of mass loss vs temperature, may be used to determine a single thermal decomposition temperature that can be used to compare the thermal characteristics of polymeric materials.

RESULTS AND DISCUSSION

FTIR Spectroscopy

FTIR spectroscopy was employed to characterize the raw material and analyze the changes in the lignin structure during the glyoxalation reaction. The FTIR spectra of (a) the original alkaline lignin, (b) the glyoxalated alkaline lignin produced after 10 h and G/L=0.5, and (c) the glyoxalated alkaline lignin produced after 10h and G/L=1.0 are given in Fig. 1. The absorption bands have been assigned as proposed by Faix (1992).

From Fig. 1 it can be seen that the (a) IR spectrum obtained for the original alkaline lignin is characterized by a broad band at 3430 cm⁻¹, which is attributed to the hydroxyl groups in the phenolic and aliphatic structures and the bands around 2935 cm⁻¹ and 2848 cm⁻¹, arising from CH stretching in the aromatic methoxyl groups and the methyl and methylene groups of the side chains. The absorbance of the weaker band of carbonyl groups is at 1717 cm⁻¹. The absorbance of the band of the phenolic hydroxyl

groups is shown at 1364 cm^{-1} and 1328 cm^{-1} . The absorbance of the C-H vibration of the aromatic ring is at 1610 cm^{-1} and 1510 cm^{-1} . The band at 1510 cm^{-1} was used for normalization and its intensity was set to 1.00. Another two bands attributed to the methoxyl groups appeared at 1459 cm^{-1} and 1425 cm^{-1} . The secondary aliphatic hydroxyl groups appeared at 1212 and the ether-O- at 1117 cm^{-1} .

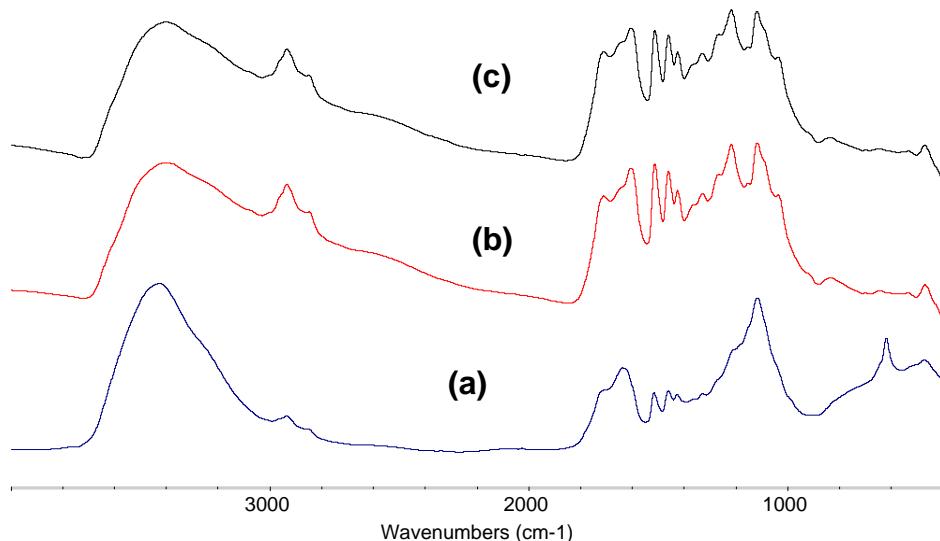


Fig. 1. FTIR spectra of (a) original alkaline lignin, (b) glyoxalated alkaline lignin produced at 10 h and $S/L=0.5$, and (c) glyoxalated alkaline lignin prepared at 10 h and $S/L=1.0$

The comparison between the IR spectra of the alkaline lignin before (Fig. 1a) and after glyoxalation (Fig. 1b and 1c) indicate that only very few main peaks increased or varied after glyoxalation. The most important one is the 1212 cm^{-1} peak. This corresponds to the C-C, C-O, and C=O stretching from the glyoxal introduced onto the lignin molecule, thus confirming that the glyoxalation reaction took place.

In order to follow the extent of the glyoxalation reaction the following ratios of relative absorbance for different functional groups were defined and the results are listed in Table 1.

$$\text{Mean value of total OH-groups} = \text{Average } (A_{3430}, A_{1364}, A_{1328}, A_{1212}) / A_{1510}$$

$$\text{Mean value of phenolic OH-groups} = A_{(1364, 1328)} / A_{1510}$$

$$\text{Glyoxalation Index (GI)} = \text{OH-aliphatic} / \text{OH-aromatic} = [(\text{OH-total} / \text{OH-aromatic}) - 1].$$

Table 1 summarizes the results of the defined ratios above. It is clear that both total OH-groups and GI-index have the same trends. Thus, the glyoxalation index can be taken into account in studying the glyoxalation reaction of lignin. This ratio increases with increasing reaction time up to 10 h, after which it begins to decrease. The first increase is attributed to the introduction of hydroxymethyl groups (-CH₂OH) into the lignin molecule, which can also be confirmed by the same tendency observed for the total-OH groups.

Table 1. Ratios of Relative Absorbance for Different Functional Groups

Samples	tr(h)	OH-aromatic		OH-total		GI	
S/L	-----	0.5	1.0	0.5	1.0	0.5	1.0
AL	0	0.45		0.76		0.68	
GAL1	1	0.44	0.44	0.85	0.86	0.93	0.95
GAL2	2	0.43	0.45	0.91	0.95	1.12	1.11
GAL3	4	0.44	0.45	0.99	1.04	1.25	1.31
GAL4	6	0.45	0.44	1.07	1.16	1.38	1.64
GAL5	8	0.44	0.45	1.12	1.25	1.55	1.78
GAL6	10	0.44	0.44	1.18	1.34	1.68	2.05
GAL7	12	0.40	0.40	1.06	1.20	1.65	2.00
GAL8	24	0.38	0.33	0.92	0.95	1.42	1.88

The decrease in GI-index can be explained by the possible degradation of the hydroxyl aliphatic of the phenyl propane units of the lignin molecule. On the other hand, the GI-index was higher in the glyoxalated lignins prepared with S/L=1.0 than those prepared with a S/L=0.5 molar ratio. This can be explained by the alkaline pH of the reaction medium in which the hydroxymethylation reaction becomes favoured (Alonso et al. 2001). The content of the aromatic OH-groups remained constant during the first 10 h and then slightly decreased, probably due to the possible secondary reaction of condensation (Malutan et al. 2008).

As a component of wood adhesives, lignin can react with an aldehyde, tannin, phenol, and isocyanate by heating under alkaline conditions to produce lignin-based polycondensate resins (Ballerini et al. 2005; El Mansouri et al. 2007a,b); however, this lignin should have a high content of aliphatic hydroxyl, which was found for glyoxalated lignin obtained at 10h and S/L=1.0. From this criterion, GAL6 prepared with S/L=1.0 at 10 h appeared to be the best of all prepared glyoxalated lignins for wood adhesives.

¹H-NMR Spectroscopy

NMR spectroscopy is a useful technique to follow the evolution of functional groups. Figure 2 displays that integration of proton signals in the ¹H NMR spectra of the lignin samples are hampered by overlap between signals. The comparison with the signal for methoxyl protons nevertheless allows for estimation of the number of protons corresponding to each functional group. The obtained results are summarized in Table. 2.

The results summarized in Table 2 show that the aliphatic acetate's protons, which correspond to aliphatic hydroxyls, increased with increasing reaction time until 10 h and then decreased. This increase is due to the introduction of hydroxymethyl groups onto the C-3 and C-5 positions in the aromatic ring of the lignin molecule, which is supported by a decrease of the aromatic protons during the first 10 h of lignin glyoxalation. This increase is more important when a S/L=1.0 molar ratio was used, which corresponds to pH of 12, because the hydroxymethylation reaction is favoured in an alkaline medium (Alonso et al. 2001). The protons of the aromatic acetates, which correspond to phenolic hydroxyls, remained unchanged during the first 10 h of the reaction, and decreased with increasing reaction time greater than 10 h. The decrease in the content of both aliphatic and phenolic hydroxyls after 10 h was probably due to the

secondary condensation reactions, which can take place under alkaline conditions (Malutan et al. 2008). Thus, the obtained hydroxymethylated lignin at 10h and with S/L=1.0 has a greater number of hydroxyl groups, and thus, it is suitable to produce lignin-based resins (El Mansouri et al. 2007a,b).

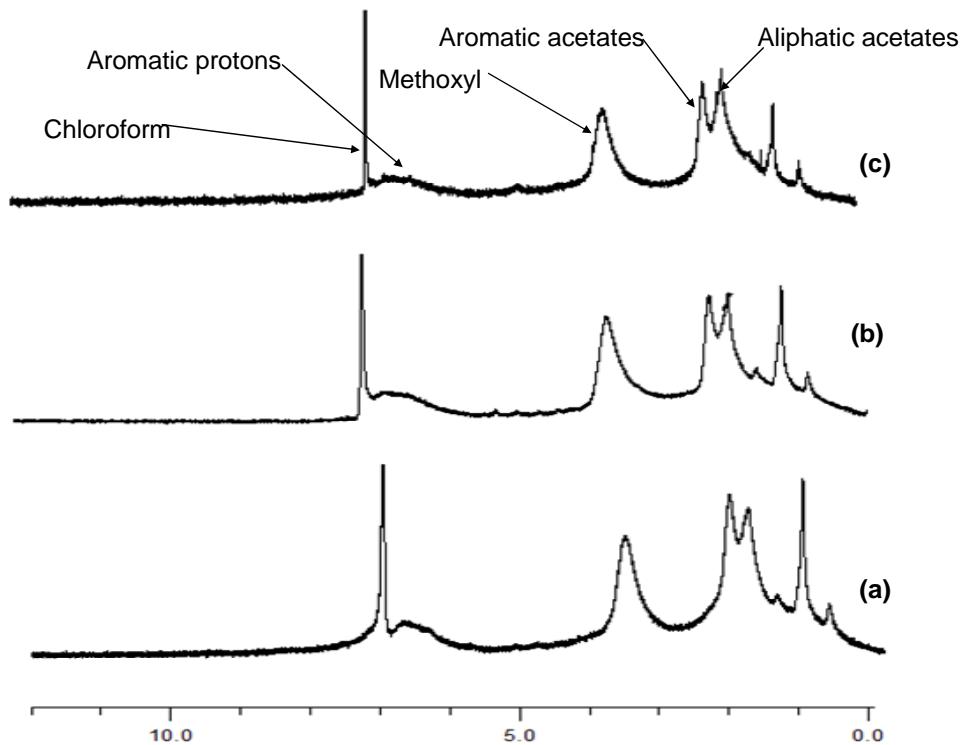


Fig. 2. ^1H -MR spectra of (a) acetylated original alkaline lignin, (b) acetylated glyoxalated alkaline lignin prepared at 10h with S/L=0.5, and (c) acetylated glyoxalated alkaline lignin prepared at 10h with S/L=1

Table 2. Average Number of Protons / Methoxyl Groups of Different Functional Groups as Estimated by ^1H -NMR Spectroscopy

Samples	tr(h)	Aliph-acetates (1.6-2.2 ppm)		Arom-acetates (2.2.-2.6 ppm)		$\text{CH}_3\text{O}-$ protons (3.0-4.0 ppm)		Aromatic- protons	
S/L	-----	0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
AL	0	1.16		0.75		1.0		0.57	
GAL1	1	1.18	1.20	0.74	0.75	1.0	1.0	0.54	0.52
GAL2	2	1.23	1.35	0.75	0.74	1.0	1.0	0.51	0.49
GAL3	4	1.28	1.45	0.75	0.74	1.0	1.0	0.51	0.47
GAL4	6	1.39	1.56	0.74	0.73	1.0	1.0	0.49	0.45
GAL5	8	1.43	1.65	0.73	0.74	1.0	1.0	0.43	0.39
GAL6	10	1.65	1.71	0.75	0.75	1.0	1.0	0.34	0.30
GAL7	12	1.44	1.59	0.71	0.70	1.0	1.0	0.32	0.30
GAL8	24	1.35	1.46	0.66	0.65	1.0	1.0	0.31	0.27

Molecular Weights Determination

Weight-average (M_w) and number-average (M_n) molecular weights, and polydispersity (M_w/M_n) of all lignin samples are shown in Table 3. The values obtained for M_w and M_n were in the range of 1050 to 1440 g/mol and 795 to 1200 g/mol, respectively. These ranges are in good agreement with the data reported in literature related to lignin molecular weight (Glasser and Jain, 1993; Angles et al. 2003; Tejado et al. 2007; El Mansouri et al. 2006b, 2011).

Table 3. Results of M_w , M_n , and Polydispersity of Acetylated Lignin Samples

Samples	tr(h)	M_w (g/mol)		M_n (g/mol)		M_w/M_n	
S/L	----	0.5	1.0	0.5	1.0	0.5	1.0
AL	0	1069		805		1.32	
GAL1	1	1060	1065	790	790	1.34	1.35
GAL2	2	1050	1060	800	810	1.31	1.31
GAL3	4	1055	1050	810	805	1.30	1.30
GAL4	6	1060	1060	805	800	1.32	1.33
GAL5	8	1065	1050	795	805	1.34	1.30
GAL6	10	1054	1060	800	810	1.32	1.31
GAL7	12	1100	1200	900	980	1.22	1.22
GAL8	24	1240	1440	1050	1200	1.18	1.20

From the results shown in Table 3, M_w and M_n remained unchanged with increasing reaction time until 10 h, after which, M_w and M_n increase significantly. The increase in M_w is due to the possible repolymerization of lignin fragments. It was reported that under alkaline conditions some α -hydroxyl groups form the quinone methide intermediate that reacts easily with other lignin fragments, giving an alkali-stable methylene linkage (Van der Klashorst et al. 1989) and consequently causing the appearance of high molecular weight molecules with higher M_w values. Polydispersity, defined by the ratio M_w/M_n , also remained practically unchanged.

Differential Scanning Calorimetry (DSC)

Lignin is a thermoplastic amorphous polymer, i.e., lignin undergoes what is known as glass transition temperature (T_g). This property is affected by several factors such as the presence of water and solvents, molecular weight, thermal history, cross-linking, and pressure (Hatakeyama 1992); however, using dried samples at 60 °C during one day under vacuum allows for relative comparison of the T_g values of different lignin samples prepared under different reaction conditions.

Table 4 lists the T_g values of the prepared glyoxalated lignin samples with S/L=1.0 that showed better structural properties. The obtained T_g for all lignin samples was in the range of 119 °C and 155°C. They are in good agreement with those reported for different lignins with T_g values between 90 °C and 180 °C (Feldman et al. 2001; Glasser and Jain, 1993; Tejado et al. 2007; El Mansouri et al. 2011).

Table 4. Results from Thermal Analysis (DSC, TGA): Values of T_g , DTG_{max}, and Residue (%)

Samples	tr(h)	Tg (°C)	DTG _{max} (°C)	Residue (%) at 800 °C
AL	0	155	370	37.3
GAL1	1	151	363	41.0
GAL2	2	145	366	41.1
GAL3	4	138	365	42.2
GAL4	6	132	365	40.6
GAL5	8	127	364	40.3
GAL6	10	119	366	41.6
GAL7	12	124	365	42.1
GAL8	24	138	365	41.3

* T_g : Glass transition temperature, DTG_{max}: maximum of thermal decomposition temperature, Residue (%): unvolatilized weight fraction at 800 °C.

After glyoxalation the glass transition temperature decreased from 155°C to 119°C after 10 h of reaction time, and then it increased to 138 °C between 10 h and 24 h. As the amount of the aldehyde substituent increased, the glass transition temperature decreased. This reduction was essentially due to the increase in free volume of the molecules as the aldehyde substituent increased. The concentration of chain ends resulting from the introduction of the hydroxyl groups on the C-3 and C-5 positions contributed to an increase in free volume of the glyoxalated lignins. This behaviour was also noted earlier in the case of lignin esters (Glasser and Jain 1993). As reported by Goring (1971) the glass transition temperature of dioxane lignin increases with the increase in molecular weights; therefore, the increase of T_g after 10 h of reaction time was a consequence of the increase in the molecular weights. This analysis seems to be valid for these experiments because of the increase of molecular weights reported earlier in the molecular weight analysis.

Thermogravimetric Analysis (TGA)

Figure 4 shows the TG and DTG curves of unmodified and some glyoxalated alkaline lignins (GAL3, GAL5, GAL6, and GAL8) prepared at different reaction times. The observation of three phase changes in the lignin samples corresponds to the moisture evaporation, main devolatilization, and continuous devolatilization. The same observation is comparable in the study of pyrolysis of biomass reported by Chen et al. (2003) and for lignin by Murugan et al. (2008). It implies that the initial weight loss of all samples starts between 40 and 50°C, with the maximum between 70 and 80°C, and an offset temperature between 110 and 120°C. This weight loss is mainly associated with moisture evaporation and loss of volatiles.

The first thermal degradation step began at 180°C for all lignin samples. Such similitude in initial degradation temperatures of lignocellulosic materials has been related to the similarity in chemical composition of the samples (Mansaray and Ghaly 1999). The weight loss at this step was almost the same for all lignin samples until a temperature of 300°C. After this temperature the difference in the weight loss of unmodified and glyoxalated lignins became evident. Thus, the rate of weight loss of modified lignins is higher than that of unmodified lignin samples in the temperature range of 300 to 550°C.

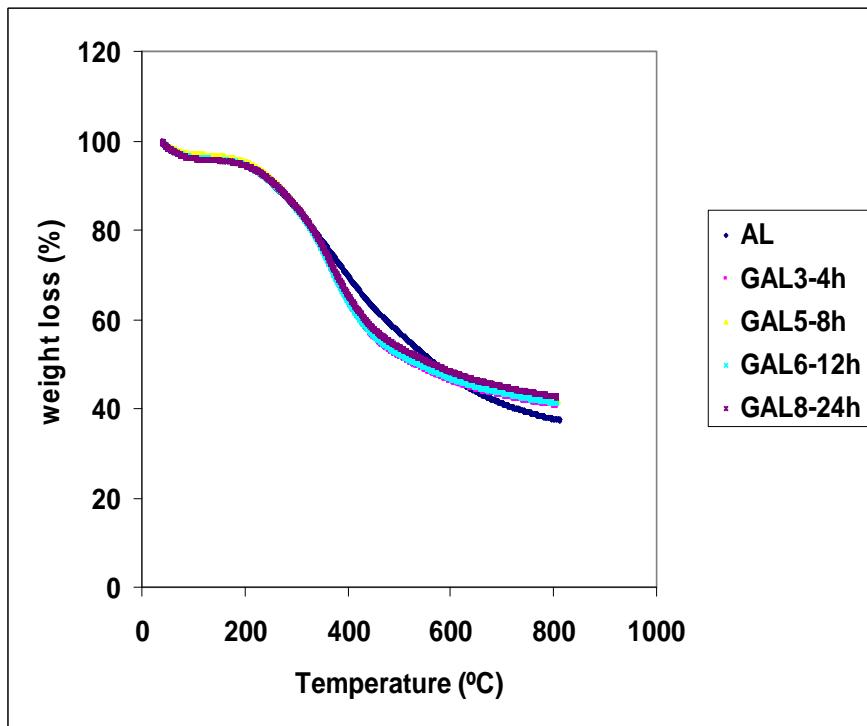
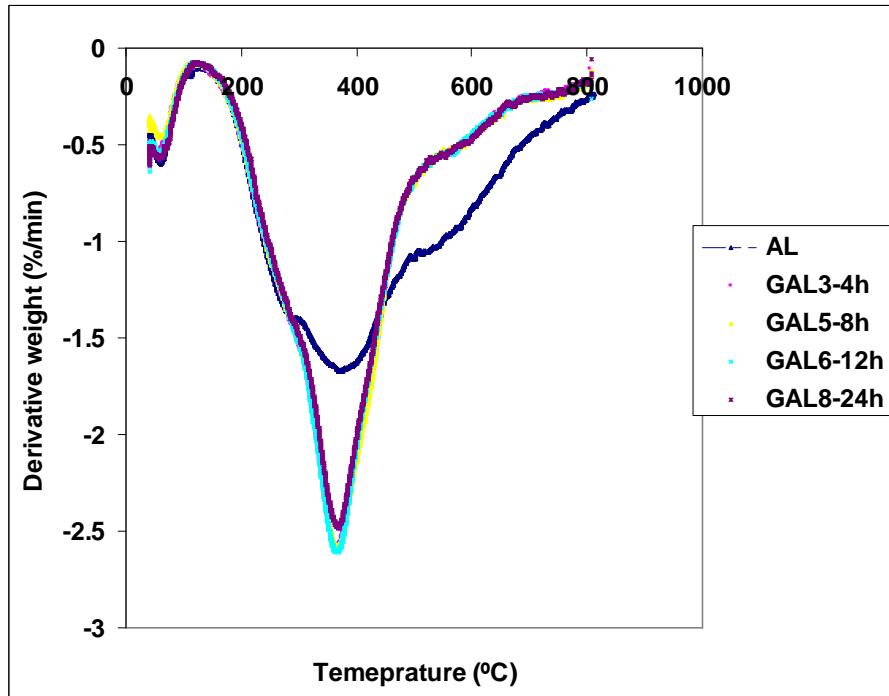


Fig. 4. (a) DTG and (b) TG curves of AL, GAL3, GAL5, GAL6 and GAL8

The peak of DTG curves (DGT_{max}) may be expressed as a single thermal decomposition temperature and can be used to compare the thermal characteristics of polymeric materials. Thus, the thermal characteristics of all lignin samples are summarized in Table 4. The obtained values of DGT_{max} for all glyoxalated lignin samples were between 363 and 366°C. There was a slight difference compared to the unmodified alkaline lignin. The residue at the end temperature of 800°C was between 40 and 42.2%, which was slightly greater after the glyoxalation reaction. From the point of view of thermal stability, the glyoxalated lignins prepared after 10h of reaction time, which presented the better structural properties, remained the most suitable for wood adhesives. This can be supported by the occurrence of the maximum rate of weight loss in phenolic resins at around 345°C, which remained less than that of GAL6.

CONCLUSIONS

1. Results of structural characterization from both FTIR and 1H -NMR spectroscopies showed that the optimum operating conditions for the glyoxalation of alkaline lignin are a sodium hydroxide-to-lignin molar ratio (S/L) of 1.0 and a reaction time of 10h.
2. Results from DSC analysis showed that T_g decreased with the introduction of glyoxal into the lignin molecule because of the increase in free volume of the molecules as the amount of aldehyde substituent increases.
3. From the point of view of thermal stability, the glyoxalated lignins prepared after 10h of reaction time, which presented the better structural properties, remained the most suitable for wood adhesives.
4. Compared to the original alkaline lignin, the improved lignin is a suitable raw material based on natural resources, such as glyoxal, for wood adhesives formulation.

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