

SYNTHESIS AND CHARACTERIZATION OF KRAFT LIGNIN-BASED EPOXY RESINS

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Epoxidization is an interesting way to develop a new application of lignin and therefore to improve its application potential. In this work, kraft lignin-based epoxy resins were obtained by the epoxidization reaction, using the kraft lignin recovered directly from pulping liquor and modified by a methylation reaction. The methylolated lignins were obtained by the reaction of original kraft lignin with formaldehyde and glyoxal, which is a less volatile and less toxic aldehyde. ¹H-NMR spectroscopy showed that methylolated kraft lignin has more hydroxymethyl groups than glyoxalated kraft lignin. For the epoxidization reaction we studied the influence of the lignin:NaOH (w/w) ratio, temperature, and time of the reaction on the properties of the prepared epoxidized lignins. The structures of lignin-based epoxy resins were followed by epoxy index test and FTIR spectroscopy. Optimal conditions were obtained for lignin-based epoxy resin produced at lignin/NaOH = 1/3 at 70 °C for 3h. Thermogravimetry analysis (TGA) revealed that the epoxidization enhances the thermal stability of lignins and may allow a wider temperature range for applications with lignin epoxy-PF blends.

Keywords: Lignin; Hydroxymethylation; Glyoxalation; Epoxidization; Epoxy resin

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INTRODUCTION

After cellulose, lignin is the most abundant organic polymer in the plant world, and its content depends on the plant species (roughly 15 to 30%) (Dence 1992). Lignin can be defined as an amorphous and polyphenolic material, arising from the copolymerization of three phenylpropanoid monomers, namely, coniferyl, sinapyl, and p-coumaryl alcohol that lead, respectively, to guaiacyl (G), syringyl (S), and p-hydroxyphenyl propane (p-H)-type units (see Fig. 1). These structures are linked by a multitude of inter-unit bonds that include several types of ether (α -O-4, β -O-4, 4-O-5) and carbon-carbon linkages. It is extracted by several pulping techniques and recently in ethanol production processes. Technical lignins are divided into two categories (Gosselink et al. 2004). The first one comprises sulphur-containing commercial lignins, including lignosulfonates and kraft lignins, which are produced in huge quantities. The second one comprises lignins without sulphur in their composition, such as organosolv, soda/antraquinone lignin, and lignin from the ethanol process production. In this last group, only the soda lignins have a short-term potential for industrial availability.

Traditionally lignins have been viewed as low value by-products of pulping and papermaking, with the only utilisation as a fuel to heat the pulping boilers. Recently the vision has been changing, and considerable interest has been shown for their use in several industrial applications, mainly those based on the use of more environmentally friendly and natural compounds. Some of these applications include biomaterials, fuels, biocides and biostabilisers, animal feed, health products, and the cultivation of crops cultivations (Lora and Glasser 2002).

In the biomaterials field, lignin has been used to synthesize several resins such as phenol-formaldehyde, polyurethanes, and epoxy resins (Nonaka et al. 1997; Thring et al. 1997; Alonso et al. 2004; Stewart Derek 2008). The epoxy resin market is important and large, and with specific reference to phenol-epoxy resins, one in which lignin could flourish as a crosslinking agent (Stewart Derek 2008). In this sense, epoxy resins are considered as an attractive area for commercial lignin applications, since they are used in adhesives, composites, and coatings.

In the past researchers have developed several methods to synthesize lignin-based epoxy resins. These methods have also been applied for polyesters and phenolic resins, and can be divided into three categories as follows: (i) Blending the epoxy resins with technical lignins obtained directly from the pulp and paper process (Feldman et al. 1991a,b; Nonaka et al. 1997). (ii) Direct modification of technical lignins by epoxides (Simionescu et al. 1993; Hofmann and Glasser 1993, 1994; Malutan et al. 2008), and (iii) Modification of lignins by several chemical reactions in order to improve their reactivity prior to the epoxidation reaction (Simionescu et al. 1993; Malutan et al. 2008). These different ways lead to different products having different physico-chemical properties, so that they may be used in different applications. The schematic representation of a lignin-based epoxy resin is presented in the Fig. 2.

Although several studies have been carried out aimed at producing lignin-based epoxy resins, modifying technical lignins by such means as an epoxidation reaction using epichlorohydrin in alkaline medium is essential to improve polymer-lignin compatibility. The water-soluble lignin prepared from calcium lignosulfonate treated with sulfuric acid and phenol has been mixed with epichlorohydrin and sodium hydroxide to obtain lignin-based epoxy resin (Sun et al. 2007). Sodium lignosulfonate was modified by reacting with anhydrides to form ester-carboxylic acid derivatives, and used to crosslink glycerol diglycidyl ether and ethylene glycol diglycidyl ether to obtain the bio-base epoxy resins, which can be used as adhesives (Ismail et al. 2010). Furthermore, there have been no extensive studies comparing the use of several lignin derivatives from the same original lignin to produce epoxidized lignins.

In this paper, kraft lignin either in its received form or modified by two chemical methods was used to produce lignin-epoxy resins suitable for the production of lignin-epoxy blends. The modification methods included methylolation and glyoxalation prior to the lignin reaction with epichlorohydrin under alkaline conditions. The synthesized products were characterized by FTIR and ¹H-NMR spectroscopies, epoxy index test, and thermogravimetric analysis (TGA).

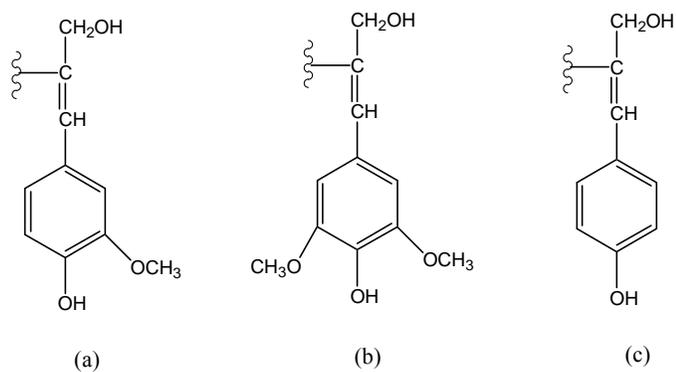


Fig. 1. Schematic representation of the structural units of lignin: (a) guaiacyl (G), (b) syringyl (S), and (c) *p*-hydroxyphenyl propane (H)

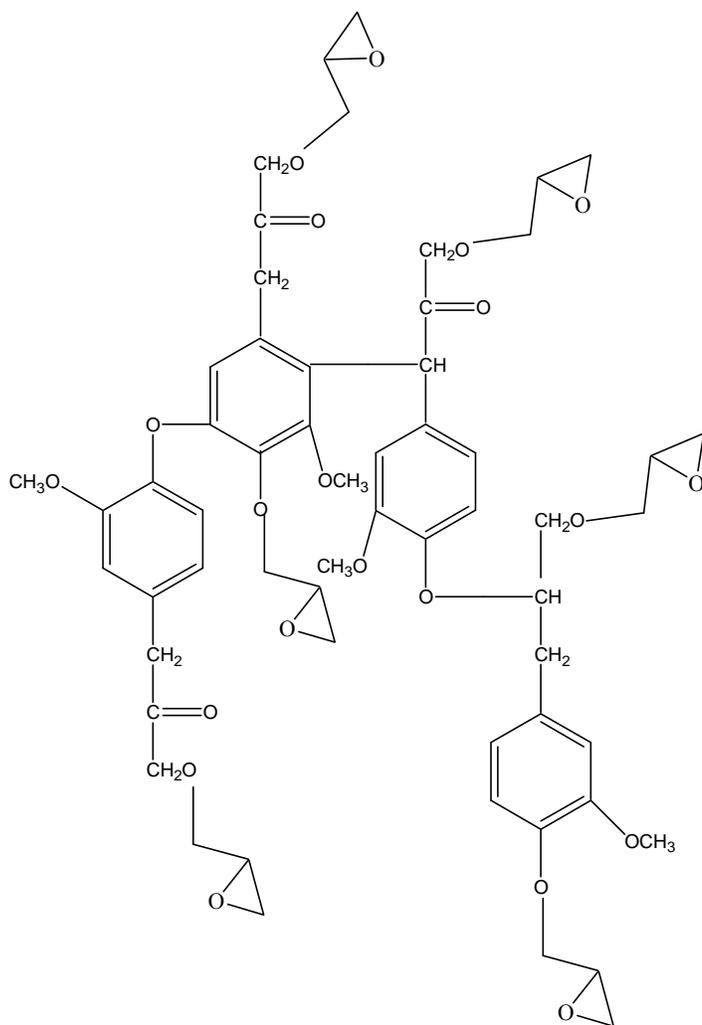


Fig. 2. Schematic illustration of lignin-based epoxy resin

EXPERIMENTAL

Materials

The kraft lignin used as a starting material for the modification reactions was purchased from Sigma Aldrich and used in its finely dry powder. Based on the elemental analysis results its molecular weight was 178 g/mol. Formaldehyde (35–40% aqueous solution), glyoxal (40%, aqueous solution), epichlorohydrin, dioxane (99%), pyridine, and acetic anhydride, used in this research work were purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purifications.

Methylolation of Lignin

Lignin powder (10 g) was slowly added to 150 mL of NaOH solution, keeping the pH of the mixed solution between 12 and 13 for better dissolution of the lignin powder, which was facilitated by vigorous stirring with an overhead stirrer. A molar ratio of NaOH to lignin of 0.8 was used, which resulted in a final pH of 12.30. A 250 mL glass flask equipped with a condenser, a thermometer, and an overhead stirrer was charged with the above solution, and then formaldehyde aqueous solution was added according to the molar ratio of 1:1 formaldehyde to lignin. The obtained mixture was heated to 50 °C and kept at that temperature for 8 hours, based on the optimum conditions determined previously in our lignin hydroxymethylation studies (El Mansouri et al. 2007a). This methylolated kraft lignin was named MKL.

Glyoxalation of Lignin

According to the preparation method reported by El Mansouri et al. (2007b), 20 parts by mass of lignin powder were slowly added to 40 parts distilled water. Then NaOH solution was added from time to time, thus keeping the pH of the solution between 12 and 12.5 for better dissolution of the lignin powder. A total of 64 parts by mass of sodium hydroxide solution (10%) was added, which resulted in a final pH near to 12.6. A 100 mL glass flask equipped with a condenser, a thermometer, and a stirrer was charged with the above solution and heated to 50°C. 20 parts by mass glyoxal (40%, in water) were added, and the lignin solution was then continuously stirred and heated for 8 hours. The obtained glyoxalated lignin was precipitated, filtered, washed, and dried in oven under vacuum overnight. The obtained glyoxalated lignin was named GKL.

Epoxidization of Lignin

The procedure for lignin epoxidation is presented in Fig. 3. Lignin powder was added to the corresponding amount of 20% (w/w) sodium hydroxide, and the mixture was stirred for 30 min before adding the epichlorohydrin. The experimental conditions are presented in Table 2. In this work, kraft lignin (KL), methylolated kraft lignin (MKL), and glyoxalated kraft lignin (GKL) were used to obtain different lignin-based epoxy resins. After lignin epoxidation, two fractions of lignin epoxy were obtained: (1) lignin epoxy soluble in water, and (2) water insoluble lignin epoxy. The solid lignin epoxy was separated by filtration and washed twice with 100 mL deionised water, and then gently dried at 30 °C under vacuum, weighted in order to determine the yields of solid epoxy-lignin resins.

Then, the obtained lignin epoxy products were characterized by epoxy index and FTIR spectroscopy to analyse the structure. Thermogravimetry analysis (TGA) was used to follow the thermal degradation, while the methylolated and glyoxalated products were characterized by proton nuclear magnetic resonance spectroscopy in order to quantify the amount of introduced aliphatic hydroxyl groups.

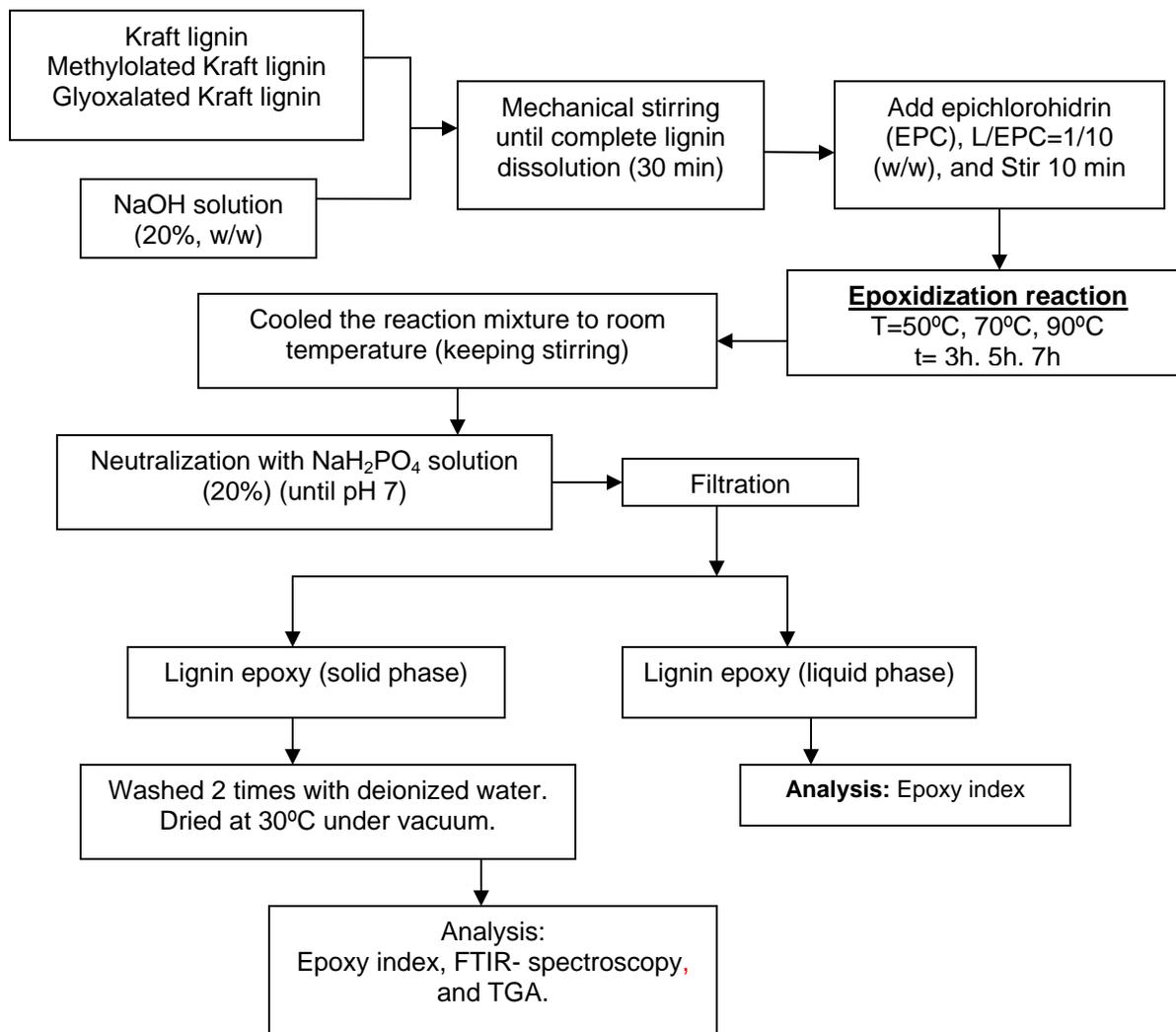


Fig. 3. Diagram of preparation of lignin-based epoxy resins

Analytical Methods

Fourier Transform Infrared Spectroscopy

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

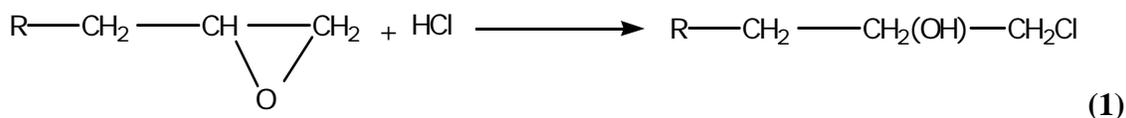
¹H-NMR spectroscopy for acetylated lignins

Acetylation of 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 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 neutral pH, and dried at room temperature.

¹H-NMR spectra of 10 mg acetylated lignin samples dissolved in 0.5 mL of CDCl₃ were recorded on a Bruker AVANCE at 500 MHz device using tetramethylsilane as internal standard. Proton signals were integrated from the baseline and referred to the integrated signal of methoxyl protons for proton quantification.

Determination of epoxy index

Determination of the epoxy groups was carried out by (0.1N) HCl addition on the epoxy group according to Reaction (1), and the titration of the acid excess with (0.1N) NaOH (Malutan et al. 2008). All samples were analyzed after drying in an oven under vacuum at 30 °C for one day. Epoxy index was determined for both lignin epoxy solid and liquid phases. The analysis was performed in triplicate, and the mean values are presented in Table 1.

*Thermogravimetry analysis (TGA)*

Thermal stability of unmodified and modified lignin samples was measured using a NETZSCH STA 409 PC/PG instrument operating from 25 °C to 600 °C at 10 °C/min under a nitrogen atmosphere. TGA analysis measures the weight change of the sample as a function of temperature or time under nitrogen atmosphere. The first derivative of the TG curve corresponding 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**¹H-NMR Spectroscopy**

NMR spectroscopy is a useful technique with which to follow the evolution of functional groups. From the spectrum of acetylated kraft lignin (A-KL) presented in Fig. 4 it can be shown that integration of proton signals in the ¹H NMR spectra of the lignin samples is hampered by overlap between signals. The comparison with the signal of methoxyl protons nevertheless allows estimation of the number of protons corresponding to each functional group. Table 1 lists the numbers of acetate groups/methoxyl of unmodified (KL), methylolated (MKL), and glyoxalated (GKL) kraft lignin samples after acetylation, as estimated from the ratios between the signals, together with the estimated ratios of aliphatic and aromatic acetate signals.

As shown in Table 1, the acetylated methylolated kraft lignin (A-MKL) exhibited a content of aliphatic acetate protons corresponding to aliphatic hydroxyls that was higher than that in the acetylated glyoxalated kraft lignin (A-GKL). These results demonstrate that although formaldehyde is more toxic and volatile than glyoxal, it is more reactive, and a higher level of methylol groups can be introduced when it is used. The increase of aliphatic hydroxyl groups after methylolation and glyoxalation is due to the introduction of more hydroxymethyl groups at C-3 and C-5 positions in the aromatic ring of the lignin molecule (the Lederer Manasse reaction), at side chain carbons α to a carbonyl group (the Tollens reaction), and at β carbons involved in α, β double bonds conjugated to a phenolic ring (the Prins reaction). Hence, the obtained methylolated lignin with formaldehyde has a higher content of hydroxyl groups and could be used with resins to form a useful material, especially in epoxy resins.

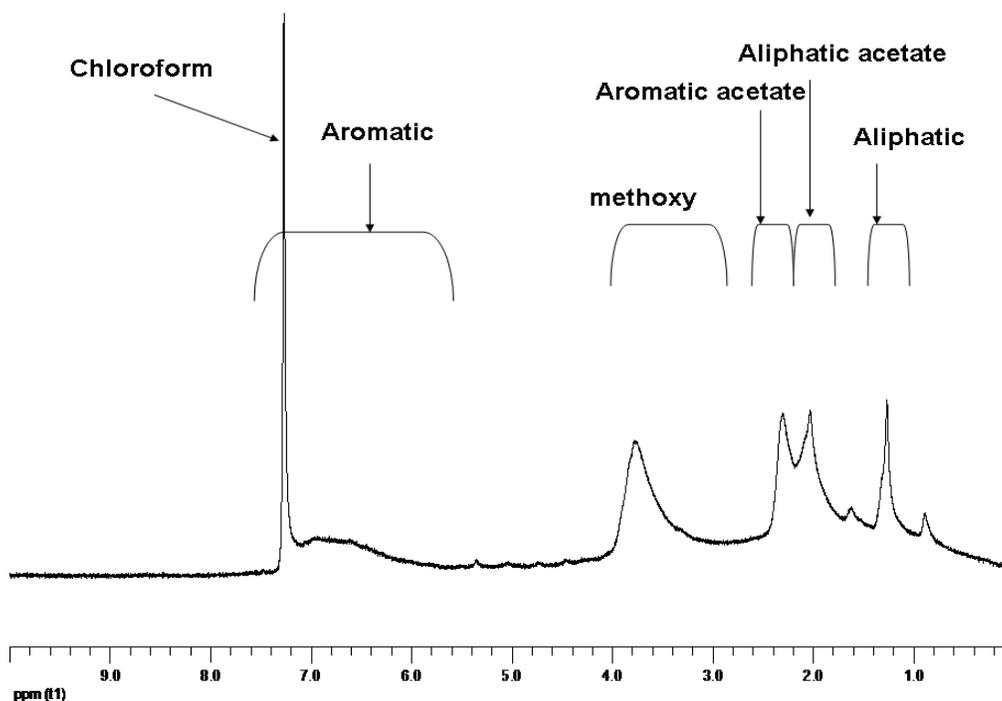


Fig. 4. ^1H -NMR spectrum of acetylated Kraft lignin (A-KL)

Table 1. Numbers of Acetate Groups per Methoxyl Groups in Various Lignins

Sample	$\text{CH}_3\text{O-}$ (4.0-3.0ppm)	Ar-acetate (2.6-2.2 ppm)	Aliph-acetate (2.2-1.6 ppm)	$\text{OH}_{\text{-Aliph}}/$ $\text{OH}_{\text{-Ar}}$
Unmodified Kraft lignin	1	0.50	0.79	1.58
Methylolated Kraft lignin	1	0.50	1.10	2.20
Glyoxalated Kraft lignin	1	0.50	0.98	1.96

Lignin Epoxidization

Table 2 shows the results of epoxy index and the obtained yields for different epoxidized lignin samples. The increase of temperature from 50 °C to 70 °C caused an increase in the epoxy index of the solid phase, but a further increasing of the reaction

temperature above this value to 90 °C resulted in large decrease in epoxy index. This decrease is probably due to the possibility of secondary reactions occurring between the formed epoxy groups and the free phenolic hydroxyl groups. The same behaviour was reported by Malutan et al. (2008) when they studied the epoxidization reaction of different alkaline lignins with epichlorohydrin under alkaline conditions. Thus, it can be expected that 70 °C is a suitable reaction temperature for lignin epoxidization. When the reaction period was increased from 3h to 5h and then to 7h, the epoxy index was decreased. This suggests that 3h reaction time is enough to generate a better epoxidized lignin. Also it can be seen that an increase of lignin/NaOH ratio had a negative effect on the epoxy index. The epoxy index has higher values for epoxidized methylolated kraft lignin (EMKL), epoxidized glyoxalated kraft lignin (EGKL), and epoxidized kraft lignin (EKL2) produced under the same experimental conditions, in that order. This difference is due to the higher content of aliphatic hydroxyl groups in both methylolated and glyoxalated kraft lignin samples. The epoxy indexes of liquid phase were between 0.13% and 0.54%, and they were in agreement with those found in literature (Malutan et al. 2008; Simionescu et al. 1993). On the other hand, the yield of epoxidized kraft lignin increased with reaction temperature and time, probably due to occurrence of crosslinking reactions.

Table 2. Experimental Conditions and Results of Epoxy Index (EI)

Samples	T (°C)	Lignin/NaOH (w/w)	Time (h)	Epoxy index (%)		Yield (%)
				Solid resin	Liquid resin	
EKL-1	70	1 / 6	3	1.56	0.13	80.0
EKL-2	70	1 / 3	3	2.29	0.16	79.0
EKL-3	70	1 / 3	5	1.63	0.41	85.0
EKL-4	70	1 / 3	7	1.54	0.38	94.0
EKL-5	50	1 / 3	3	2.01	0.35	81.0
EKL-6	90	1 / 3	3	1.15	0.37	93.0
EMKL	70	1 / 3	3	3.30	0.54	82.0
EGKL	70	1 / 3	3	2.95	0.15	80.0

EKL: Epoxidized kraft lignin, EMKL: Epoxidized methylolated kraft lignin, EGKL: Epoxidized glyoxalated kraft lignin

FTIR Spectroscopy

FTIR spectroscopy was employed to characterize the raw materials and analyze the changes in the lignin structure during its modification reactions, mainly to observe the introduction of new functional groups or disappearances of the existent ones. The FTIR spectrum of unmodified kraft lignin (KL) is presented in Fig. 5, and the attribution of the absorption peaks in lignin molecule were used as suggested by Faix (1992). The introduction of epoxy groups in lignin structure is usually indicated by the presence of the bands at 910 cm^{-1} , 850 cm^{-1} , and 750 cm^{-1} after the epoxidization reaction (Feldman et al. 1991a).

The FTIR spectrum of original kraft lignin was characterized by an O-H band at 3445 cm^{-1} , an intense C-H band at 2935 cm^{-1} , and another at 2848 cm^{-1} , which are typical vibrations of methoxyl groups. The absorbance of carbonyl groups conjugated with

aromatic ring was manifested by a band at 1648 cm^{-1} . The phenolic hydroxyl groups appeared at 1364 and 1328 cm^{-1} . The absorbance of the C-H vibration of aromatic ring was at 1615 cm^{-1} and 1514 cm^{-1} . Another two bands attributed to methoxyl groups appeared at 1459 cm^{-1} and 1425 cm^{-1} . The secondary aliphatic hydroxyl groups appeared at 1218 cm^{-1} and the ether (-O-) at 1043 cm^{-1} .

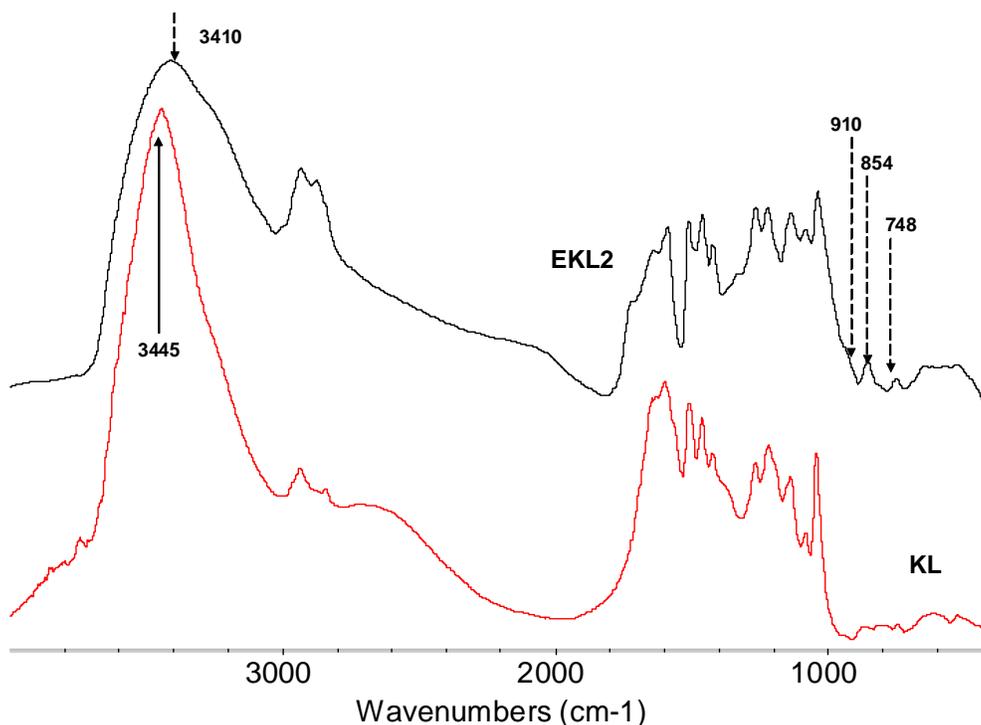


Fig. 5. FTIR spectra of original kraft lignin (KL) and epoxidized kraft lignin (EKL2)

The FTIR spectra of the kraft lignin after epoxidizing EKL-2, EMKL, and EGKL presented in Figs. 5 and 6 indicate that some of the main peaks decreased or appeared after epoxidization. All the spectra of epoxidized kraft lignin samples from EKL-1 to EKL-6 were similar, and for this reason just EKL-2 is presented for comparison. The most important peak is at 3445 cm^{-1} which decreased and shifted to 3410 cm^{-1} , indicating the occurrence of reaction at 1364 cm^{-1} and 1218 cm^{-1} respectively, and the appearance of new characteristics bands of epoxy groups at 910 cm^{-1} , 854 cm^{-1} , and 748 cm^{-1} . The peak at 1720 cm^{-1} corresponds to carbonyl groups in lignin.

Thermogravimetry Analysis

Table 3 shows the thermal characteristics of the unmodified and modified kraft lignins. The lowest value of DGTmax from peak2 for all lignin samples was obtained for KL, methylolated lignin (MKL), and glyoxalated lignin (GKL), while the highest values were obtained for epoxidized lignins (346°C to 362°C). The high values were found in the case of EMKL and EGKL with DGTmax of 362°C and 368°C , respectively. In contrast, the loss of mass at 600°C was very important for EGKL, EMKL, and EKL-1~6 in this order, and less important in non-epoxidized products.

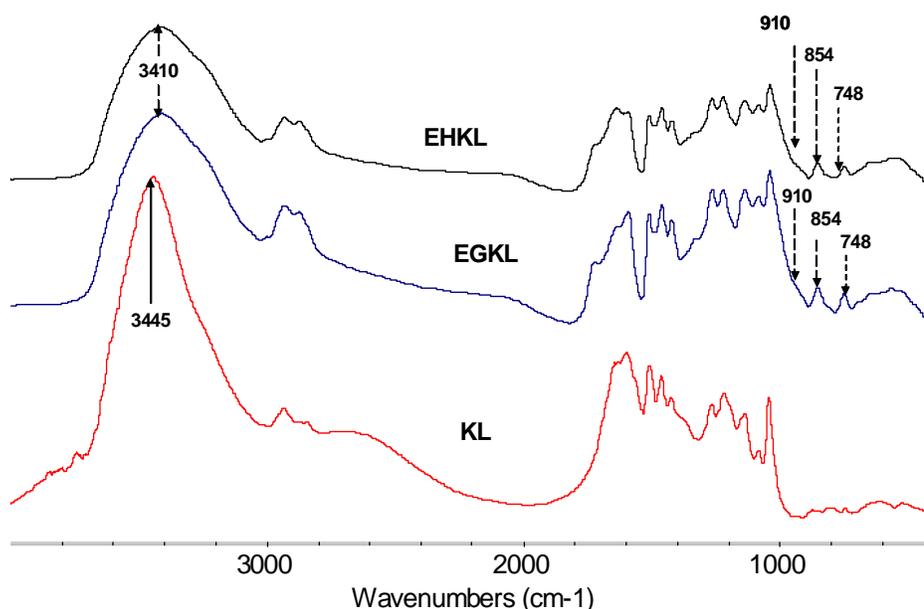


Fig. 6. FTIR spectra of original kraft lignin (KL), epoxidized methylolated and glyoxalated kraft lignins (EGKL) and (EMKL)

When raw lignin material was heated in the temperature range 350 to 450 °C, pyrolytic degradation occurred, involving fragmentation of inter-unit linkages, releasing monomeric phenols into the vapor phase, while above 500 °C the process was related to the decomposition of some aromatic ring (El-Saied and Nada 1993; Sun et al. 2000; Tejado et al. 2007). The range of DGT_{max} obtained is in agreement with the literature (El-Saied and Nada 1993; Sun et al. 2000; Tejado et al. 2007). On the other hand, the maximum rate of loss in phenolic resins occurred at around 345°C. Therefore, the blend of epoxy lignins with phenolic resins, especially those with higher thermal stability, will lead to higher thermal decomposition temperatures. This enhanced thermal behavior may suppose a wider temperature range of application for lignin epoxy-PF blends.

Table 3. Results of Thermogravimetric Analysis of Unmodified and Modified Lignins

Samples	Peak 2			R (%)
	T_{onset} (C°)	DGT_{max} (°C)	T_{offset} (°C)	
KL	281.5	319.7	363.2	59.08
EKL1	305.1	359.0	408.7	39.22
EKL2	311.3	346.3	376.3	37.76
EKL3	315.2	356.2	377.1	31.91
EKL4	314.2	352.3	381.5	34.08
EKL5	305.6	353.6	382.9	34.76
EKL6	323.0	353.5	378.3	43.85
MKL	292.6	328.5	380.6	60.15
EMKL	325.5	362.3	394.6	46.98
GKL	302.5	336.9	388.0	57.83
EGKL	302.0	368.3	412.4	29.39

R: Residue at 600 °C.

CONCLUSIONS

1. Kraft lignin-based epoxy resins were obtained by the epoxidization reaction, using both kraft lignin recovered directly from pulping liquor and the lignin modified by the methylolation reaction. The methylolated lignins were obtained by the reaction of original kraft lignin with formaldehyde and glyoxal, which is an aldehyde less volatile and less toxic than formaldehyde. Proton NMR spectroscopy showed that methylolated kraft lignin had more hydroxymethyl groups than glyoxalated kraft lignin.
2. The epoxidization reaction of unmodified kraft lignin was optimized to produce lignin epoxy with better epoxy index, and the optimum reaction conditions were found with lignin/NaOH = 1/3 at temperature 70 °C for 3h.
3. FTIR spectroscopy showed the presence of bands at 910 cm⁻¹, 854 cm⁻¹, and 750 cm⁻¹, which indicated the epoxidization of lignin molecule.
4. Thermogravimetry analysis showed that the thermal stability of hydroxymethylated and glyoxalated lignins was not essentially influenced, but the epoxidization reaction increased the thermal stability of the lignin-epoxy resins. This may permit a wider temperature range application for lignin epoxy-PF blends.

ACKNOWLEDGMENTS

Authors wish to thank the support of the Commission for Universities and Research of the DIUIE of the Generalitat of Catalonia and the company Henkel KGaA.

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Article submitted: February 25, 2011; Peer review completed: April 28, 2011; Revised version received: May 5, 2011; Accepted: May 7, 2011; Published: May 10, 2011.