

LIGNIN MODIFICATION BY EPOXIDATION

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The chemical modification of lignin through hydroxymethylation and epoxidation is a way to develop new application fields and improvement of lignin performances. In this paper the influence of reaction conditions was studied using different samples of unmodified and modified lignins from annual plants (Wheat straw and Sarkanda grass). The progress of reactions was monitored by evaluating the epoxy index. The resulting products were characterized by FTIR-spectra, UV-Vis spectroscopy, and thermogravimetry analysis. The products obtained were tested to be used in composite formulation for wood applications.

Keywords: Lignin; Epoxidation; FTIR Spectroscopy; Thermogravimetry

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INTRODUCTION

The reactivity of lignin is determined both by its particular structure with specific functional groups and by its structural modifications induced by separation methods used for different raw materials (Popa 1983). Lignins have phenolic hydroxyl groups and aliphatic groups at C- α and C- γ positions on the side chain. The presence of the hydroxyl groups, both phenolic and aliphatic, in lignin has enabled its utilisation as a partial substitute for phenol in the synthesis of products with a lot of applications.

In recent decades (Zhao et al. 2001; Popa et al. 2003), lignin-based polymers have been increasingly considered as a potential way to use lignin reasonably on a large scale. In this paper we discuss two ways to achieve lignin modification: hydroxymethylation and epoxidation. Hydroxymethylation of lignin consists of reaction of lignin with formaldehyde in alkaline medium. Through this type of reaction, hydroxymethyl groups are introduced in the lignin's reactive positions, mainly in *ortho* positions (in relation to phenolic OH groups) of aromatic rings. The second possibility to obtain lignin-based epoxy resins is an epoxidation reaction, using both the alkali lignin precipitated from black liquor and hydroxymethylated lignin. In this paper results are presented for lignin epoxidation.

EXPERIMENTAL

The epoxidation of lignin samples with epichlorohydrin was studied. The influence of reaction conditions of epoxidation of alkali lignin was followed by modifying the temperature, reaction time, NaOH/lignin, and respectively epichlorohydrin/lignin ratios. The alkali lignin L₁ (from *Wheat straw* 100-W-A) and L₂ (from *Sarkanda grass* 100-S-A), as well as Protobind 1000 hydroxymethylated were used for epoxidation. The

procedure of lignin hydroxymethylation was presented in a previous paper (Malutan et al. 2008). The epoxy products were characterized through UV-Vis and FTIR-spectroscopy, thermogravimetry analysis, as well as by epoxy index. The procedure of lignin chemical modification is presented in Fig. 1.

By lignin epoxidation, in alkaline medium, two fractions of lignin-epoxy were obtained: (1) a brown-reddish liquid, totally soluble in water, and (2) a brown-reddish or brown-yellow water-insoluble solid. The solid lignin-epoxy was separated from the liquid lignin-epoxy by centrifugation (15 minute at 2500 rpm), washed two times with 100 mL distilled water, and gently dried at 30°C, in vacuum.

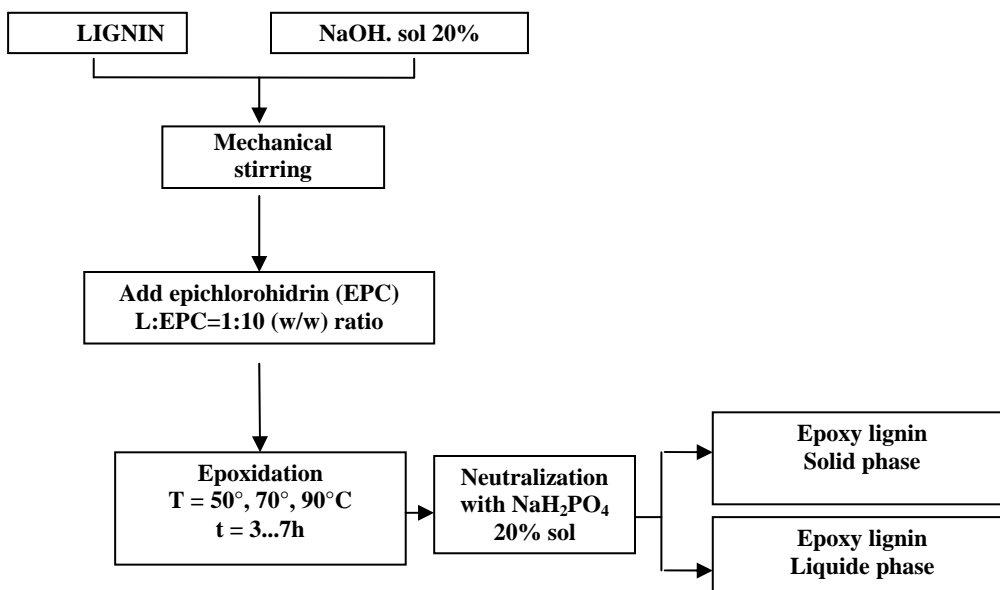


Fig. 1. Scheme of lignin epoxidation

Epoxidation index

Determination of the epoxy group was carried out by HCl addition on the epoxy group and titration of the acid excess with NaOH solution 0.1N:



FTIR Spectroscopy.

Infrared (IR) spectra of the modified and unmodified lignins were recorded on a Digilab FTS 2000 Fourier transform spectrometer, domain: 4000-400 cm^{-1} , resolution 4 cm^{-1} , 32 scans.

Termogravimetry Analysis

Thermal stability was studied via thermogravimetric analysis (TGA) on a Mettler Toledo instrument. Temperature ramps between 25 and 900°C at 15 °C/min under nitrogen were performed to determine the mass loss of material as a function of temperature.

RESULTS AND DISCUSSION

Lignin Epoxidation

The lignin samples and their derivatives were characterized by FTIR and UV-Vis spectroscopy, thermogravimetry, and epoxy index. The results obtained for lignin epoxidation are presented in Table 1, and the influence of the lignin/sodium hydroxide ratio on the epoxy index and lignin epoxidation yields is shown in Fig. 2.

Table 1. Results Obtained in the Lignin Epoxidation

Sample	T, °C	L:NaOH ratio, (w/w)	t, min	Epoxy index, %		Ash, %
				solid phase	liquid phase	
L ₁ (<i>Wheat straw</i> lignin)	70	1:6	180	1.18	0.19	4.18
	70	1:3	180	1.76	0.60	1.31
	70	1:3	300	1.60	0.38	1.06
	70	1:3	420	1.44	0.32	0.77
	50	1:3	180	1.84	0.54	8.79
	90	1:3	180	1.09	0.07	1.09
L ₂ (<i>Sarkanda grass</i> lignin)	70	1:6	180	1.21	0.21	4.65
	70	1:3	180	1.65	0.43	1.24
	50	1:3	180	0.49	0.12	9.71
Pb1000 (<i>Protobind</i> 1000)	70	1:6	180	1.14	0.20	9.62
	70	1:3	180	1.62	0.61	0.98
(L ₁ H)E	70	1:3	180	1.27	0.39	1.68
(L ₂ H)E	70	1:3	180	1.58	0.56	3.65
(Pb1000H)E	70	1:3	180	1.34	0.58	1.58

(L₁H)E – *Wheat straw* lignin hydroxymethylated and epoxidated

(L₂H)E – *Sarkanda grass* lignin hydroxymethylated and epoxidated

(Pb1000H)E – *Protobind 1000* lignin hydroxymethylated and epoxidated

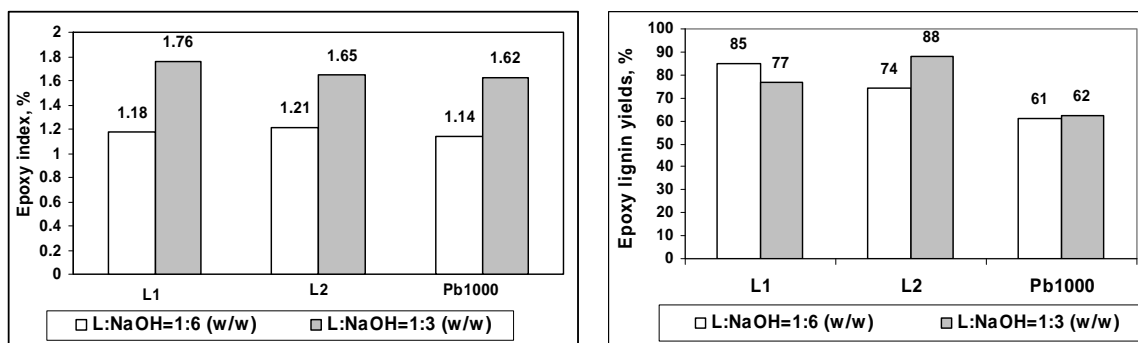


Fig. 2. Influence of lignin:NaOH ratio upon epoxy index and yield for lignin epoxidation (T = 70 °C, reaction time 180 min)

From the data obtained it can be seen that increase of temperature had a negative effect on the epoxy index. The epoxy index values obtained at high temperature (90 °C)

were lower in comparison with those obtained at 50 °C, probably due to secondary reactions.

When reaction time increased from 30 min to 7 hours, the epoxy index decreased, but the mass increased, probably due to crosslinking reactions (Fig. 3). The epoxy index had lower values in epoxy lignin hydroxymethylated for (L₁H)E, (L₂H)E and (Pb1000H)E samples, as compared with epoxy lignin for all lignin samples studied.

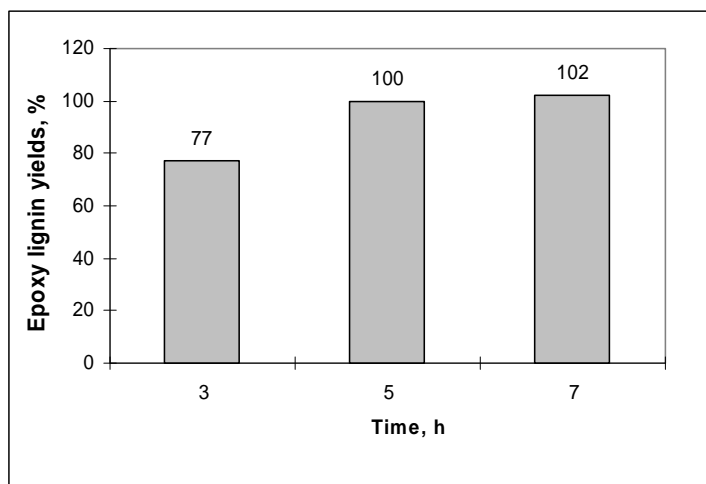


Fig. 3. Influence of reaction time upon yield during *wheat straw* lignin epoxidation ($T = 70\text{ }^{\circ}\text{C}$, $L_1:\text{NaOH}$ ratio = 1:3 (w/w))

FTIR Spectroscopy

The FTIR spectra of unmodified and epoxy lignin are shown in Fig. 4 (Protobind 1000 lignin). The FTIR spectra of unmodified lignin were characterized by a broad O-H band at 3400 cm^{-1} , an intense C-H band at 2927 cm^{-1} , and another at 2854 cm^{-1} , typical of methoxyl groups. The aromatic skeletal vibration occurred at 1600 cm^{-1} and 1515 cm^{-1} . The C-H deformations band of asymmetric methyl and methylene appeared at $1460\text{--}1470\text{ cm}^{-1}$, and carbon-oxygen ether bands at $1400\text{--}1000\text{ cm}^{-1}$. The band at 1370 cm^{-1} is due to the bending vibration of the phenolic OH groups. Bands at 1140 and 1035 cm^{-1} are characteristic of secondary and primary OH groups.

The FTIR spectra of epoxy lignin and unmodified lignins clearly reflected structural differences between them. The epoxidation reaction changed the structure of lignin when the characteristic peak of the epoxy ring appeared distinctly at $1230\text{--}1280\text{ cm}^{-1}$, 910 cm^{-1} , and 854 cm^{-1} . The new band at 1725 cm^{-1} in FTIR spectra of epoxy lignin is characteristic of carbonyl stretching.

Termogravimetric Analysis

The thermogravimetric data are presented in Table 2. The DTG_{max} (T_m , peak 2) appeared between 360 and $381\text{ }^{\circ}\text{C}$, and the loss of mass between 58% and 70% for epoxidated lignin sample was analyzed. The lowest values for peak 2 were obtained for hydroxymethylated epoxy lignin, but the loss of mass was very important, in comparison with raw lignin samples.

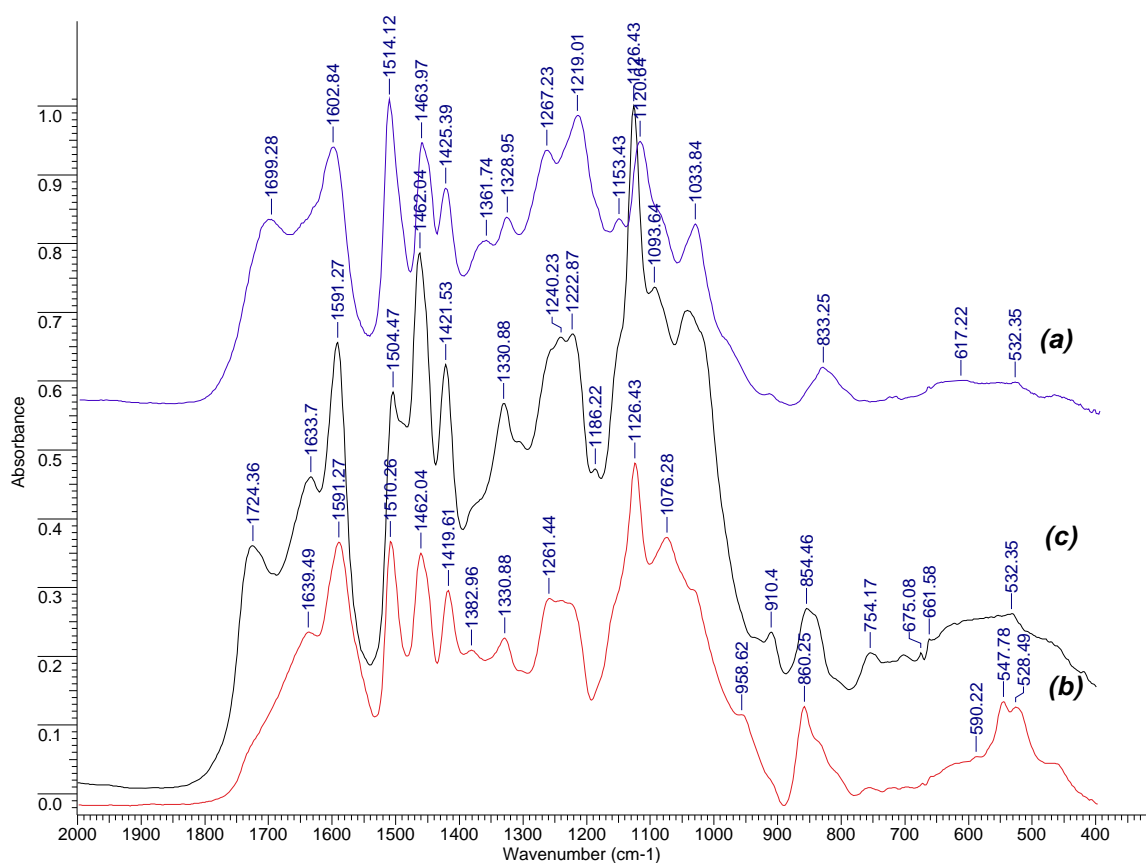


Fig. 4. FTIR spectra of Protobind 1000 lignin: unmodified (a), hydroxymethylated (b), and epoxidated (c)

UV-Spectroscopy

The maximum UV absorptions of the unmodified and epoxidated lignin samples are presented in Table 2. From these data one can observe that the epoxidation reaction moved the maximum UV absorptions from 281 nm to 275-277 nm (hypsochromic shift) due the substituent effects.

Table 2. Maximum UV Absorptions of Modified and Unmodified Lignins

Sample	λ max, nm	
L ₁ (Wheat Straw lignin)	258	281
L ₂ (Sarkanda grass lignin)	259	281
Pb1000 (Protobind 1000)	258	282
L ₁ E (3h_70_L/NaOH_1:3)	252 s	277
L ₂ E (3h_70_L/NaOH_1:3)	251 s	275
Pb1000E (3h_70_L/NaOH_1:3)	-	277
L ₁ HE	-	276
L ₂ HE	257	276

DMSO – solvent; s - shoulder

CONCLUSIONS

1. The reactivity of different kinds of lignin versus epichlorohidrin was studied. The highest reactivity was found for the *Sarkanda grass* lignin, as compared with *Wheat straw*, and *Protobind 1000* lignin.
2. The introduction of functional groups in lignin could be appreciated by following the ratios of relative absorbances established by FT-IR spectroscopy for different groups.
3. The reaction time had a positive influence on the yield for epoxy product, but the epoxy index decreased when time increased from 30 min to 7 h.
4. The thermal stability of hydroxymethylated lignin was not essentially influenced by reaction conditions, but the epoxidation reaction decreased the thermal stability of the products.
5. For chemical modification of lignin, the hydroxymethylation alone or successive hydroxymethylation and epoxidation can be used.

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