APPLICATIONS OF EPOXIDATED LIGNINS FOR BIOPROTECTION OF LIGNOCELLULOSIC MATERIALS

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This paper presents the results obtained by the modification of lignins through epoxydation. The reaction of lignins (commercial products Protobind 1000, Protobind 2000, Protobind 3000) with epichlorohydrin was performed in basic catalysis aiming to increase their functionality. The resulting products were characterized in terms of functionality (content of epoxy groups) and by FTIR, fluorescence and ^{1}H NMR spectroscopy. The chemical and spectral characterization showed that the Pb3000 lignin was the most reactive substrate in terms of functionality. The efficiency of unmodified and epoxidated lignin derivatives was tested in biocide systems in order to ensure the protection of lignocellulosic materials. It has been noticed that the chemical modification of lignin assures a higher capacity of biostabilisation for the protection of cellulose fibers, compared to the unmodified product.

Keywords: lignin, epoxidation, FTIR spectroscopy, fluorescence, ^{1}H NMR, biocide systems

INTRODUCTION

Due to its capacity to regenerate through photosynthesis, biomass, as well as its components (including lignin), will become a source of raw material with a high recovery rate in the future. Considering the greater possibilities of using lignin nowadays, an increasing number of studies has been noted, aiming to improve the processes of separation, by clearing up its structure and its chemical characterization, by analyzing the reactivity and the functional properties of this biopolymer.[1] From the chemical point of view, lignin is a macromolecular compound with a more resistant polyaromatic structure, made up of thousands of phenylpropane monomers, connected through different chemical bonds into a highly cross-linked structure, which makes biodegradation difficult and moreover reduces the access of microorganisms to the other constituents of the cell wall.[2,3,4,5]

Worldwide, lignin resulting from pulping or biomass hydrolysis can be considered a raw material with high potential for recovery, due to its origin from renewable resources and its low price. Nearly 50 million tons of lignin is processed annually; only 6-8% of it is employed as raw material in the chemical industry, the rest being used to produce energy.

The key roles of lignin in plants are strictly related to its particular structure and its distribution in the plant tissue. It is known that wood lignin provides resistance to mechanical demand and effort, inhibiting the enzymatic degradation of wood, protecting against microorganisms attack, while controlling the humidity, it acts as a natural glue, at the same time being a binding agent to microfibers in the secondary cell wall and middle lamella of cells, and last but not least, it helps to improve soil properties during natural degradation.[1,6]

Technical lignin is industrially produced by treating the wood with alkalies,[1] when lignin undergoes numerous chemical transformations accompanied by high depolymerization during the delignification process. Depending on the type and the duration of the chemical process, but also on the type of plant materials, it can be noticed that transformations occur in the lignin macromolecule and they affect the molecular

mass, the functional groups, the condensation level, the type of intermonomeric bonds and the type and the ratio of the monomeric units.

Lignin reactivity is determined both by its peculiar structure, where specific functional groups can be identified, and by the structural modifications caused by the methods used when it is separated from the wood. With this purpose in view, one of the objectives of this study was to modify the properties of lignin resulted from chemical processing of wood and annual plants, through reactions that may increase its applicability in various areas of use. From this point of view, the modification reactions offer significant opportunities for the increase of lignin functionality, which may thus become a significant component in different adhesive systems etc.[7,8]

By introducing the epoxy cycle in the molecules of natural polymers (lignin, cellulose, lignocellulose), the adhesion between the latter and the synthetic polymer matrix is increased and this obviously leads, on the one hand, to an increase of dimensional stability, of thermal resistance and resistance against microorganisms and, on the other hand, to an improvement of the physical-mechanical properties of the synthetic/natural polymer mixtures and practically to a decrease of the water absorption capacity.[9,10,11] Lignin modification through epoxidation offers many possibilities of improving its features, allowing to extend the application area for the synthesized derivatives.[12,13,14,15]

Taking all these aspects into account, the objectives of this study are to modify some lignins through epoxidation, carried out in alkaline medium in the presence of epichlorohydrin, and to characterize the lignin derivatives by chemical and spectrophotometric methods (fluorescence, FTIR and ^{1}H NMR).[15,16,17]

It is known that wood is commonly degraded by a series of biological agents whose action can be increased by climate factors and by the types of environment where it is temporarily kept or after processing. In other words, the composition and the structure of wood make it vulnerable to the attack of some natural destroying factors (damaging factors) both biotic (biological) and abiotic, physical and chemical (environment factors, fire). They produce specific phenomena of degradation represented by the alteration of physical, mechanical and/or biochemical characteristics of wood. In order to control and to adjust the biodegradation process of the lignocellulose composite elements, various bioprotection methods have been designed based on both modern and traditional techniques developed for wood preservation (chemical change, thermal treatment, superficial or depth treatment with resins, polymers and polymerizable substances, impregnation with inorganic salts and other compounds, inclusions in composite materials (other materials), protection, gluing.

Thus, the efficiency of unmodified and epoxy-lignin has been tested in order to achieve biocide systems (systems based on unmodified products/epoxy lignin and copper solutions) for the bioprotection of some lignocellulosic materials (birch veneer samples). The efficiency of the obtained systems was assessed by determining the mass loss and the contact angle for treated veneer samples.

EXPERIMENTAL

Materials

In this study, the following materials have been used: commercial products based on lignins (Protobind 1000 noted Pb1000, Protobind 2000 noted Pb2000 and Protobind 3000 noted Pb3000) isolated through the alkaline delignification process and offered by Granite Company, Switzerland. Also, birch veneer samples with dimensions of 1x10 cm and equilibrium relative humidity of 7%, copper chloride ($CuCl_2$) (5%), tetraaminocopper hydroxide (Cuam) (5%) and furfuryl alcohol (100%) were used.

Methods

Epoxidation reaction

Epoxidation was performed using epichlorohydrin in a basic medium, according to the literature.[15,18,19]

Epoxidation index

The assessment of the epoxy groups was carried out by adding a hydrochloric acid solution and titrating the acid excess with 0.1 N NaOH solution.[15,20]

Fluorescence spectroscopy

The fluorescence emissions of both unmodified and modified lignins were registered on a luminescence spectrometer Perkin Elmer LS 50 B, by using fluorescence cells with a liquid volume of 1 mL, 10 mm path length and 350 nm excitation wavelengths, in the 400÷600 nm absorption region. The lignins and their derivatives were dissolved in 70% dimetil sulfoxide (DMSO).

FTIR spectroscopy

FT-IR spectra were recorded on KBr pellet using a DIGILAB-Excalibur FTS 2000 spectrometer, equipped

with a heating device. The working parameters were: spectral range 4000-400 cm^{-1}, resolution 4 cm^{-1} and 32 scans.

Proton nuclear magnetic resonance (^{1}H NMR)

The nuclear magnetic resonance (NMR) offers the richest and most complex information on the structure of organic compounds. For this purpose, a Bruker Avance DRX 400 MHz spectrometer was used.

For the investigation, it was necessary to use unmodified acetylation[20] and epoxidized lignins for better dissolution in DMSO-d6. To obtain a "good" spectrum, it is required to have concentrations of about 0.2 mmol/mL. Spectra processing was performed with a specialized program from SpectraManager series.

Treatment of birch veneer samples with unmodified and epoxidated lignin, and copper solutions

We used birch veneer samples for the treatment with lignins dissolved in furfuryl alcohol as follows:

- Birch veneer samples were immersed in solutions containing copper ions (copper chloride or copper ammonia solutions) for 5 minutes, followed by drying at room temperature (laboratory conditions);
- The samples were immersed in unmodified and modified lignin solutions for five minutes and dried under mild conditions.

The treated birch veneer samples were weighed before and after treatment to determine the quantity of material retained on the surface of the samples and then they were buried in soil under laboratory conditions for a period of six months, with regular watering to maintain specific soil moisture. The degree of biodegradation was evaluated by determining the mass loss and the contact angle measured on the surface of the birch veneer treated with lignin derivatives and copper solutions.

Determination of mass loss

The biocide treated and untreated veneer samples were weighed on an analytical balance before and after they were kept in soil for 6 months, to assess the mass loss, expressed in percentage.

Contact angle determination

Contact angle measurements were made with a Kruss Model FM40 Easy Drop Goniometry apparatus. The assay and image processing were consistent with the SR.EN.828/2001-L73 standard. The device software allows surface energy assessment, video recording and experimental data storage. The contact angle was measured on the veneer surface using distilled water as solvent, with 5 µL droplets.

RESULTS AND DISCUSSION

Modification of lignin by epoxidation

The characterization of the lignin products (Table 1) has been achieved for the three modified samples used in the synthesis reactions, by monitoring the influence of temperature (50 °C and 70 °C, respectively), the mass ratio between the lignin (L) and NaOH (L:NaOH = 1:3 and 1:6) and the reaction duration (3, 5 and 7 hours respectively).

Table 1
Characteristics of lignins modified by epoxidation

Samples	T, °C	L:NaOH (w/w)	t, h	CE, %		η, %	U, %	Ash, %	Consist. f.liq., %
				f.sol.	f.liq.				
	70	1:6	3	1.14	0.20	61	6.22	9.62	15.8
	70	*1:3*	*3*	*1.62*	*0.61*	*62*	*4.36*	*0.98*	*17.4*
Pb1000E	50	1:3	3	1.52	0.4	52	4.8	4.90	12.3
	70	1:3	5	1.32	0.52	60	5.12	3.21	11.32
	70	1:3	7	1.54	0.36	58	4.87	5.65	13.50
	70	1:6	3	1.20	0.21	50	5.5	8.12	16.40
	70	*1:3*	*3*	*1.70*	*0.64*	*64*	*5.1*	*2.1*	*18.20*
Pb2000E	50	1:3	3	1.85	0.36	60	7.2	7.85	16.25
	70	1:3	5	1.50	0.32	69	6.78	6.22	12.32
	70	1:3	7	1.63	0.40	52	6.27	5.63	15.30
	70	1:6	3	1.25	0.25	58	5.7	8.14	16.3
	70	*1:3*	*3*	*1.80*	*0.70*	*68*	*6.8*	*4.42*	*17.56*
Pb3000E	50	1:3	3	1.32	0.28	64	5.31	6.30	14.15
	70	1:3	5	1.40	0.42	58.2	5.47	5.13	15.12
	70	1:3	7	1.46	0.30	60.5	6.20	7.10	14.44

T (°C) – reaction temperature, L:NaOH – lignin:NaOH mass ratio, t (h) – reaction time, CE – epoxy index, f.sol. – solid fraction, f.liq. – liquid fraction, η – yield; U – relative humidity, Consist. f.liq. – consistency of liquid fraction

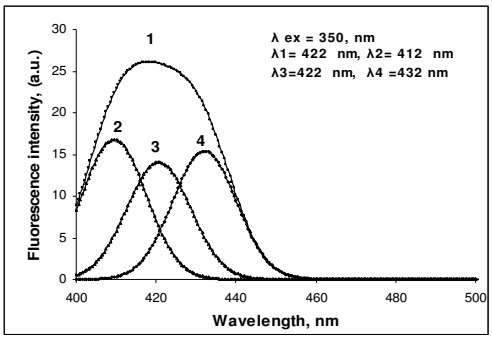

Figure 1: Deconvolution of fluorescence spectra for unmodified Pb1000 commercial lignin

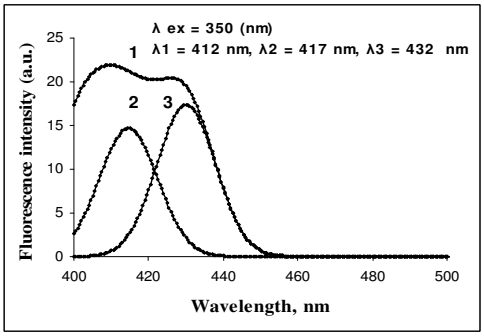

Figure 2: Deconvolution of fluorescence spectra for modified Pb1000E commercial lignin

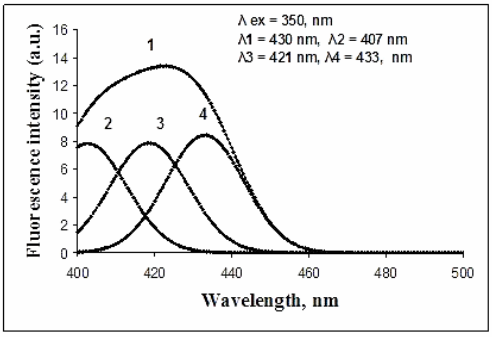

Figure 3: Deconvolution of fluorescence spectra for unmodified Pb2000 commercial lignin

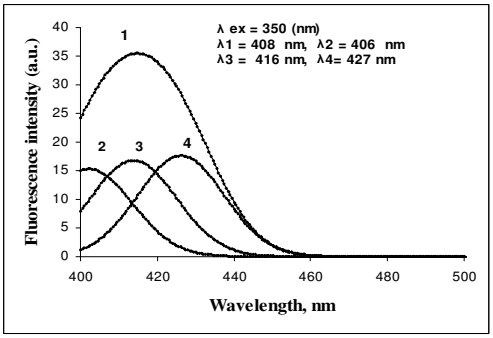

Figure 4: Deconvolution of fluorescence spectra for modified Pb2000E commercial lignin

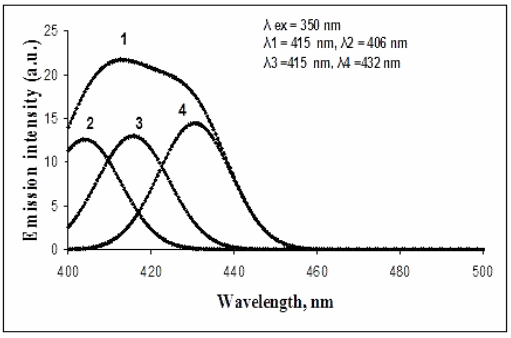

Figure 5: Deconvolution of fluorescence spectra for unmodified Pb3000 commercial lignin

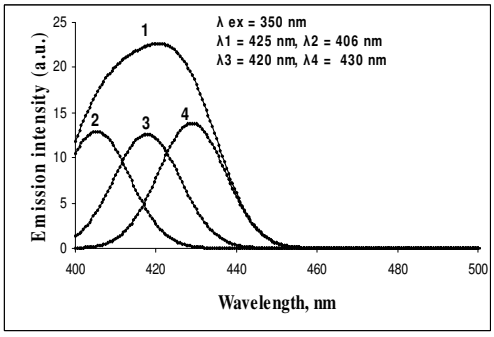

Figure 6: Deconvolution of fluorescence spectra for modified Pb3000E commercial lignin

Table 2
Characteristic spectra of the studied lignin derivatives

Characteristic bands, cm^{-1}	Samples					
	Pb1000	Pb1000E	Pb2000	Pb2000E	Pb3000	Pb3000E
	3427	3410	3425	3415	3414	3414
	2922	2922	2920	2920	2922	2920
	2850	2862	2850	2860	2850	2860
	1704	1716	1703	1722	1688	1722
	1602	1621	1602	1635	1602	1635
	1512	1595	1514	1599	1512	1595
	1462	1460	1460	1400	1460	1460
	1370	1421	1370	1380	1370	1330
	1219	1249	1217	1257	1232	1255

Subsequently, the yield of epoxidized solid product, the epoxidation number, the humidity, the ash content and the consistency of the aqueous phase resulted after the separation of the epoxidized derivatives have been determined.

It can be noticed from Table 1 that the best results can be obtained when the reaction is achieved at 70 °C, for a L:NaOH=1:3 ratio and for a three-hour reaction duration, all appreciated as being the optimal reaction conditions. The reaction yield was included in the 50-90% interval, while related to the mass of the reactants and it differs according to the type of the substrate and the purification degree after washing the derivatives. The Pb3000 lignin represents the most reactive substrate in terms of functionality. It should also be noticed that along with an increase in temperature and reaction duration, from 3 to 7 hours, a decrease of the epoxidation number is registered. This can be explained through the initiation of side reactions, namely of reticulation reactions between the lignin macromolecules, reactions which are also favored by the substitution of the epoxide cycles. The chemical modifications produced inside the structure of the epoxidized lignin samples, which were obtained under optimal reaction conditions, have been analyzed both chemically and spectrally (fluorescence, FTIR and ^{1}H NMR spectroscopy).

Fluorescence spectroscopy

The use of fluorescence spectroscopy has allowed a comparative analysis of the initial lignins and of the synthesized derivatives. For a detailed analysis, the deconvolution of the fluorescence spectra was carried out for the fractions soluble in DMSO, thus allowing determining more precisely the wavelengths at which the emission of radiation was produced for the unmodified and epoxidized samples (Figs. 1-6).

The analysis by deconvolution of the fluorescence spectra indicates the fact that the registered emissions can be characterized by the appearance of several bands, which can be identified separately for different wavelengths specific to the various groups present in the lignin structure. The emission power values may indicate structural modifications of the lignin samples during the epoxidation reaction. After analyzing the curves resulted as a consequence of deconvolution, three significant drops for each type of lignin and epoxidized derivative have been distinguished.

The maximum value on the deconvolution curves in the case of epoxidized lignins moves towards lower intensity values, which confirms the presence of new functional groups in the lignin structure. This fact influences the answer of the substituted aromatic nucleus. Although this technique does not offer clear information about the modifications produced, it adds up to the other methods, which certify the development of the reaction.[18,21,22]

FTIR spectroscopy

The three types of lignin modified under optimal reaction conditions have been spectrophotometrically analyzed, checking the presence of functional groups in their structure and correlating the data obtained with the results of the chemical analysis (Table 2). In the case of the epoxidized Protobind 1000 sample, a slight displacement of the drop of absorption is registered from 1716 cm^{-1}, compared to the case of the unmodified lignin. This displacement was caused by the carbonyl and carboxyl groups, whose absorption intensifies in the case of the epoxidized lignin due to the stimulation of the aromatic nucleus. The absorption bands at 1631-1595 cm^{-1} are due to the epoxy groups and to the formation of the ether (C-O-C) bonds, with the participation of OH phenol and alcohol groups from the lignin structure.

The FTIR spectra of the epoxidized Protobind 2000 and Protobind 3000 lignin are similar with regard to the presence of some absorption bands, probably because of the epoxy index, which has close values in the case of the two types of lignin. In both cases, absorption at 1722 cm^{-1} is noticed, as well as the bands at 1635-1595 cm^{-1}, which are ascribed to the epoxy groups. In the area 1400-800 cm^{-1}, both vibrations of the guaiacyl units and of the ether bonds established through the medium of the OH alcohol groups can be encountered. Vibrations corresponding to the C-O, C-H and C=O groups are present in the area 1300-1000 cm^{-1}.

The band at 1400 cm^{-1} is more difficult to be attributed, being the result of more complex contributions, which characterize monolignol subunits from the lignin structure. Absorptions, typical to the guaiacyl (1260-1255 cm^{-1}) and syringyl (1325-1330 cm^{-1}) units can be noticed in all the registered spectra.

^{1}H NMR spectroscopy

The NMR analysis is a useful technique for structural investigations, accurately reflecting the chemical structure, functions and the type of chemical bonds in the lignin macromolecule.

^{1}H NMR spectroscopy, used to characterize both unmodified and modified lignin, shows clear results on the structure of the biopolymer.

^{1}H NMR spectra allow determining both the total content of acetyl groups and the ratio of aliphatic and aromatic substituents. By integrating different signals, the following parameters can be calculated: the G/S ratio and the aromatic protons content, the methoxyl and hydroxyl total groups, the phenyl propane units (C9) and the ratio of phenolic and aliphatic hydroxyl groups.[23]

Figures 7 and 8 show the ^{1}H NMR recorded spectra for the unmodified and epoxidized commercial product Protobind 1000. The interpretation of the spectra is however difficult because of the structural complexity.

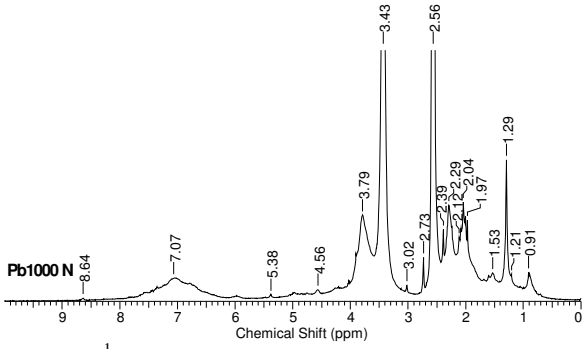

Figure 7: ^{1}H-NMR spectra for unmodified Pb1000 lignin

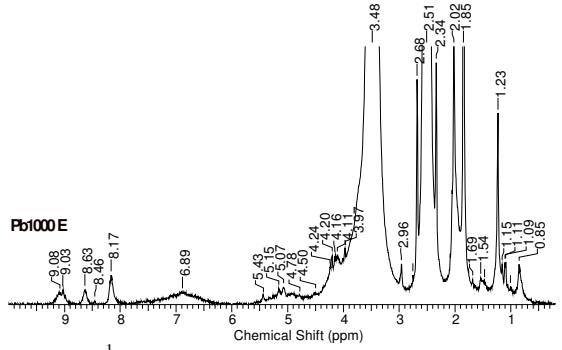

Figure 8: ^{1}H-NMR spectra for modified Pb1000 lignin

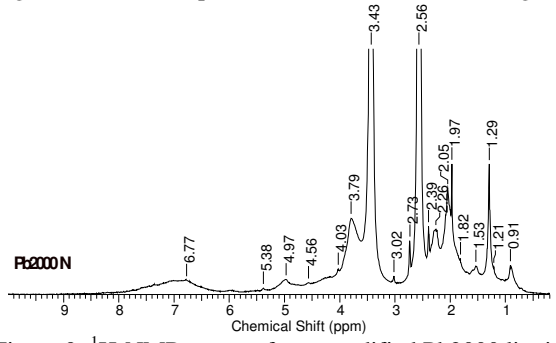

Figure 9: ^{1}H-NMR spectra for unmodified Pb2000 lignin

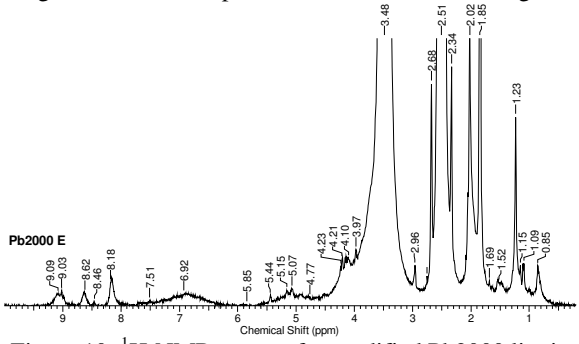

Figure 10: ^{1}H-NMR spectra for modified Pb2000 lignin

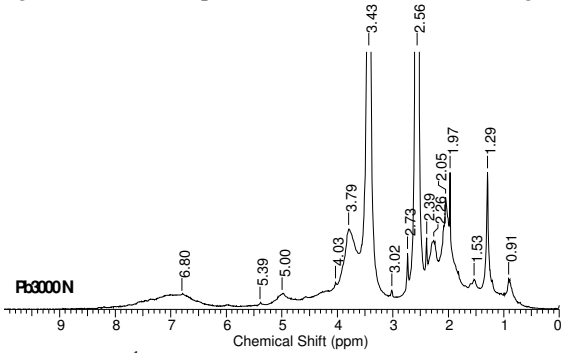

Figure 11: ^{1}H-NMR spectra for unmodified Pb3000 lignin

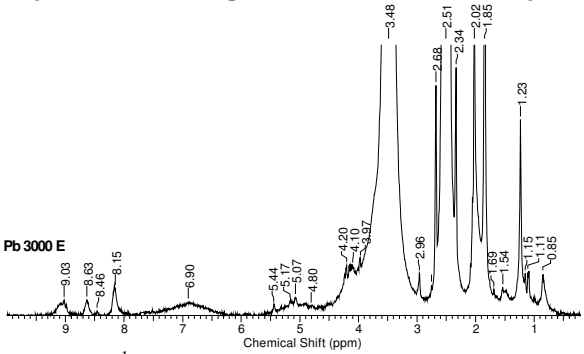

Figure 12: ^{1}H-NMR spectra for modified Pb3000 lignin

In the spectra of both types of lignins, the appearance of some clearly defined signals in the aromatic domain can be noted, which is specific to the protons from phenolic OH. The signals

from 9.08-7 ppm confirm the presence of epoxy groups in the lignin structure. Also, the signals of methoxyl and acetyl groups stand out, being more intense in the spectra of epoxidized lignin. Although the products present a high degree of complexity, the spectrum confirms the presence of epoxy groups in the modified lignin structure. Figures 9-12 show the spectra for unmodified and epoxidized Pb2000 and Pb3000 lignins. The spectra of these two types of lignin have similarities due to the fact that they are structurally related and confirm the structural transformations produced by the epoxidation reaction. Thus, there are intense signals in the range of 9.0-8.0 ppm, specific to the protons of phenolic OH groups from the lignin structure.

The methoxyl groups are more visible in the case of epoxy-lignin, compared with unmodified lignin. For both types of lignins, there are signals in the 6.80-6.90 ppm domain, specific to the protons of guaiacyl units.

As can be seen in Figures 10 and 12, there are intense signals in the 5-4 ppm domain, which are more pronounced in epoxidized lignins due to epoxy groups binding to the OH groups.

The binding of epoxy groups in the lignin structure can be the result of the signals from 3-2.22 ppm domain, attributable to the protons of aliphatic OH groups.

The analysis of the presented spectra leads to the conclusion that the epoxy groups are present in the structure of the lignin macromolecule, this being confirmed by the presence of specific signals related to these functional groups.

Mass loss and contact angle of veneer samples treated with unmodified and epoxidized lignins, and copper solutions

Firstly, the mass loss was determined for each birch veneer sample after six months of burial in soil. The results of mass loss for different veneer samples treated with various biocides containing unmodified lignin or epoxy lignin and copper ions are presented in Figures 13-15. It can be observed that in the case of the samples containing lignin or lignin derivatives and copper ions, the degradation process is inhibited and the degree of biostability is higher for the complex combinations of treatment components.

The presented results have led to the idea that the effectiveness of the surface treatment of a wood product depends on the type of the treatment components and on the degree of functionality of the samples. The analysis of the mass loss variations seems to indicate that the slightest mass loss occurred in specimens treated with copper ions and in epoxidized lignin complexes. In addition, the birch veneer samples treated only with copper ($CuCl_2$ or Cuam) present a high inhibition degree of biodegradation. Copper compounds are substances that produce effective bioprotection of timber. The obtained results show the following scale of efficiency (with respect to the different biocides): $CuCl_2$ > Cuam > $CuCl_2$Pb1000N > CuamPb2000E > $CuCl_2$Pb3000E, presenting mass loss in the range of 3-12%. The most significant mass loss occurred in the case of the veneer samples treated with epoxy lignin and unmodified lignin, the mass loss reaching up to almost 99% (the case of Pb1000E lignin). This situation may be explained by the low level of interaction between the veneer and the product used for the treatment and by the higher accessibility of several components from the tested samples to the action of soil microorganisms. These can be considered favorable conditions for the development and deep attack of the wood substrate.

To test the effectiveness of the applied treatments on the veneer surface, the contact angle was also determined. The high values for the contact angle show high efficiency of the treatment. Figure 15 presents the variation of the contact angle for samples of birch plywood treated with various biocide systems based on copper ions, modified and unmodified lignin and their complexes.

As can be observed in Figure 15, the treatments performed using only unmodified and epoxidated lignins in the treatment of wood surface produce a penetration capacity even higher than distilled water in solid media.

The treatments with copper solutions, especially tetra amino copper hydroxide (Cuam), together with their complexes with various epoxidized lignins, decisively influenced the contact angle. The highest contact angle values were observed for the samples treated with the following biocides: Cuam > CuamPb1000N > CuamPb2000E > CuamPb3000N > CuamPb3000E > $CuCl_2$, and the results are consistent with the lowest values of mass loss.

Although the contact angle value is higher in the case of the samples mentioned above, water penetrates rather rapidly the wood substrate, and the contact angle showed a slighter decline just for the samples treated with copper ions only. It can be concluded that the chemical modification

of lignin ensures a higher biostabilisation of the wood surface in comparison with the cases where unmodified lignins are used as components of the treatment.

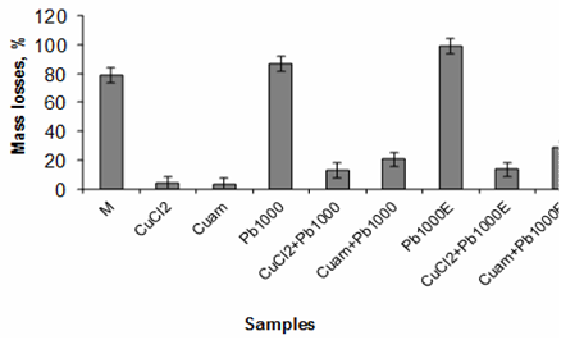

Figure 13: Variation of mass losses for untreated (M) and treated veneer samples

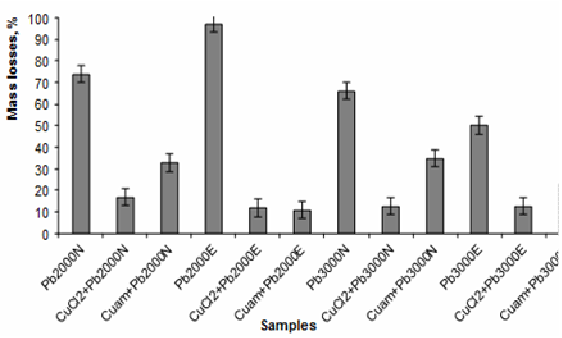

Figure 14: Variation of mass losses for untreated (M) and treated veneer samples

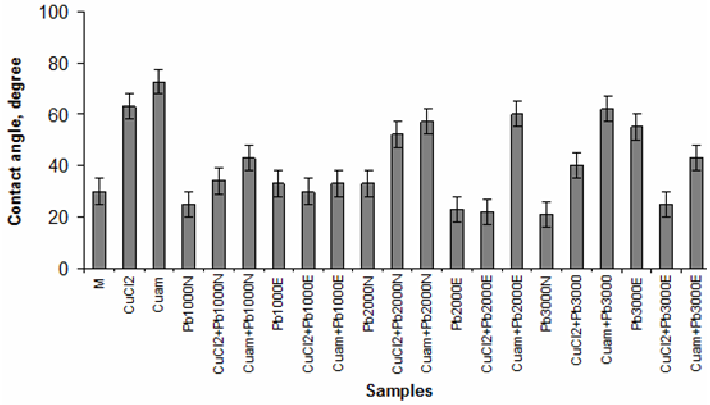

Figure 15: Variation of contact angle for untreated (M) and treated veneer samples

CONCLUSION

1. The epoxidation reaction determined an increase in the reactivity and functionality of lignin, as shown by chemical and spectrophotometric methods.
2. The influence of the factors affecting the epoxidation reaction was studied and thus it was possible to establish the conditions that ensure an optimal content of epoxy groups (L:NaOH of 1:3, temperature of 70 ^{o}C, three-hour duration of reaction). It could be thus inferred that the best reactivity appears in the case of the Protobind 3000 lignin.
3. The FT-IR, ^{1}H NMR and fluorescence spectroscopy have proved the modification of lignin through epoxidation and implicitly the amplification of its functionality. The wavelength intensity for epoxy lignins confirms the presence of epoxy groups in their structure.
4. The application of lignin modified by epoxidation provides higher biostability of the wood substrate than that of unmodified products, the mass loss being much lower in this case.
5. The treatments with different copper ion solutions ensure a higher degree of protection, as expected, the biostability being even higher than in the case of lignin products.
6. Applying complexes of lignin and its derivatives (epoxidized lignins) with copper ions increases the stability of the veneer samples, but it still remains lower than the one produced by the simple copper ions.

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