CELLULOSE CHEMISTRY AND TECHNOLOGY

VALORIZATION OF LIGNIN MODIFIED BY HYDROXYMETHYLATION TO ENSURE BIRCH VENEER BIOPROTECTION

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The present paper focused on the effect of unmodified and modified lignins and copper ions on the interaction between birch veneer and some biocides. The aim of the present study was to modify commercial lignins (Protobind 1000, Protobind 2000, Protobind 3000) by the hydroxymethylation reaction in an alkaline medium and to describe the lignin derivatives by chemical, spectral (^{1}H NMR) and thermal analyses (TG). The studies revealed some functional changes, which are correlated with both the different reactivity of lignins and the reaction conditions. Also, lignin derivatives were observed by thermal analysis, which allowed establishing a correlation between the modification degree and the thermal stability. Treatments with unmodified and hydroxymethylated lignins were applied to birch veneer strips by immersing them in copper chloride solutions. The lignin products were dissolved in 0.1 N ammonia solution of 5% concentration. The biostability of the treated veneer was tested by burying the product in the soil for six months. The samples were then characterized as to their weight loss of and contact angle values. The obtained results show that the treatment of veneer with a complex of hydroxymethylated lignin derivatives and copper ions determines higher stability of the wood substrate, compared to the treatment with unmodified products.

Keywords: lignin, hydroxymethylation, ^{1}H NMR spectroscopy, thermogravimetry, birch veneer, biostability

INTRODUCTION

In the last decades, the research in the lignin area has sought not only to determine the most efficient extraction processes, but also to elucidate the structure of the products separated from various vegetal sources, to understand their chemical characteristics, reactivity and functional properties, as well as to develop new applications.[1,2] Lignin is a macromolecular compound, much more active than cellulose or other natural polymers, due to the functional groups contained in its macromolecule. It constitutes the main aromatic component of vegetal tissues and it represents about 20-40% of the higher mass of the plant, located in the cellular wall and in the intercellular spaces. Globally, lignin is regarded as a raw material with high recovery potential, accessible from renewable sources, with low costs and a negligible pollution degree.[3-5]

The reactivity of lignin is determined by its particular structure, which comprises specific functional groups, but also by the structural modifications induced by the methods used for its separation from wood.[6-9] It is known that lignin has a very complex structure, which varies depending on the plant species, on the separation method and the modification reactions that may induce particular characteristics. Regarding the functional groups, lignin presents at least three main functional groups in its structure: methoxyl, hydroxyl (alcoholic and phenolic) and a side propane chain.

Alongside these functional groups, in lower amounts, there can be found carbonyl groups (about 1 group of CO at 5 C9 units), most of them being fixed onthe side chain.[6,10-12] In some cases, the presence of carboxylic groups in the lignin structure can be noticed in the form of phenol carboxylic acids or of small quantities of lactone groups.[7,13,14]

Lignin is resistant to biological attack and thus it grants mechanical resistance to wood. However, its relatively low stability against the action of environmental factors requires the use of chemical compounds for protection against biological agents attack. Currently, toxic, environmentally incompatible products are used for wood protection against microorganisms and insects. Also, aqueous chemical protective agents are known and their efficiency is due to the presence of copper.[15-18] Part of the copper ions are fixed in the wood substratum by the hydroxyl or carboxylic ionized groups in the wood at high pH. Thus, lignin and tannins,[8] which are known due to their resistance and toxicity against microorganisms, could represent a solution to create "green biocides". A green biocide either is degraded as it kills the microorganisms and the resulting end products are harmless, or causes little damage to the environment.

The discovery of new chemicals from plants has drawn much attention to wood decay, which is an age-old problem since humans began building with wood thousands of years ago. When trees with natural durability were available, they were commonly used, but the scarcity of durable timber in some areas of the world, coupled with the need to make enduring wood products and structures, led to the development of wood preservation techniques.

Nowadays, it is important to replace synthetic wood preservatives with more environmentally friendly natural products. New natural wood preservatives could be obtained from the residues of agricultural, forest, pulp and food industries. This will also benefit the environment by diminishing the already existing problem of vegetal waste disposal.

On the other hand, the application of copper compounds in wood protection, due to their fungicidal activity, is an old well-known method. Although such protection is very commonly used, the mechanisms of copper action and its way of binding to wood are still to be established accurately. A possible binding site for copper is lignin, due to the various different functional groups present in its structure and its abundance in wood.

The aim of the present study was to modify commercial lignins (Protobind) during the reaction of hydroxymethylation produced in an alkaline medium in the presence of formaldehyde and to characterize the lignin derivatives by using chemical, spectral (^{1}H NMR) and thermogravimetric methods. Also, this paper presents the results obtained in the biostabilization of birch veneer in the presence of non-modified (N) and modified (H) lignin, their complex with copper ions along with inorganic compounds of copper.

EXPERIMENTAL

Materials

In this study the following materials were used: birch veneer samples with sizes of 1x12 cm, tetra amino copper hydroxide (Cu am), copper chloride ($CuCl_2$) and 0.1N ammonia solution, as well as three types of commercial lignins (Protobind 1000 – (Pb1000 N), Protobind 2000 – (Pb2000N) and Protobind 3000 – (Pb3000N) offered by Granit Recherche Developement S.A., Lausanne-Schwitzerland, to be used in the Ecobinders project. The chemical characteristics of the lignins are presented in Table 1.

Methods

Hydroxymethylation reaction

The method used to hydroxymethylate the three lignin products was carried out in a basic medium, in the presence of formaldehyde (37%), according to the literature.[1,9,17]

Determination of total hydroxyl groups

The total OH groups content was determined by the chemical method with acetic anhidryde in pyridine medium[6] and from FT-IR spectral analysis.[19] The Ar-OH group content was determined by the UV-VIS method.[11]

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

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, the acetylation of lignin and derivatives[20] was necessary to achieve better dissolution in DMSO-d6. The acetylation reaction of lignin also allowed highlighting the functional groups.

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.

Thermogravimetry

The thermal analysis was performed using the METTLER TOLEDO derivatograph in N_2 atmosphere with a flow of 20 mL/min and a heating rate of 15 ºC/min, in the temperature range 25-800 °C. The sample mass was 4-6 mg.

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

We used birch veneer samples (size 1x10 cm) for the treatment with lignins dissolved in 0.1N ammonia solution, at a concentration of 5%, as follows:

- the birch veneer samples were immersed in solutions containing copper ions (copper chloride or tetra amino copper hydroxide 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 laboratory conditions.

The treated birch veneer samples were first weighed to determine the quantity of the retained material on the surface of the samples and then they were buried in the soil under greenhouse 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 burying them in the soil for six months, to assess the mass loss, expressed in percentage.

Contact angle determination

Contact angle measurements were made with a Kruss Model FM40 Easy Drop Goniometer. The software of the device allows surface energy assessment, video recording and experimental data storage. The contact angle was measured on the veneer surface using distilled water as a solvent, with 5 µL droplets.

Table 1
Characteristics of Protobind lignin samples

Characteristics	Protobind 1000	Protobind 2000	Protobind 3000
Solids, %	97.5-98.6	95	95
Ash, %	1.4-1.8	1.3	1.3
pH (10% dispersion)	~ 3.5	4.80	6.20
Density, g/mL	~ 0.3	~ 0.6	~ 0.3
Aromatic OH, mmole/g	1.8-1.9	1.6-1.8	1.9
COOH, mmole/g	2.1-2.3	2.1-2.3	2.6-2.7
T softening, °C	~ 200	~ 130	~ 200
Solubility in furfuryl alcohol, %	40.1	41	42.10
Solubility in aqueous alkali, %	94	95	93.8

RESULTS AND DISCUSSION

Characteristics of the lignins

The hydroxymethylation of the three types of lignin was performed varying the reaction conditions (temperature: 50 °C and 90 °C, duration of three hours, and pH 10.5 and 12) in order to obtain highly functional products. It has been determined that the most reactive lignin product obtained is the type Pb2000 modified under conditions of pH 10.5 and 90 °C temperature. This indicates a high functionality, compared to that of the products resulted from the other two types of lignin (Pb1000 and Pb3000). Table 2 presents the content of the functional groups of the modified and unmodified lignins.

As can be noticed in Table 2, the content of functional groups varies for each type of lignin according to the applied reaction conditions. The content of the functional groups was determined according to the methods proposed by different research groups.[1,7,9,17]

The determination of the total hydroxyl groups was done by comparing the UV-VIS spectra of the samples before and after chemical modification with acetic anhydride in pyridine medium, in the same manner. The phenolic OH group content was established using the UV-VIS method. In addition, the determination of the total hydroxyl groups was performed by analyzing the FTIR spectra.

In addition, chemical characterization was performed through the determination of carboxyl, metoxyl and aromatic hydroxyl groups, the calculation of the phenolic groups/aliphatic groups ratio, and the determination of syringyl/guaiacyl units ratio (S/G).

The data thus acquired allowed determining the optimal reaction conditions, namely:

temperature of 90 °C, pH 10.5 and duration of three hours.

The lignin products obtained under the optimal conditions were characterized by spectroscopy and thermogravimetry and were used for the treatment of birch veneer with copper compounds to provide high biostability of wood.

Table 2
Content of functional groups in modified and unmodified lignins

Samples	T, °C	pH	OH total groups	Ar-OH groups	OCH_3 groups	Ak/Ar ratio	C=O groups	S/G ratio
Pb1000	-	-	1.11	0.89	1.05	1.17	0.89	0.83
	90	12.0	1.23	0.98	1.15	1.27	0.95	0.96
	90	*10.5*	*1.15*	*0.98*	*1.13*	*1.20*	*0.91*	*0.96*
	50	10.5	1.14	0.98	1.12	1.22	0.95	0.96
	50	12	1.16	0.99	1.14	1.21	0.94	0.96
Pb2000	-	-	1.10	0.92	1.1	1.19	0.90	0.92
	90	12.0	1.20	0.94	1.11	1.24	0.95	0.94
	90	*10.5*	*1.17*	*0.99*	*1.18*	*1.28*	*0.94*	*0.98*
	50	10.5	1.26	0.99	1.15	1.22	0.94	0.95
	50	12	1.14	0.98	1.15	1.20	0.95	0.97
Pb3000	-	-	1.13	0.90	1.09	1.13	0.87	0.86
	90	12.0	1.19	0.92	1.13	1.17	0.91	0.90
	90	*10.5*	*1.15*	*0.97*	*1.16*	*1.24*	*0.93*	*0.95*
	50	10.5	1.16	0.93	1.15	1.20	0.93	0.92
	50	12	1.17	0.95	1.12	1.19	0.93	0.95

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

Of all the spectral techniques, nuclear magnetic resonance (NMR) is the one that offers the richest and most complete structural information on organic compounds. Unlike FT-IR spectroscopy, UV-VIS and Fluorescence, the NMR technique allows all signals to be interpreted relatively easily. NMR spectra, both the ^{1}H and ^{13}C, contain the exact required information, which can be linked directly to the structural formula of the substance. Developed by analogy with electronic resonance, high resolution nuclear magnetic resonance was initially applied to study protons and subsequently extended for a number of other nuclides: ^{13}C, ^{31}P, ^{17}O etc. It has now become the most important method to study the structure and the configuration of organic compounds.[21]

In the literature, there are specific signals in the ^{1}H-NMR spectra of lignin functional groups,[13,20,22] and for the hydroxymethyl it is given therein. For the characterization by ^{1}H-NMR spectroscopy, lignin samples were subjected to acetylation to aid dissolution in the solvent used (DMSO-d6).

Figures 1 and 2 show the ^{1}H-NMR spectra for Pb1000 unmodified (Pb1000N) and hydroxymethylated (Pb1000H) lignin, and the results were interpreted using the literature data. As seen from previous results, Pb1000 lignin is a mixture of three types of lignin from different plants. The spectra recorded for the two lignin samples appear with weak signals in the aromatic domain at 8.64 ppm and in the methoxyl groups. The recorded spectra show binding hydroxymethyl groups in the Pb1000H lignin structure. Figures 3 and 4 present the ^{1}H-NMR spectra of commercial Pb2000 unmodified (Pb2000N) and hydroxymethylated (Pb2000H) lignin.

The analysis of the spectra evidenced the modifications occurring in the lignin structure after hydroxymethylation and the most affected domain is that of the aromatic and phenolic OH groups. Signals are likely due to the high inhomogeneity of lignin and its degree of dissolution in the solvent used for analysis. The modifications are noticed in the domain from 5.32-4.03 ppm specific to methoxyl groups, the signal intensity being weak in this case.

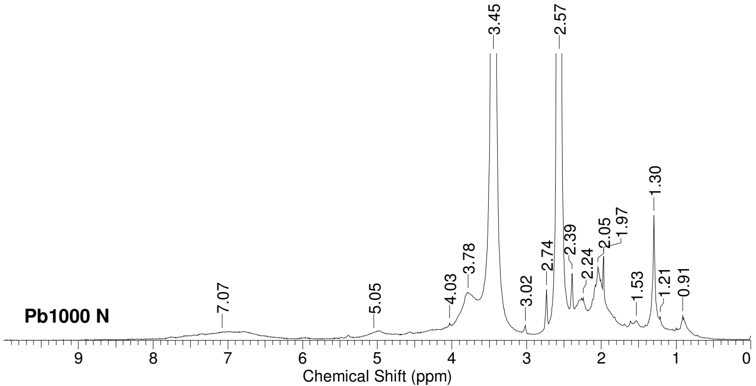

Figure 1: ^{1}H-NMR spectra for unmodified lignin Pb1000N

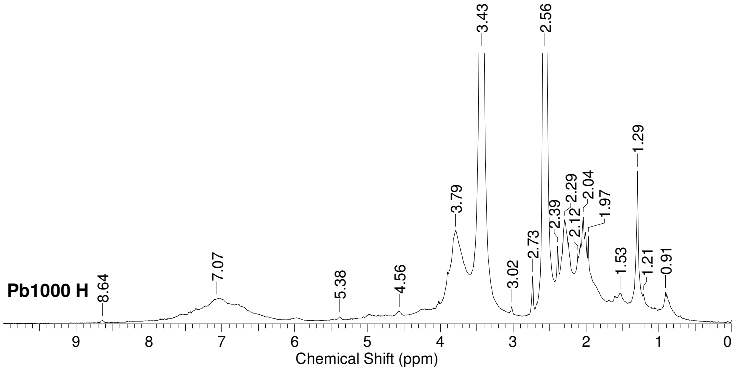

Figure 2: ^{1}H-NMR spectra for modified lignin Pb1000H

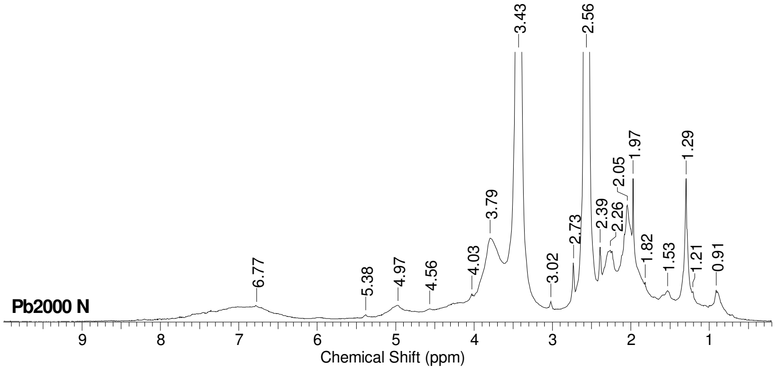

Figure 3: ^{1}H-NMR spectra for unmodified lignin Pb2000N

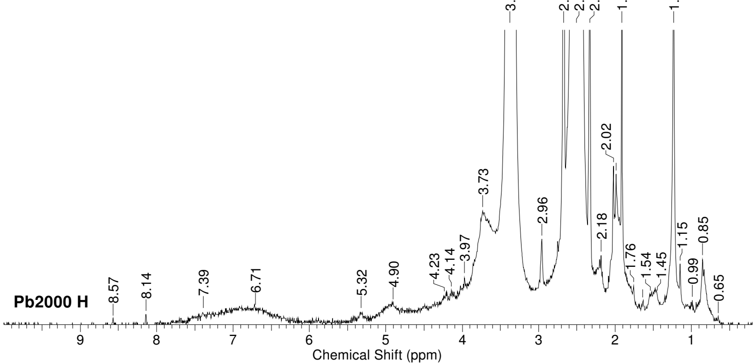

Figure 4: ^{1}H-NMR spectra for modified lignin Pb2000H

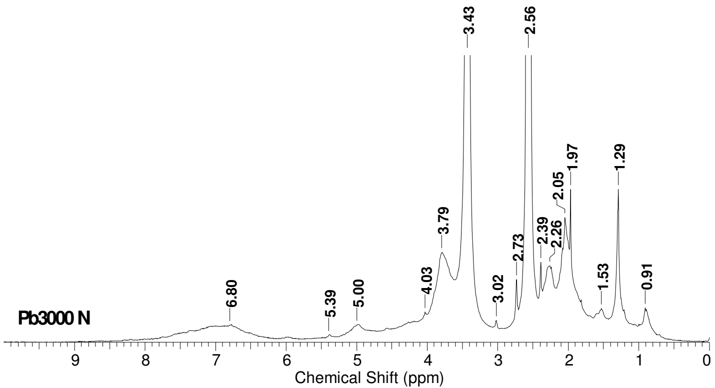

Figure 5: ^{1}H-NMR spectra for unmodified lignin Pb3000N

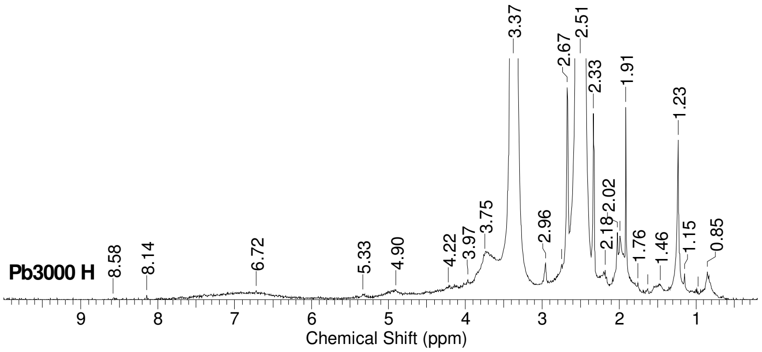

Figure 6: ^{1}H-NMR spectra for modified lignin Pb3000H

Figures 5 and 6 present the ^{1}H-NMR spectra for Pb3000 unmodified (Pb3000N) and modified (Pb3000H) lignin.

The ^{1}H- NMR spectroscopy results confirm the presence of the specific signals of OH phenolic groups in the domain 8.5-7 ppm.

It is difficult to interpret the ^{1}H-NMR spectra recorded for commercial Pb3000 unmodified lignin and that modified by hydroxymethylation, since the substrate subjected to reaction is a mixture of two types of lignins from different sources. Therefore, there is an overlapping of the signals corresponding to certain functional groups in their structure.

The spectra show a high content of guaiacyl groups confirmed by the presence of signals at 6.80-6.72 ppm found in both studied samples. The binding of hydroxymethyl groups in the structure of Pb3000 lignin can be correlated with the presence of signals in the range 5.33-4.22 ppm, specific to methoxyl groups. Also, at 2.96 ppm characteristic proton signals occur in methyl and methylene groups.

Thermal stability

The thermal degradation of the Protobind commercial products, as well as of the lignins modified through hydroxymethylation, represents a three-step process. The most significant mass loss can be noticed in the last stage. In order to achieve that, the temperature under which the maximum degradation rate can be reached is approximately the same ($T_{max} \approx 370$ ºC) for all the analyzed samples. While the first stage, during which the water is removed from the sample, is neglected, by analyzing the initial temperature at which the degradation process starts (T_i) in the second stage, it can be noticed that the thermostability of the lignins modified through hydroxymethylation increases with approximately 10-30 ºC. As a consequence of the thermal analyses, it can be noticed that the modified products have a higher degradation temperature in the third stage, compared to the unmodified samples. The highest temperature values have been recorded in the case of the modified lignin Pb2000H, where the final temperature reaches 580 ºC.

Table 3
Characteristics of the thermal degradation process of the lignin derivatives

Samples	Degradation stage	T_i (°C)	T_{max} (°C)	T_f (°C)	Mass losses (%)
Pb1000	I	52	77	106	3.31
	II	229	267	330	17.05
	III	330	383	532	42.47
Pb1000H	I	64	83	122	4.71
	II	244	264	341	14.03
	III	341	379	523	34.28
Pb2000	I	63	75	110	1.86
	II	205	234	326	22.78
	III	326	381	496	39.23
Pb2000H	I	56	79	115	5.06
	II	216	248	328	12.90
	III	329	3374	580	36.37
Pb3000	I	54	72	88	2.18
	II	147	196	267	11.01
	III	267	369	479	46.73
Pb3000H	I	54	77	116	6.53
	II	241	257	330	13.50
	III	330	379	570	31.49

T_i – initial temperature when the degradation starts; T_{max} – temperature corresponding to the maximum rate of degradation, T_f – final temperature and W – mass losses %

The thermal stability can also be associated with the structural (S/G ratio) and functional (carbonyl, hydroxyl, aromatic and aliphatic groups) characteristics. In addition, the mass loss, in the case of the modified lignins, presents lower values compared to the unmodified samples.

Use of unmodified and modified lignins in birch veneer treatment

Determination of mass loss

Birch veneer was chosen for testing because it has a large usage in the wood industry.

The results related to the mass loss of the samples treated with the products having biocide potential and buried in the soil for six months are presented in Figs. 7-9. In these cases, the applied treatments were more convenient to reduce the mass loss, which was more evident than in the cases where complexes of lignin obtained with copper chloride were used.

Thus for all the samples treated with lignins and their derivatives, an increased hydrophobicity was observed as compared with the reference (M). In the case of the complexes with copper ions, the situation seems to be different for the two systems used to obtain a complex combination. These differences could be explained by a different mechanism of complex formation and by a different interaction of the complexes with soil microorganisms. From this point of view, the best results were obtained in the case of the modified lignins and their complexes with copper ions.

Following the tests performed, it was found that the efficiency of the treatment applied to the wood surface depends on the type of the product used and on the degree of modification and complexation.

The stabilizing effect of copper is clearly manifested. At the same time, one can see the influence of lignin or one of its derivatives is different depending on their initial structure and the functionality introduced by the modification. When using copper ammonia solution in all the cases, the stronger action is probably due to pronounced tissue penetration of the wood, propitious for the interaction between the functional groups of the wood components and copper ions. Considering the results obtained, in terms of the bioprotection degree, the study established the following efficiency order of the tested products: $CuCl_2$ > $CuCl_2$Pb3000H > Cuam > CuamPb2000H > CuamPb3000H.

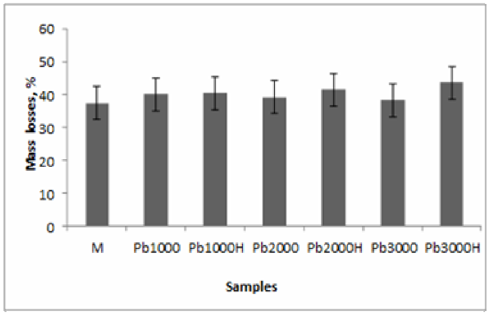

Figure 7: Variation of mass loss for the veneer samples untreated (M) and treated with: Pb1000, Pb1000H, Pb2000, Pb2000H, Pb3000, Pb3000H

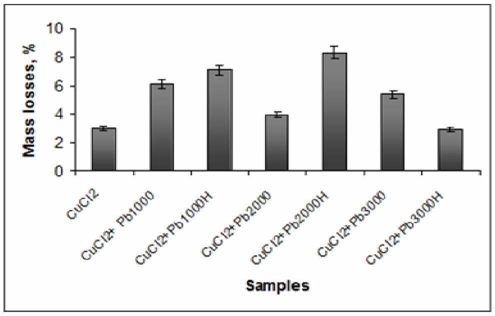

Figure 8: Variation of mass loss for the veneer samples untreated (M) and treated with: $CuCl_2$, $CuCl_2$ Pb1000, $CuCl_2$ Pb1000H, $CuCl_2$ Pb2000, $CuCl_2$ Pb2000H, $CuCl_2$ Pb3000, $CuCl_2$ Pb3000H

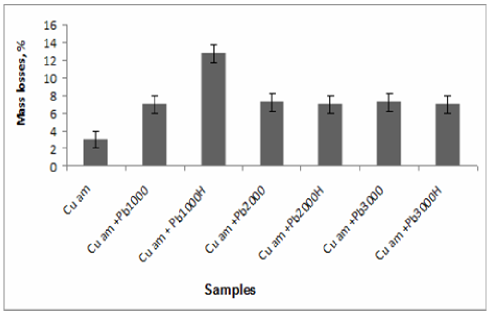

Figure 9: Variation of mass loss for the veneer samples untreated (M) and treated with: Cu am, Cu am Pb1000, Cu am Pb1000H, Cu am Pb2000, Cu am Pb2000H, Cu am Pb3000, Cu am Pb3000H

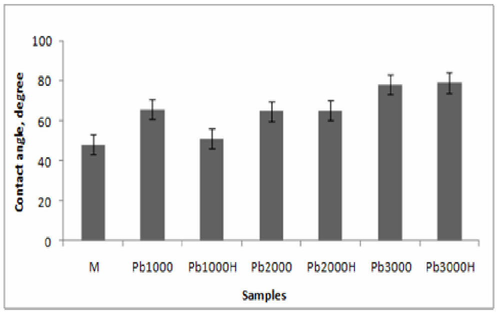

Figure 10: Variation of contact angle for the veneer samples untreated (M) and treated with: Pb1000, Pb1000H, Pb2000, Pb2000H, Pb3000, Pb3000H

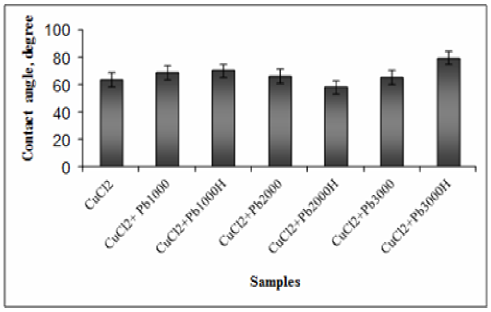

Figure 11: Variation of contact angle for the veneer samples treated with: $CuCl_2$, $CuCl_2$ Pb1000, $CuCl_2$ Pb1000 H, $CuCl_2$ Pb2000, $CuCl_2$ Pb2000H, $CuCl_2$ Pb3000, $CuCl_2$ Pb3000H

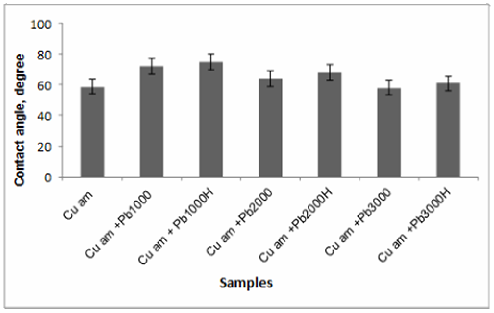

Figure 12: Variation of contact angle for the veneer samples treated with: Cu am, Cu am Pb1000, Cu am Pb1000 H, Cu am Pb2000, Cu am Pb2000H, Cu am Pb3000, Cu amPb3000H

Contact angle determination

To assess the effectiveness of the treatments applied on veneer surface, another important parameter was determined, that is the contact angle.[16] Contact angle decrease is an evidence of substrate hydrophilicity and increases its wetting capacity. Figures 10-12 present the variation of the contact angle determined for the samples of birch veneer treated with various biocide based systems of unmodified/hydroxymethylated lignin and copper ions, after burial in the soil for a period of six months.

From Figure 10, one can see that the most important values of the contact angle were found in the samples of veneer treated with modified lignins, thus recording over 79° for Pb3000 commercial lignin (Pb3000H). Introducing functional groups in the lignin structure on the veneer surface allows further interaction; thereby it stabilizes the effective action of microorganisms.

On the other hand, there was a higher mass loss in the samples treated with these lignins. The lack of consistency between the mass loss and the wetting angle could be attributed to the changes caused by microorganisms. These are known to contribute to the degradation accessible fraction, which explains the mass loss. At the same time, they take part in some humification processes, by initiating several reactions, specific to condensation. Contact angle values were determined for veneer samples treated with copper solutions and lignin derivatives, which permitted a comparison of the results obtained in terms of their efficiency (Figs. 11-12).

As seen from the contact angle variation for the studied samples, its value increases for the veneer samples treated with copper solutions and hydroxymethylated lignins. For the specimens treated only with lignin products, the angle decreases greatly due to their high degree of degradation in the soil. The chemical composition and the type of veneer products with potential biocide action are just some of the elements that exert a direct influence on the contact angle and thus on the wetting capacity and biodegradation.

The treatment with copper solutions ($CuCl_2$ and Cu am) and their complexes with different types of lignin caused a certain wetting degree and reflected a high contact angle, providing advanced biostability. The highest efficiency was found for the veneer samples treated with copper ions and modified lignins: Pb3000> Pb3000H > $CuCl_2$Pb1000H > CuamPb1000H > $CuCl_2$Pb3000H. One can appreciate that by the chemical modification of lignin, a higher protection capacity can be achieved for cellulose fibres, compared to the unmodified product. Figure 13 presents the time variation of the contact angle measured on the surface of the birch veneer sample treated with hydroxymethylated lignin and copper solutions ($CuCl_2$ + Pb3000H).

The data indicate that the contact angle reaches higher values (74.5-80^o) in the case of the samples treated with copper complexes with lignin derivatives, compared with the control samples or with those samples for which copper ion solutions or unmodified lignin were used. Therefore, these treatments confer biological stability and hydrophobycity to wood surfaces, due to the more efficient action of the lignin modified in the presence of copper ions, which were better fixed on the wood substrate. In this way, better protection against microbiological attack was ensured. During the contact angle measurement, it was observed that the hydrophilic surface presented a very low value, as in some cases the water drop penetrated the wood surface and its evolution showed insignificant variations in time (Figs. 13, 14).

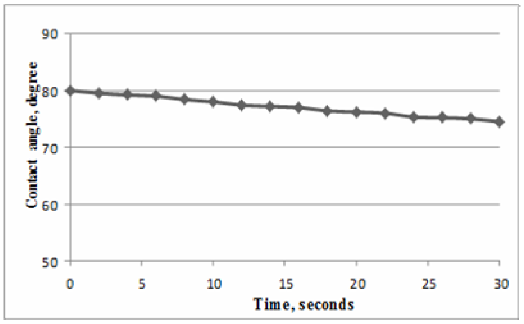

Figure 13: Variation in time (seconds) of contact angle of specimen surface of birch veneer treated with $CuCl_2$ + Pb3000H

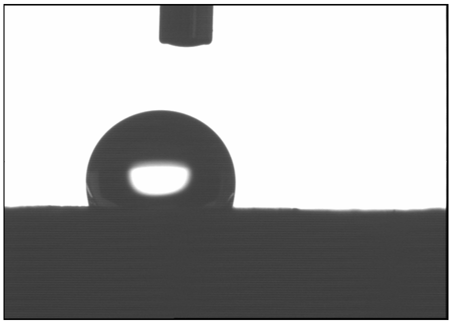

Figure 14: Image of a water drop on the surface of birch veneer treated with modifed lignin and copper solutions ($CuCl_2$ + Pb3000H)

CONCLUSION

1. The reactivity of the three types of lignin towards formaldehyde in an alkaline medium has been studied at two different temperature values, 50 °C and 90 °C, and pH 10.5 and 12.0, respectively. As a result, the Pb2000 product has been found to have the highest reactivity. The optimum reaction conditions were determined in order to obtain the maximum content of functional groups: T = 90 °C and pH = 10.5.

2. The initial lignins and the resulted derivatives have been investigated by means of spectral techniques (^{1}H NMR spectroscopy) and

this revealed the functionality modifications induced by the hydroxymethylation reaction.

3. The thermogravimetric analyses have proved that thermal degradation occurs in two or three stages, according to the type and the modification degree of the tested products. The hydroxymethylated derivatives proved to have higher thermostability, compared to the unmodified lignins.

4. The purpose of modifying these products was to increase their applicability in adhesive systems and in composite materials.

5. The modification of lignins increased their capacity to interact with copper ions and with the veneer samples. Also, it was possible to establish a correlation between lignin samples, the modification degree, the capacity of complex formation, the mass loss and the wetting angle, as a measurement of surface hydrophobicity.

6. The obtained results proved the possibility to improve the biostability of wood by treating it with unmodified and modified lignins and their complexes with copper ions.

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