3rd International Conference
″Advanced Composite Materials Engineering″
COMAT 2010
27- 29 October 2010, Brasov, Romania

STUDIES CONCERNING THE OBTAINING OF NANOPARTICLES WITH BIOCIDES PROPERTIES BASED ON MODIFIEED LIGNINS

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Abstract: *In this paper are presented the results of a study concerning the obtaining and characterization of nanoparticles based on hydroxymethyl lignin and interaction between them and birch veneer. The lignin derivatives were synthesized using lignin from annual plants (wheat straw and Sarkanda grass) and commercial products Protobind offered by the company Granit (Switzerland), in specific conditions to ensure the obtaining of nanoparticles. The birch veneer samples were successively immersed in copper (II) solutions and unmodified and modified lignin (5% concentration in 0.1 N ammonia solutions) in order to realize in situ complexes between the two partners. The biostability of veneer samples thus treated was assessed by their burial in soil for six months and was characterized by mass loss and contact angle values variations. The obtained results show that treatment of birch veneer with complexes of nanoparticles with copper provides high stability of the woody substrate.*
Keywords: *lignin, nanoparticles, veneer, biocides, biostability.*

I. INTRODUCTION

The researches in the lignin area, in the last decades, were focused not only on the extraction process but also on structures elucidation of products separated from different vegetal raw material, on chemical and reactivity characterization, functional properties and new application directions. Lignin accessibility from renewable resources and its environment compatibility, lately enlarge the researches area in lignin modification reactions. The previous studies evidenced that the antimicrobial properties of aromatic polymers can be amplified through chemical modification and complexation with cooper ions (Măluţan Th. et al., 2007, 2008, Popa VI, 1983, Căpraru A.M et al., 2008, 2009). The favorable results previously obtained permitted the synthesis of nanoparticles from modified lignins through hydroxymethylation, in special reaction conditions (Schilling P., 1993). The aim of this work was to test the capacity of nanoparticles obtained from different lignins and copper ions in ensuring birch veneer biostability. The results evidenced that in these conditions it was possible to assure a better interaction between lignin and wood by copper ions supplementations, which promoted the increasing of wood stability. Wood stability was quantified through mass loss and contact angle.

2. MATERIALS AND METHODS

Materials: In this study we used the following materials: birch veneer samples sizes (1x10) cm, wheat straw and Sarkanda grass lignins, along with three commercial products: Protobind 1000 Protobind 2000 Protobind 3000, dissolved in 0.1 N ammonia solution, in 5% concentration (unmodified products - from Granite Company-Switzerland in the European research program-Ecobinders) and laboratory modified lignin by hydroxymethylation reaction under appropriate conditions to obtain nanoparticles, cupric chloride and cuproxam. To evaluate the biostability degree the birch veneer specimens treated with lignin derivatives and solutions containing copper ions were buried in soil for six months. The influence of tratments applied was monitored by mass loss and contact angle.

Methods

1. The synthesis of nanoparticles by hydroxymetylation of lignins: 10 g lignin were suspended in 47 mL of distilled water under stirring for two hours at room temperature. After obtaining the lignin suspension 1.29 g of 50% NaOH solution were added and 3.14 g of 25% NH_4OH solution as a catalyst, and the mixture was shaken for two hours. Afterwards, 6.7 g of 37% formaldehyde were introduced in the system and the reaction was performed at 85 ^{0}C for 4h in a water bath. The resulted product was recovered by precipitation at pH 2 with 1N HCl solution and then it was separated by centrifugation. The solid phase was washed twice with distilled water and then dried and weighed (P. Schilling et al., 1993). The resulting product was subjected to nanoparticles dimensional distribution analysis using Multi Seiser.

2. Treatment of birch veneer samples with unmodified lignin, lignin-based nanoparticles and cupric solutions

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

- 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);
- 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 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 the birch veneer treated with lignin derivatives and copper solutions.

3. RESULTS AND DISCUSSIONS

The possibilities of obtaining of nanoparticles based on ligins or its derivatives could, properly represent a new direction to study both applicative and fundamental character. In figures 1-5 it is presented the nanoparticle size distribution curves obtained in dimensional analysis of the five types of lignin's submitted to modification. The registered data evidenced that, depending on the substrate hydroxymethylation, resulted nanoparticles with different sizes and distributions.

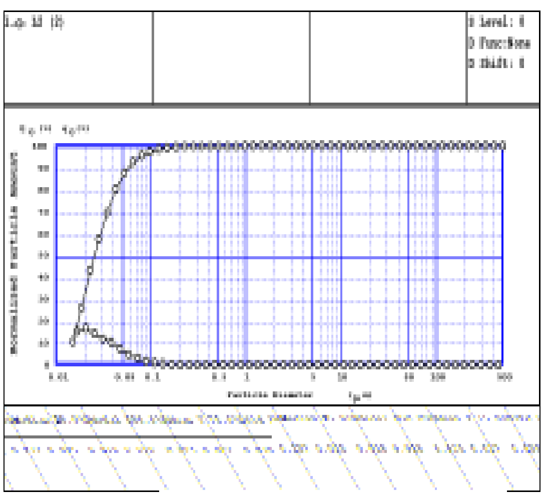

Figure 1: Dimensional distribution curve for nanoparticles synthesized from hydroxymethylated grass lignin (L2)

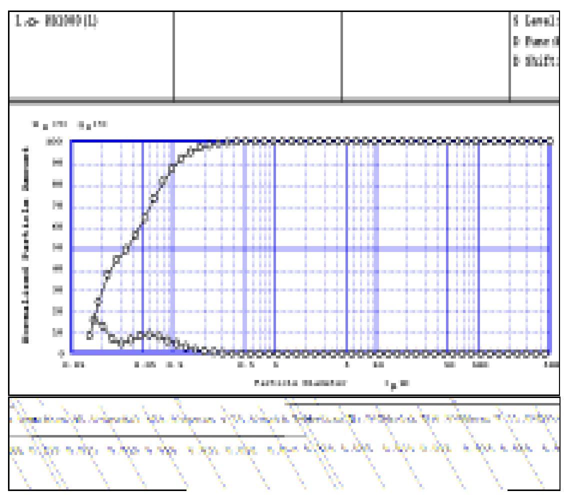

Figure 2: Dimensional distribution curve of nanoparticles synthesized from hydroxymethylated Protobind 1000 (Pb1000) lignin

Comparative analysis of lignin synthesized derivatives of straw and Pb1000 commercial product showed that in the first case a unimodal curve was registered meanwhile for the second one it was obtained a bimodal distribution and wider size nanoparticles. Nanoparticles from the other three types of commercial lignins were characterized by a stronger uniform distribution and different dimensional range depending on the substratum nature.

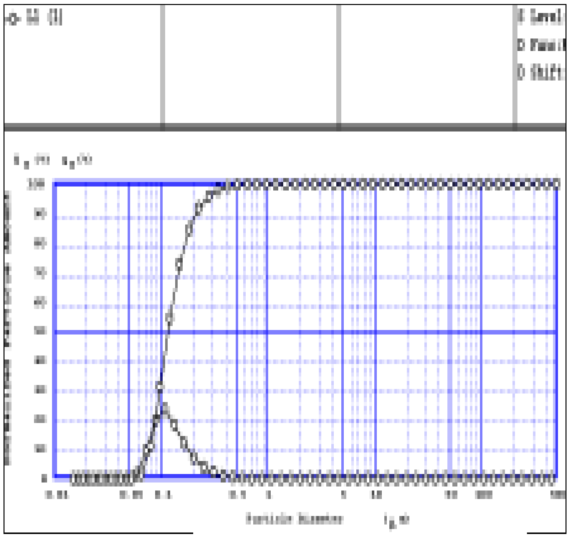

Figure 3: The dimensional distribution curve of nanoparticles synthesized from hydroxymethylated wheat straw lignin (L1)

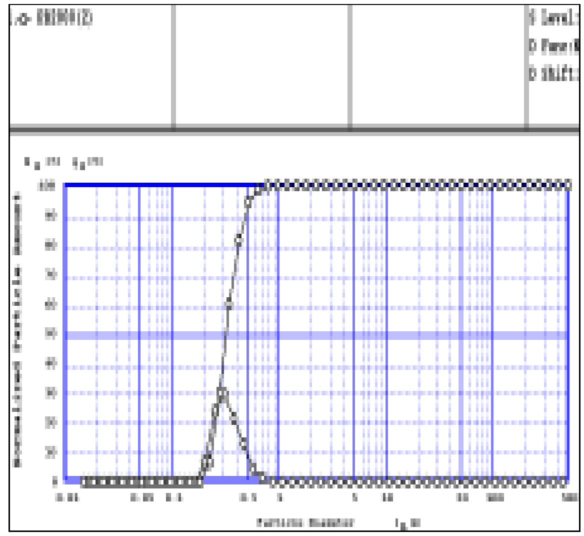

Figure 4: The dimensional distribution curve of nanoparticles synthesized from hydroxymethylated Protobind 2000 (Pb2000) lignin

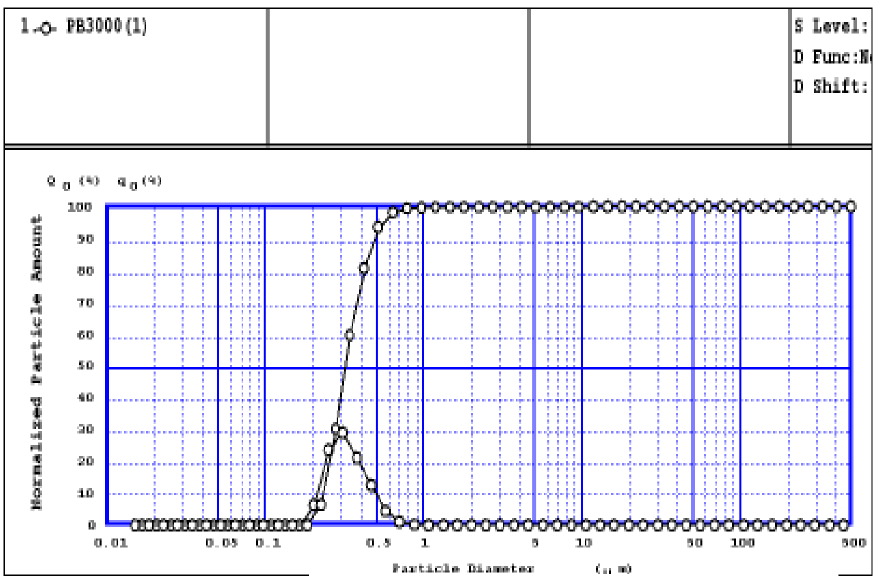

Figure 5: The dimensional distribution curve of nanoparticles synthesized from hydroxymethylated Protobind 3000 (Pb3000) lignin

Dimensional distribution domains for nanoparticles obtained through the hydroxymethylation reaction of the five types of lignin are presented in table 1:

Table 1: The size medium for nanoparticles five types of lignins

Samples	**Size medium,µm**
$L1_{nano}$	0.123
$L2_{nano}$	**0.027**
$Pb1000_{nano}$	**0.038**
$Pb2000_{nano}$	0.327
$Pb3000_{nano}$	**0.329**

Thus, it appears that the structural characteristic of lignin's used in the modified reaction induced different characteristics in nanoparticles size and distribution. In the case of grass lignin (L2) particles presented a lower average size and a more uniform distribution. For the commercial lignin Pb1000 it can be also observed reduced size of nanoparicles but with larger distribution. The other derivatives presented larger sized and high uniformity.

Mass loss determination recorded for birch veneer samples treated with nanopartciles based on hydroxymetylated lignin

The veneer samples were treated with nanoparticles based on hydroxymethylated lignin, with their copper complexes and with copper solutions ($CuCl_2$ and Cuam). The biodegradation degree of samples thus obtained was determined by mass loss after burial in soil for six months. In figures 6-7 there are shown mass loss variations as recorded in samples of birch veneer.

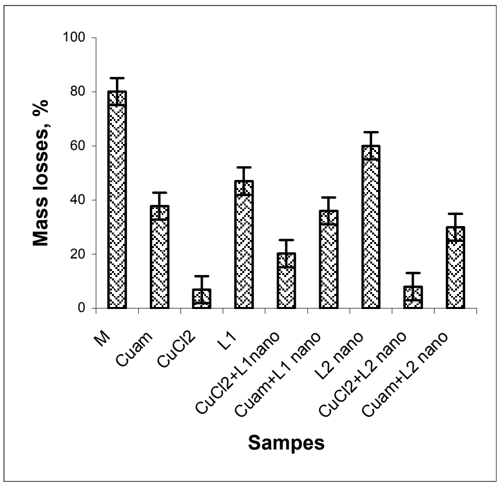

Figure 6: Variation of mass loss for the birch veneer samples non-treated (M) and treated with $CuCl_2$, Cuam, L1nano, $CuCl_2$L1nano, Cuam L1nano, L2nano, $CuCl_2$L2nano, CuamL2nano

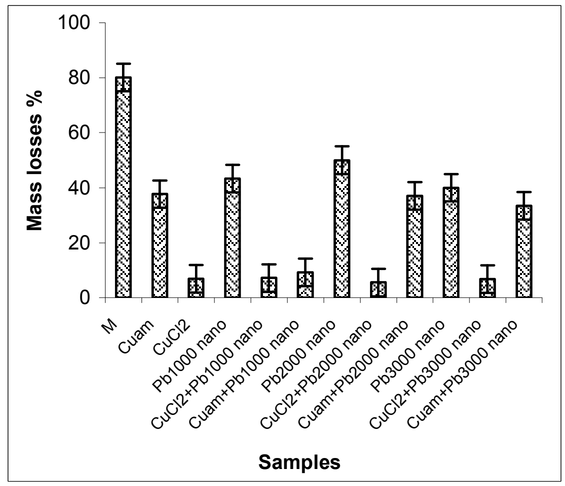

Figure 7: Variation of mass loss for the birch veneer samples non-treated (M) and treated with $CuCl_2$, Cuam, Pb1000nano, $CuCl_2$Pb1000nano, Cuam Pb1000nano, Pb2000nano, $CuCl_2$Pb2000nano, CuamPb2000nano, Pb3000nano, $CuCl_2$Pb3000nano, CuamPb3000nano

The data obtained for samples treated with lignin based nanoparticles and copper compounds show that the mass loss is lower compared to untreated samples. The lower mass loss was due to copper's toxic effects, to lignin's derivatives and to the two components' complexes, which limit and inhibit the microorganisms' attack. The treatment of wood surface with copper containing solutions, especially when provided by the chloride derivative and the lignin nanaoparticles, proved to be more efficient. Lignin-copper complexes derivatives fall in order as follows: Pb2000nano> Pb3000nano> Pb1000nano> L2nano> L1nano, in terms of assurance of wood biological stability. This situation may be correlated with their various functionalities induced thru hydroxymetylation, consequently resulting in different degrees of copper complex forming and wood surface interaction.

Determination of contact angle of the veneer samples treated with nanoparticles based on hydroxynmethylated lignin

The contact angle values for veneer specimens, buried into the soil for six months, were done to monitorize the efficiency of surface treatment and to establish the correlation between this parameter and weight loss recorded (Fig. 8, 9).

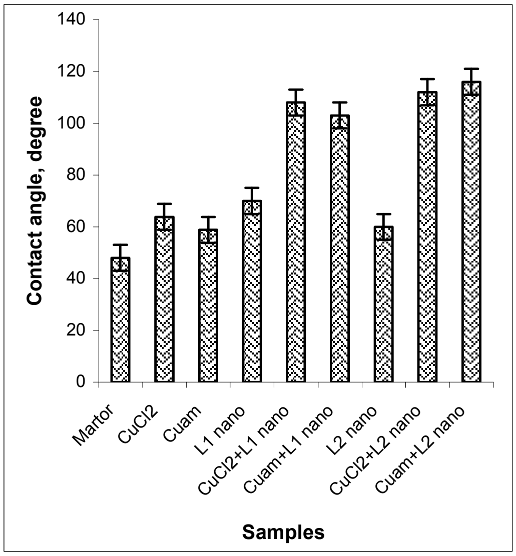

Figure 8: Variation of contact angle for the veneer samples non-treated (M) and treated with Cuam, $CuCl_2$, L1nano, $CuCl_2$L1nano, CuamL1nano, L2nano, $CuCl_2$L2nano, CuamL2nano

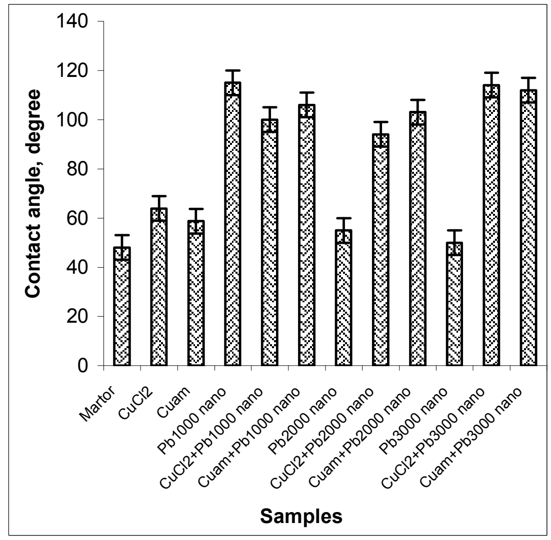

Figure 9: Variation of contact angle for the veneer samples non-treated (M) and treated with Cuam, $CuCl_2$, Pb1000nano, $CuCl_2$Pb1000nano, CuamPb1000nano, Pb2000nano, $CuCl_2$Pb2000nano, CuamPb2000 nano, Pb3000nano, $CuCl_2$Pb3000nano, CuamPb3000 nano

The data showed that the contact angle reaches higher values (94 -116 ^{o}) in the case of samples treated with copper complexes lignin derivatives, compared with the control or with those samples for which it was used copper ions solutions or unmodified lignin.

Therefore, those treatments provide biological stability and hydrofobycity of wood surfaces due to the more efficient action of lignin nanoparticles in the presence of copper ions which were better fixed on wood support. That is how it was assured a better protection against microbiological attack. During the contact angle measurement, it was observed that the hydrophilic surface has a very low level, the drop of water in some cases penetrated the wood surface and its evolution showed insignificant variations in time (Fig. 10, 11).

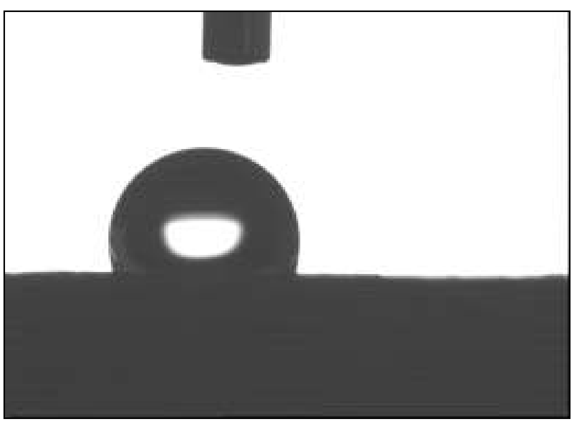

Figure 10: The image of drop of water on the surface of birch veneer based nanoparticles treated lignin and copper solutions (Cuam+L2nano) measured of Kruss Goniometry

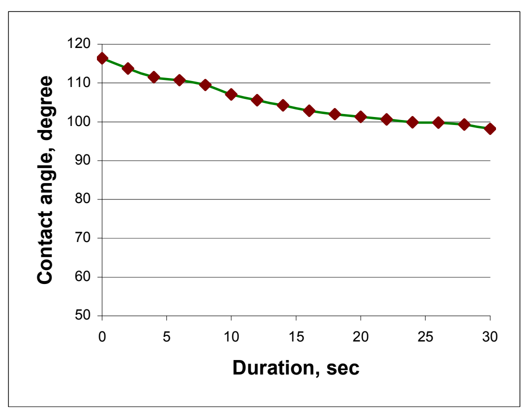

Figure 11: Variation in time of contact angle of specimen surface of birch veneer treated with Cuam+ L2nano

The image of drop of water on the surface of birch veneer treated with nanoparticles based hydroxymethyl lignin and copper solution (Cuam+L2) is presented in figure 10. Water droplet stability was found at over 100 degrees for angle values registered. In figure 11 it could be observed the slow decrease of contact angle during the measurement for 30 seconds.

4. CONCLUSIONS

1. A modified method of hydroxymethylation made possible the synthesis of nanoparticle from five types of lignin products from different sources with different reactivity capacity.
2. The nanoparticles obtained in hydroxymethylation were characterized by different dimensional size and distribution depending on studied lignin type.
Synthesized derivatives have been used to treated birch veneer in order to ensure its protection against microbiological attack followed by burial in soil samples for a period of six months.
The biological stability was assessed by determining mass loss and contact angle reported to the distilled water.
5. The data showed that the use of hydroxymethyl lignin-based nanoparticles and their complexes with copper provides good protection reducing mass losses and high values of contact angle. It was also observed certain hydrophobicity effects and a decreasing in the penetration level of water into the substrate timber.

5. ACKNOWLEDGEMENTS

The authors would like to thank to the Granit Recherché Développement SA, Trans Furans Chemicals bvba, for supplying the lignin and the furan resin samples, and to ECOBINDERS (SIXTH FRAMEWORK PROGRAMME, NMP2 – CT – 2005 - 011734) and CEEX-CNCSIS, LIGNOMAT, 4153/2006 for their financial support.

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