AGENTS FOR WOOD BIOPROTECTION BASED ON NATURAL AROMATIC COMPOUNDS AND THEIR COMPLEXES WITH COPPER AND ZINC

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The paper discusses the interaction between birch veneer and wheat straw lignin (L1) and Sarkanda grass lignin (L2), offered by Granit Recherche Development SA, Lausanne-Switzerland, both unmodified and modified (through a hydroxymetylation reaction which allows obtaining of nanoparticles), along with their complexes with copper and zinc. The treatments of birch veneer samples involve their successive immersion for 2 h into the products selected for testing. Solutions with 5% concentrations of lignin products in 0.1N ammonia solutions were used. The biostability of the thus treated veneer samples was assessed by burying them into soil cultivated with wheat plants and keeping them there for six months. The efficiency of the treatments was assessed by determining mass loss, contact angle and their variation during measurements.

Keywords: lignin, hydroxymethylation, nanoparticles, bioprotection, birch veneer

INTRODUCTION

Lignin biosynthesis and structure have been extensively studied along the years, the interest being explained by its abundance in nature and by its economic importance, *i.e.* the special performance of the end products.[1-3] The obtained data confirm that the lignin structure is that of a complex polymer characterized by a high diversity of monomeric units and also by various ways of connecting these building blocks (Fig. 1). The presence of phenolic and aliphatic hydroxyl groups in the lignin macromolecule explains its use as a partial substitute for phenol in multiple applications, such as biocide systems, adhesive systems or material composites.

Recent applications have been devoted to inserting lignin derivatives into composite materials and to employing them in treatments of wood, to increase its biological stability, or in bioremediation processes.[4]

The chemically modifying/modified substances used in wood treatments cause changes in its attributes, so that wood-derived materials are obtained.[5-7] From this perspective, lignin and the polyphenolic compounds are noteworthy. Therefore, solutions based on the known stability properties of the biological compounds are considered, while the elucidation of their action mechanisms will allow the development of replacing or additional systems for the currently used products.[8,10,11] Nanotechnology is the study and engineering of matter at 1-100 nm dimensions, whose physical, chemical or biological properties are fundamentally different from those of the bulk material. The nanotechnology paradigm is to modify bulk properties and functionality by controlled manipulations at nanoscale. Nanotechnology research has dramatically grown in the last 10 years, due to recent developments in nanoscale characterization techniques, processes and understanding of material behavior at nanoscale. An extension of the present understanding and control of matter at such levels will open new ways in product development. Nano-based science has applications across nearly all economic sectors, allowing the development of new technologies with higher commercial potential in the forest products industry.[12] At the same time, the possibilities of attaining water soluble and environmentally friendly biosafety systems are analyzed. This paper reports the biocide effects of lignin products in biostabilization treatments of birch veneer.

EXPERIMENTAL

Materials

Birch veneer samples (1x12 cm), copper chloride, zinc acetate, 0.1N ammonia, unmodified wheat straw lignin (L1N) and unmodified grass lignin (L2N) provided by Granite Recherche Development Company, wheat straw lignin (L1H), grass lignin (L2H),[5,6] nanosized wheat straw lignin (L1Hnano) and nanosized grass lignin, all modified through hydroxymethylation (L2Hnano), were employed in the experiments.[6,9]

Method

The veneer samples were subjected to the following treatments, on using the above-mentioned lignin products dissolved in 0.1N ammonia solutions to a final concentration of 5%:

a) immersion of samples for 2 h into the working solutions, followed by drying;

b) immersion of samples into zinc and/or copper compounds solutions, followed by drying, treatment with lignin products ammonia solutions, and again drying.

The treated samples were previously weighed to determine the mass retained on the wood surface. The treated birch veneer samples were buried in soil cultivated with wheat plants and maintained under laboratory conditions for 6 months, with specific soil moisture provided through regular watering. The biodegradation degree was assessed by measuring mass loss and contact angle. The mass loss of the biocide-treated birch veneer samples was determined by weighing on an analytical scale. Weighing was performed both before and after the treatment, which permitted to follow the mass increase after drying under laboratory conditions (25 ºC). After being dug up, the samples were weighed and the mass loss percentage was determined. Also, contact angle measurements were performed with Kruse Goniometry.[4]

RESULTS AND DISCUSSION

The study aims at establishing the efficiency of biocide products, based on unmodified/modified lignin and Cu and Zn ions, used in surface treatments of wood, to protect it against the action of the microorganisms present in the soil.

Figures 2 to 5 show the mass loss variation for birch veneer samples treated with unmodified/modified lignin and copper chloride and zinc acetate solutions, after their recovery from soil.

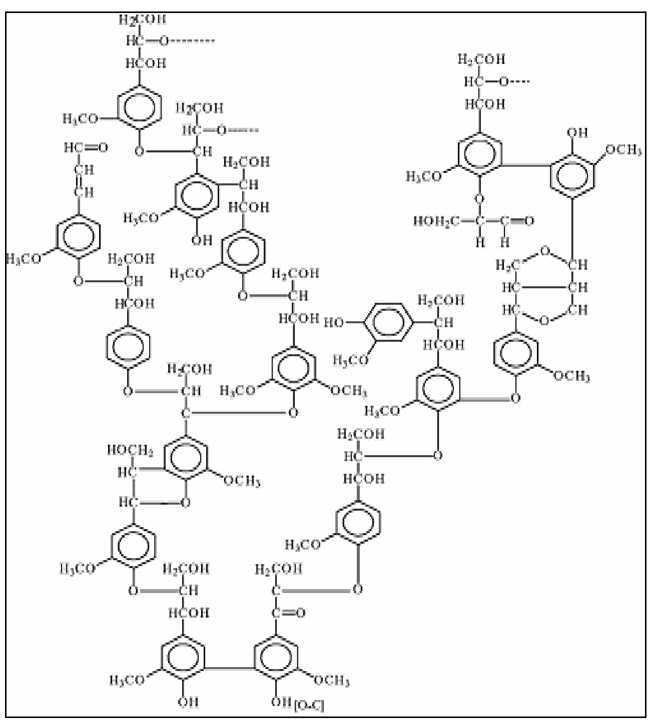

Figure 1: Structure of coniferous lignin proposed by Adler[1] in 1997

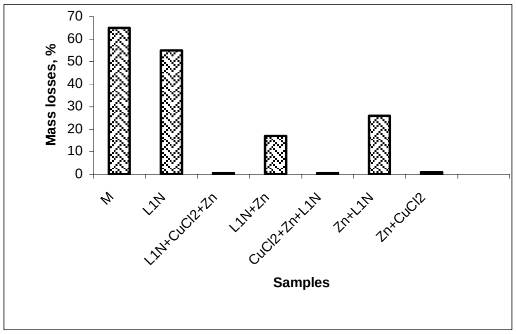

Figure 2: Variation of mass losses for birch veneer samples, non-treated (M) and treated with L1N, L1N+$CuCl_2$+Zn, L1N+Zn, $CuCl_2$+Zn+L1N, Zn+L1N, Zn+$CuCl_2$, Zn

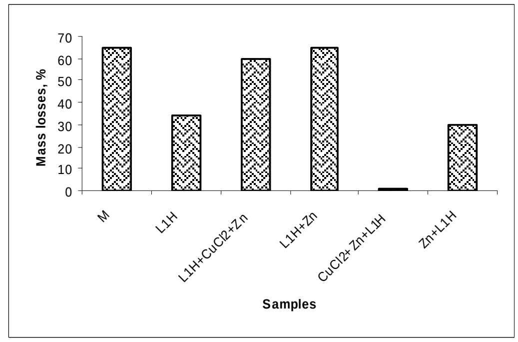

Figure 3: Variation of mass losses for birch veneer samples, non-treated (M) and treated with L1H, L1H+$CuCl_2$+Zn, L1H+Zn, $CuCl_2$+Zn+L1H, Zn+L1H

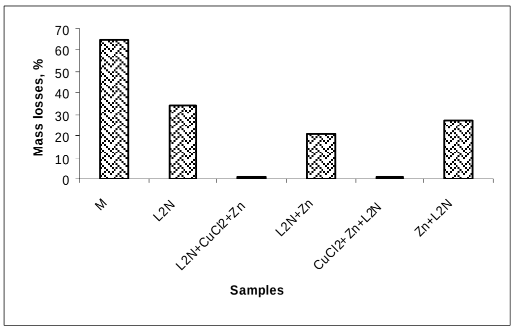

Figure 4: Variation of mass losses for birch veneer samples, non-treated (M) and treated with L2N, L2N+$CuCl_2$+Zn, L2N+Zn, $CuCl_2$+Zn+L2N, Zn+L2N

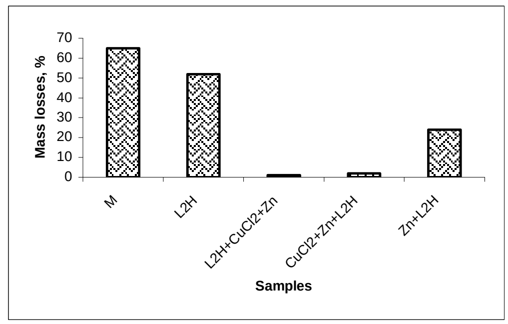

Figure 5: Variation of mass losses for birch veneer samples, non-treated (M) and treated with L2H, L2H+CuCl2+Zn, CuCl2+Zn+L2H, Zn+L2H

The treatment of the birch veneer samples with unmodified and modified lignin from wheat straw and from grass, led to the conclusion that the mass loss was low in the samples treated with lignin and copper and zinc compounds. Therefore, it could be argued that the presence of copper and zinc ions in the treatment

The data showed that the contact angle reaches higher values in the samples applied has an important role, leading to up to 0.5% mass loss.

The low mass losses are due both to lignin modification through hydroxymethylation – permitting its easier penetration into the veneer surface, granting it strength – and to copper and zinc ions, known for their protective effect against the microorganisms present in soil. The mass losses recorded for the treatment of birch veneer samples with wheat straw and grass lignin nanoparticles are shown in Figures 6 and 7.

As observed from the obtained data, the mass loss observed for specimens treated with modified lignin nanoparticles and copper and zinc solutions led to satisfactory results in terms of birch veneer stability. In this case, the biodegradation process is represented by the changes occurring in birch veneer samples in the presence of soil microorganisms. The effectiveness of the wood surface treatment applied depends on the nature of the product used., on the order of application and extent of change and complexation. treated with copper and zinc complexes lignin derivatives, compared to the control, or in the samples for which copper ion solutions or unmodified lignin were used. Therefore, such treatments provide biological stability and hydrophobicity of the wood surfaces, due to the more efficient action of lignin nanoparticles in the presence of copper ions, which were better fixed on the wood support. This assured better protection against the microbiological attack.

Contact angle measurements on the treated veneer surface led to the conclusion that the used products provide a high stability rate.

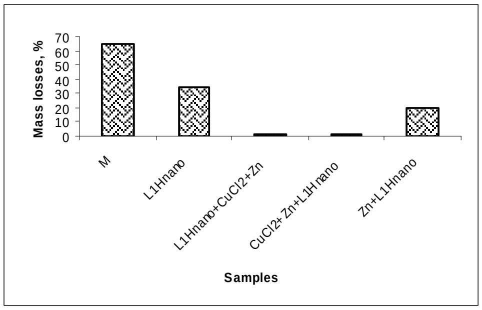

Figure 6: Variation of mass losses for birch veneer samples, non-treated (M) and treated with L1Hnano, L1Hnano+$CuCl_2$+Zn, $CuCl_2$+Zn+L1Hnano, Zn+L1Hnano

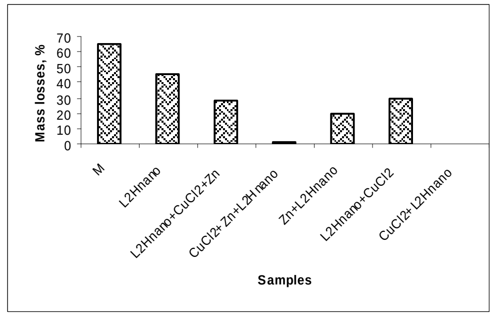

Figure 7: Variation of mass losses for birch veneer samples, non-treated (M) and treated with L2Hnano, L2Hnano+$CuCl_2$+Zn, $CuCl_2$+Zn+L2Hnano, Zn+L2Hnano, L2Hnano+$CuCl_2$, $CuCl_2$+L2Hnano

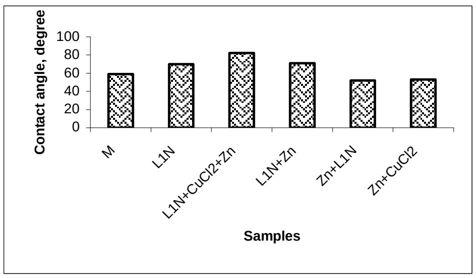

Figure 8: Variation of contact angle for veneer samples, non-treated (M) and treated with L1N, L1N+$CuCl_2$+Zn, L1N+Zn, $CuCl_2$+Zn+L1N, Zn+L1N, Zn+$CuCl_2$

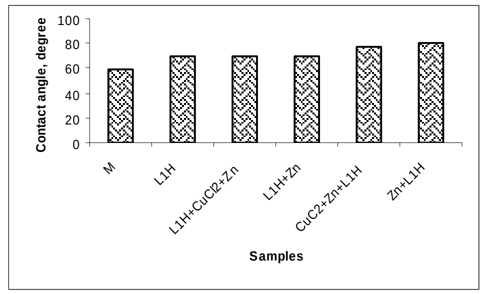

Figure 9: Variation of contact angle for veneer samples, non-treated (M) and treated with L1H, L1H+$CuCl_2$+Zn, L1H+Zn, $CuCl_2$+Zn+L1H, Zn+L1H

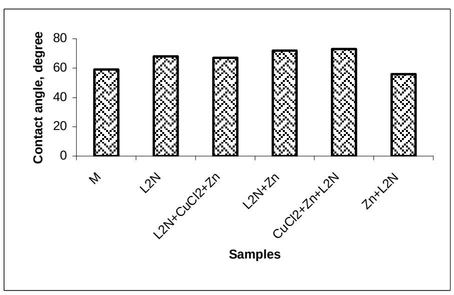

Figure 10: Variation of contact angle for veneer samples, non-treated (M) and treated with L2N, L2N+$CuCl_2$+Zn, L2N+Zn, $CuCl_2$+Zn+L2N, Zn+L2N

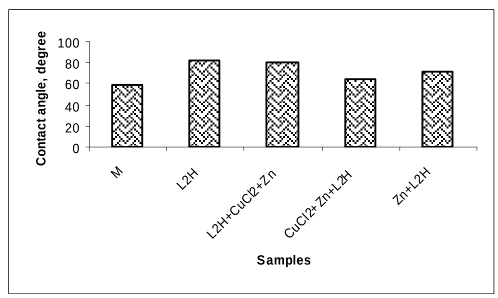

Figure 11: Variation of contact angle for veneer samples, non-treated (M) and treated with L2H, L2H+CuCl2+Zn, CuCl2+Zn+L2H, Zn+L2H

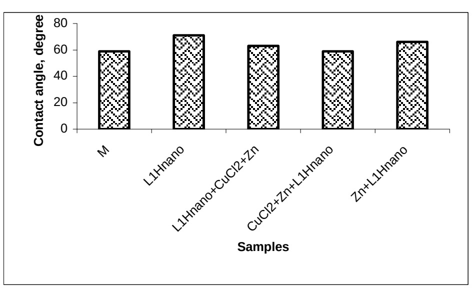

Figure 12: Variation of contact angle for veneer samples, non-treated (M) and treated with L1Hnano, L1Hnano+$CuCl_2$+Zn, $CuCl_2$+Zn+L1Hnano, Zn+L1H nano

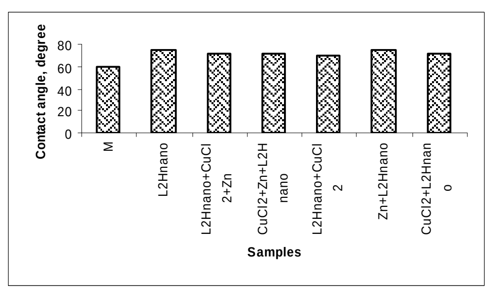

Figure 13: Variation of contact angle for veneer samples, non-treated (M) and treated with L2Hnano, L2Hnano+$CuCl_2$+Zn, $CuCl_2$+Zn+L2Hnano, Zn+L2H nano, L2Hnano+$CuCl_2$, $CuCl_2$+L2Hnano

Thus, it was confirmed that unmodified/modified lignin and zinc- and copper-based compounds confer biological stability to the wood substrate. The use of copper chloride and zinc acetate intensifies the response, probably due to wood tissue penetration, making it more resistant. The action of copper and zinc ions might be explained by their retention by the functional groups of the wood components, where lignin plays an important role.

CONCLUSIONS

1. The potential biocide effect of some lignin derivatives was studied by treating birch veneer samples with test solutions. The effects were monitored by burying the samples in wheat-cultured soil for 6 months.
2. The tests performed to evaluate the efficiency of lignin product treatment in the presence of copper and zinc ions substantiated the compounds' ability to ensure a high biological stability of wood, as assessed through mass loss and contact angle measurements.
3. The performed assays led to the conclusions that the best treatments applied to birch veneer were those involving modified lignin and copper and zinc solutions, which assured a high hydrophobicity degree and biological stability.

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REFERENCES

[1] G. Cazacu and M. I. Totolin, in "Lignina, sursă de materii prime şi energie" (in Romanian), Pim Publishing House, Iasi, 2010, pp. 3-10.

[2] Gh. Petrovici and V. I. Popa, in "Chimia şi prelucrarea chimică a lemnului" (in Romanian), Lux Libris Publishing House, Braşov, 1997, vol. 2, pp. 170-178.

[3] Gh. Rozmarin, in "Fundamentări macromoleculare ale chimiei lemnului" (in Romanian), Tehnica Publishing House, Bucuresti, 1984, pp. 55-70.

[4] A. M. Căpraru, E. Ungureanu and V. I. Popa, *15th International Symposium on Wood*, *Fibre Pulping Chemistry*, Oslo, Norway, 2009, pp. 50-55.

[5] Th. Măluţan, R. Nicu and V. I. Popa, *Bio/Resources*, **3**, 13 (2008).

[6] Th. Măluţan, in "Valorificarea complexă a biomasei" (in Romanian), Performantica Publishing House, Iaşi, 2008, pp. 25-31.

[7] Th. Măluţan and V. I. Popa, in "Protecţia lemnului prin metode specifice" (in Romanian), Cermi Publishing House, Iaşi, 2007, pp. 141-153.

[8] V. I. Popa, I. Spiridon and N. Anghel, in "Procese biotehnologice în industria de celuloză şi hârtie" (in Romanian), Media-Tech Publishing House, Iaşi, 2001, pp. 30-35.

[9] P. Schilling, US Patent no. 5,192,361, March 9, 1993.

[10] M. I. Totolin and G. Cazacu, in "Adezivi, materiale compozite şi alte aplicaţii pe bază de lignină" (in Romanian), Pim Publishing House, Iaşi, 2010, pp. 195-197.

[11] V. I. Popa, in "Tehnologii de valorificare a ligninei" (in Romanian), Publishing House of the Polytechnic Institute of Iaşi, 1983, pp. 30-41.

[12] L. Wagner, "Overview of the Forest Products Industry", Nanotechnology for the Forest Products Industry – Vision and Technology Roadmap, 1998.