STUDY ON BIOCIDAL PROPERTIES OF SOME NANOPARTICLES BASED ON EPOXY LIGNIN

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The abundance and relatively low price of lignin has always captured researchers' interest. To increase the reactivity of lignin, a series of reactions, such as epoxidation, hydroxymethylation, carboxymethylation etc., are used. The aim of this study has been to use the liquid supernatant phase generated from the epoxidation reaction of comercial lignins Pb1000, Pb2000 and Pb3000 (from Granit, Switzerland) in biocide systems. This supernantant phase proved to contain lignin micro- and nanoparticles. With these nanosuspensions, treatments on poplar and oak veneer were carried out. Then the treated and untreated veneer samples were buried in cultivated garden soil for six months. The biodegradation degree was assessed by contact angle and mass loss. Treatment efficiency was found to be dependent on the treatment with lignin and on the wood species used for the substrate. For poplar veneer, epoxidated Pb 3000 was the best protection agent, while the derivative of Pb1000 was efficient for oak veneer protection.

Keywords: epoxidation, nanosuspensions, nanolignin, bioprotection, poplar and oak veneer

INTRODUCTION

Although in recent years in building materials industry many new products with special characteristics and relatively low production costs have appeared, wood is still preferred due to its properties (recycling, low density and high mechanical resistance, low thermal conductivity coefficient and low coefficient of linear thermal expansion on the fiber length). Nevertheless, there are a number of shortcomings, such as significant loss of mechanical properties with increasing humidity, the existence of natural defects in wood structure, appearance of degradation as a result of environmental factors and the action of microorganisms. Some of these deficiencies can be eliminated using specific treatments of the wood surface, whose efficiency depends on the retention of the products applied. From the chemical point of view, wood is composed up to 95% of cellulose, hemicelluloses and lignin, the rest representing extractive substances.[1] In the technology of wood pulping, significant amounts of lignin are removed from the raw material; in the case of wood species, lignin represents up to 25% of the wood mass.[2] Most of lignin is incinerated to obtain energy and recover chemicals necessary in pulping processes.[3] On the other hand, lignin, which is an aromatic polymer with a complex structure, may be used to obtain biofuels or to partially substitute the phenols in the synthesis of products of wide range application.[4] The abundance and relatively low price of this renewable resource are good reasons for searching for ways of high valorisation. The reactivity of lignin can be modified by using different reactions, such as epoxidation, hydroxymethylation and carboxymethylation.[5-9] The introduction of epoxy groups in the lignin structure is achieved by its reaction with epichlorohydrine in alkaline medium. The reaction products can be used to obtain epoxy resins, where the phenolic component is partially or completely substituted with lignin derivatives, according to the reaction presented in Figure 1.[8] The use of the epoxidation reaction also allows the obtaining of micro- and nanoparticles evidenced in the supernatant resulted from the epoxidation of commercial lignins (Pb1000, Pb2000, Pb3000). In this study, the lignin derivatives thus synthesized were tested for their biocidal properties and the results obtained are presented. It is worth mentioning that macro- and nanoparticles could be identified only in the liquid phase resulting from the modification of these lignins (epoxidation). The nanosuspensions thus obtained were applied on poplar or oak veneer with the objective of improving the biostability of woody substrates. The biostability was investigated by determining weight loss and contact angle variation in time for the samples, after they had been buried in cultivated soils for six months.

EXPERIMENTAL

Materials

Commercial lignins Pb1000, Pb2000 and Pb3000 (from Granit, Switzerland) with the characteristics presented in Tables 1 and 2 were used for the epoxidation experiments.

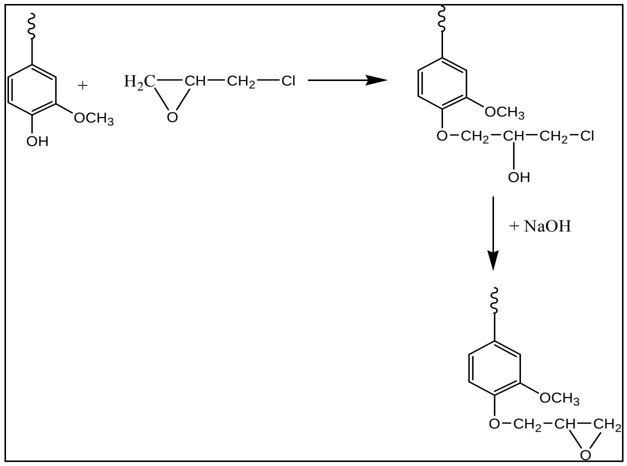

Figure 1: Lignin epoxidation

Table 1
Origin of Protobind lignins

Type of lignin	Characteristics	Origin	Raw materials
Protobind 1000	Unmodified lignin	Laboratory	Hard wood
		Pilot	Wheat straw
		Pilot	Grass (*Saccharum munja*)
		Industrial	Wheat straw and grass
Protobind 2000	Low softening temperature /compatibility with furfuryl alcohol	Pilot	Wheat straw and grass
Protobind 3000	High reactivity	Pilot	Wheat straw and grass

Table 2
Characteristics of commercial Protobind lignins

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% aqueous suspension)	~3.5	4.80	6.20
Particle size	>99% less than 210 μm	>96% less than 200 μm	>98% less than 200 μm
Density, g/mL	~0.3	~0.6	~ 0.3
OH aromatic, 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
Softening temperature, °C	~200	~130	~200
Furfuryl acohol solubility	40.1%	41%	42.10%
Solubility in alcalii, pH=12	94%	95.2%	93.8%

The reaction medium was composed of sodium hydroxide (NaOH 20%), epiclorohydrin and sodium dihydrogen phosphate NaH_2PO_4. For the biostability tests, specimens of poplar and oak veneer (120x15x1.5

mm) were used and were treated with the synthesized micro- and nanodispersion (epoxidation supernatant with a solids content of 8-12%).

Methods

Epoxidation reaction was performed under previously established optimum conditions: temperature 70 °C, lignin:NaOH mass ratio = 1:3, reaction time two hours. 10 g lignin (a.d.) were weighed and dissolved in 150 mL NaOH 20% solution, and stirred for one hour at 40 °C, in a water bath. After one hour of stirring at 40 °C, the temperature was raised to 45 °C and 85 cm^3 of epichlorohydrin was added to the reaction vessel. The temperature was further raised to 70 °C and maintained constant for two hours under continuous stirring. After the reaction time expired, the mixture was cooled under a water jet and neutralized with NaH_2PO_4 up to a pH higher than 10. The solution was centrifuged at 2500 rpm. The solid material was washed twice with distilled water and dried.[5,8] Particle size distribution of the epoxidated lignin present in the nanosuspensions was analyzed with SALD 7001 device, which uses a light power laser source that allows the evaluation of an average particle size ranging from 15 nm to 500 µm. The samples of oak and poplar veneer were immersed for 30 minutes in the nanosuspensions obtained after the epoxidation of the three types of lignin, then were dried at room temperature and weighed to assess the retention degree. The samples were then buried in garden soil sown with wheat. These experimental conditions combine the effects of microorganisms with those of rhisosphere. After six months, the samples were extracted from the soil, washed and dried to determine mass loss. The mass loss of the biocide-treated poplar and oak veneer samples was determined by weighing, which was carried out both before and after introduction into soil, thus permitting to assess mass variation under laboratory conditions (25 °C). The variation of contact angles for both initial samples and those kept in the soil were determined by the sessile drop method, at constant temperature and controlled humidity, by placing 4 µL drop of liquid on the veneer surface and until the drop disappeared, using a CAM-200 instrument from KSV, Finland. The contact angles of double-distilled water were measured on veneer to estimate wettability. Contact angle measurements were done at least 5 times in different locations on the surface. The average values were used in contact angle analysis.

RESULTS AND DISCUSSION

It is known that in plants lignin performs several functions: it confers resistance to roots and stems, acts as an adhesive for cellulose fiber, or as a matrix of phenolic and aliphatic substances, protects carbohydrates against microorganism and insect attack.[4,10]

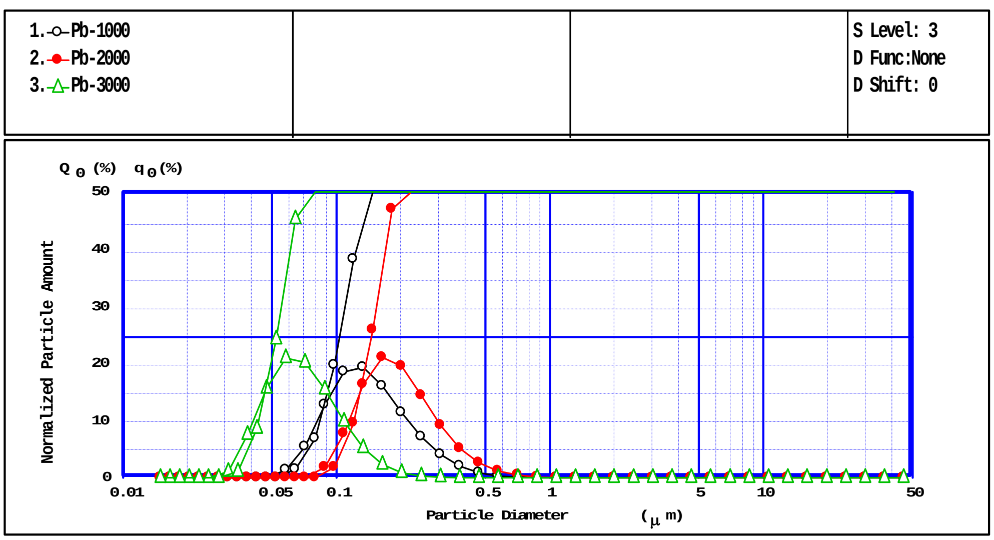

Figure 2: Average size distribution of nanoparticles after epoxidation of Pb1000, Pb2000, Pb3000

Knowing the biological role of lignin in wood, which is to ensure biological stability, and taking into account the favorable results previously obtained,[11,12] we have proposed to extend our studies to other species of wood and under the conditions of wheat sown soil. The surface roots of this plant are considerable and ensure an accelerated development of microorganisms. For this purpose, to increase durability of wood veneer, nanodispersions resulted from the epoxidation of Pb1000, Pb2000 and Pb3000 have been tested as bioprotection systems through application on the material surface. Particle size distribution data of micro- and nanoparticles resulting from epoxidation of Pb1000, Pb2000, and Pb3000 are presented in Figure 2, with averages between 70 and 200 nm.

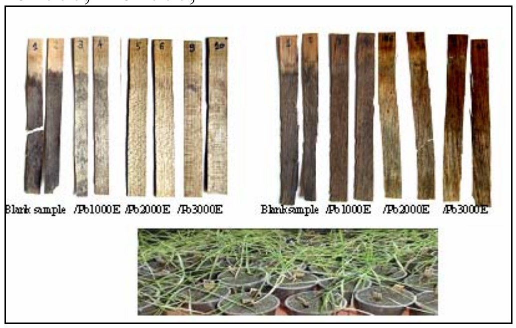

Figure 3: Samples of poplar and oak veneer after six months in soil

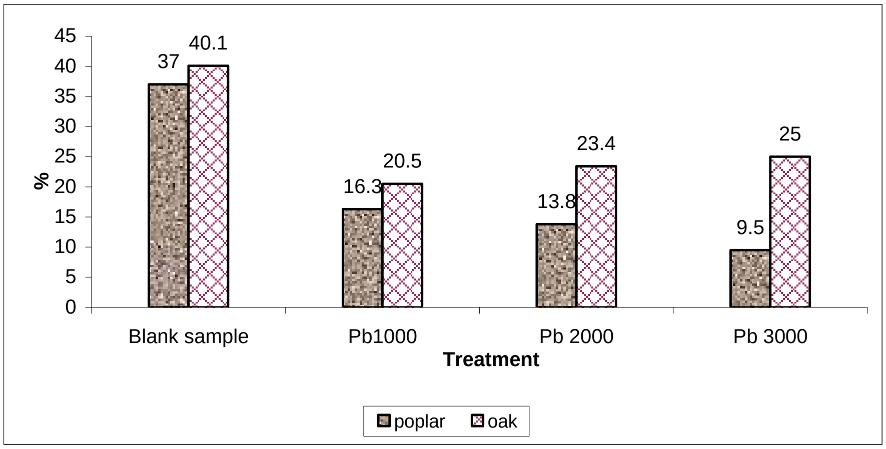

Figure 4: Variation of mass loss for poplar and oak veneer treated with Pb1000, Pb2000, Pb3000 lignin nanosuspensions

After the treatment of poplar and oak veneer with unmodified lignins, it was observed that the hydrophilic character of wood was increased. Compared to commercial Protobind products, nanosuspensions resulting from epoxidation are retained better on the veneer surface. The specimens treated with nanodispersions become more hydrophilic, in comparison with treatments with unmodified lignin. As a result, it was concluded that epoxy products improve the biostability of oak and poplar veneer. This is evidenced by the reduced mass loss of the treated samples buried in soil for six months. The efficiency of the treatment depends on the type of product used and also on the species of treated wood. Poplar veneer thus treated was found to be more stable in cultivated soil, compared to oak veneer (Figure 4). The application of nanodispersions resulting from the epoxidation reaction on veneer confers biostability and, in addition, increased capacity for liquid adsorption on the surface (Figures 5-10). This characteristic may improve the retention of some products that could be applied after biostabilization treatments. The behavior of the wood subjected to different treatments was evaluated by assessing the evolution in time of the average value of contact angle. Thus, the determination of contact angle values, perpendicularly to the fiber axis, was done until the drop of liquid on the surface examined disappeared. Low water adsorption and the weigh loss values (up to 40% of the sample) recorded for the blank show that microorganisms from the soil have consumed a large part of the polysaccharides, so that the lignin content increased in the samples. On the other hand, the mass of the treated specimens dropped to a lower extent, the losses being below 25%. It was also observed that the contact angle values underwent no significant change, compared to those recorded for the reference samples, and the wood (especially poplar) maintained a part of its initial characteristics conferred by the treatment, even after it was kept in the soil for six months.

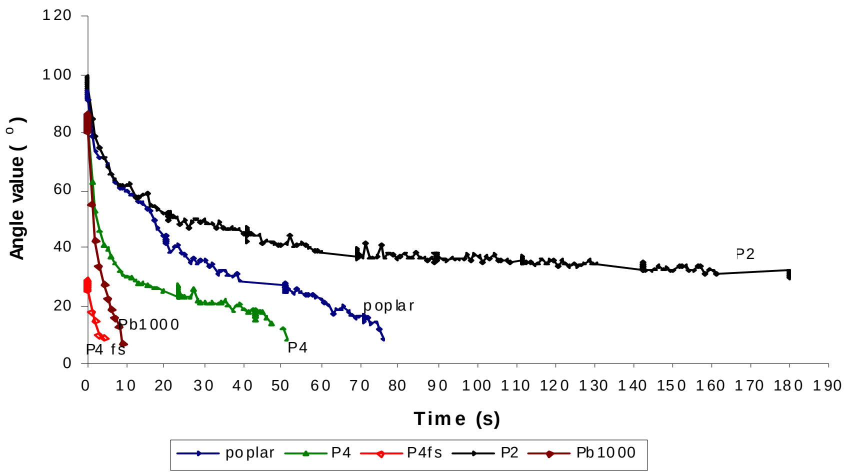

Figure 5: Variation of contact angle in time for poplar veneer samples: non-treated (poplar), non-treated after six months in soil (P2) and treated with Pb 1000 nanosuspensions: P4, P4fs (before burying in the soil), Pb 1000 (unmodified lignin)

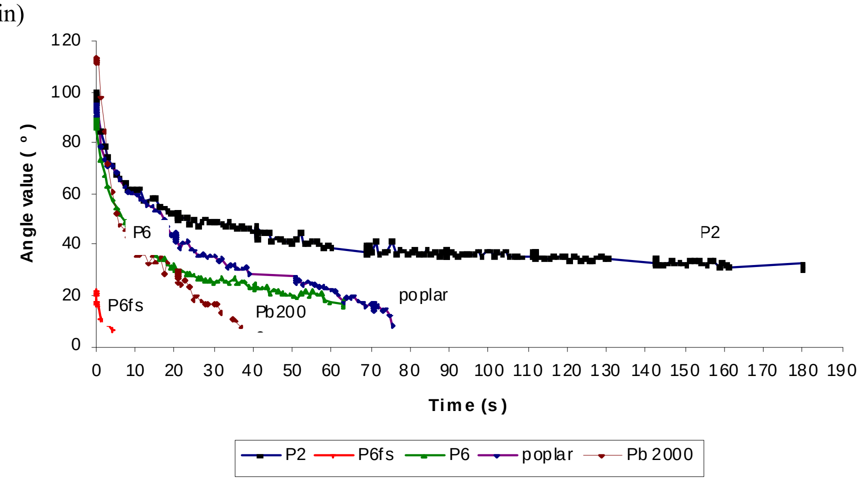

Figure 6: Variation of contact angle in time for poplar veneer samples: non-treated (poplar), non-treated after six months in soil (P2) and treated with Pb 2000 nanosuspensions: P6, P6fs (before burying in the soil), Pb 2000 (unmodified lignin)

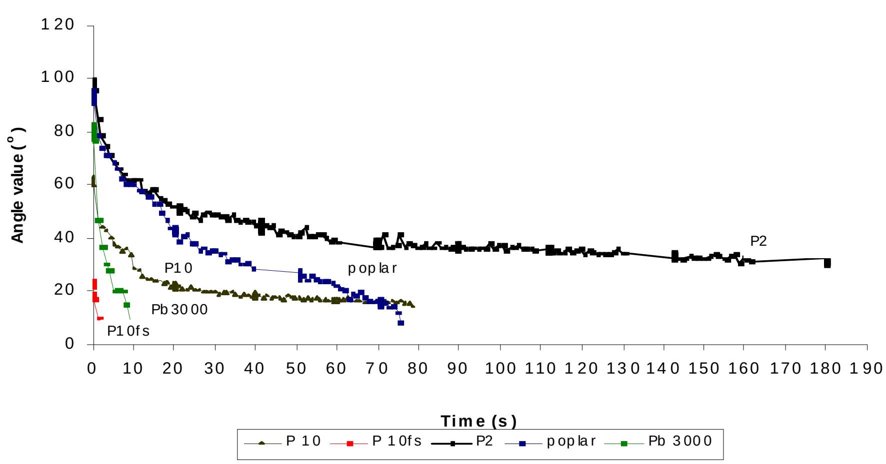

Figure 7: Variation of contact angle in time for poplar veneer samples: non-treated (poplar), non-treated after six months in soil (P2) and treated with Pb 3000 nanosuspensions: P10, P10fs (before burying in the soil), Pb 3000 (unmodified lignin)

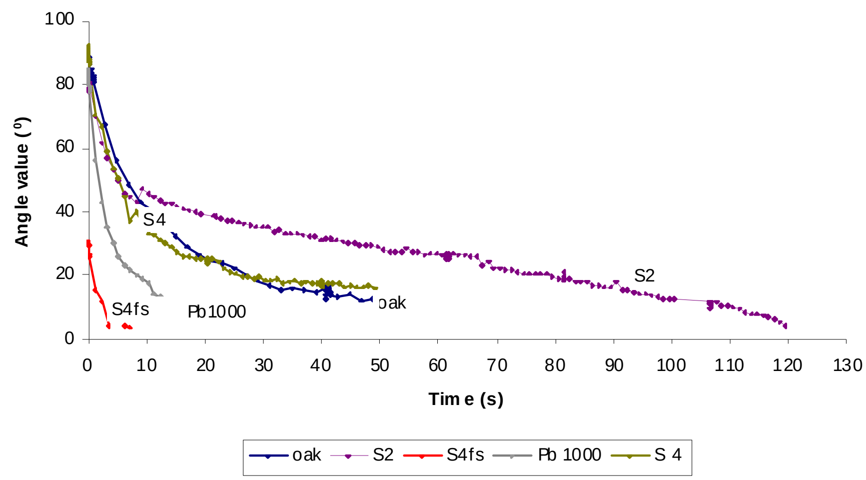

Figure 8: Variation of contact angle in time for oak veneer samples: non-treated (oak), non-treated after six months in soil (S2) and treated with Pb 1000 nanosuspensions: S4, S4fs (before burying in the soil), Pb 1000 (unmodified lignin)

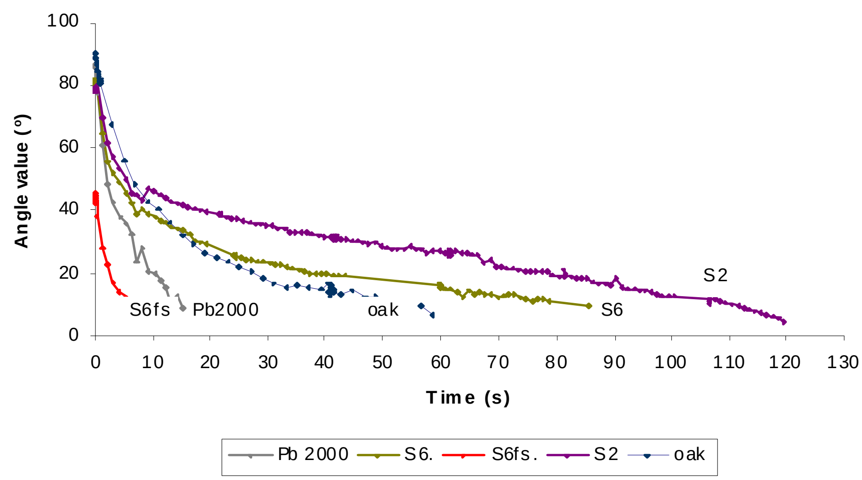

Figure 9: Variation of contact angle in time for oak veneer samples: non-treated (oak), non-treated after six months in soil (S2) and treated with Pb 2000 nanosuspensions: S6, S6fs (before burying in the soil), Pb 2000 (unmodified lignin)

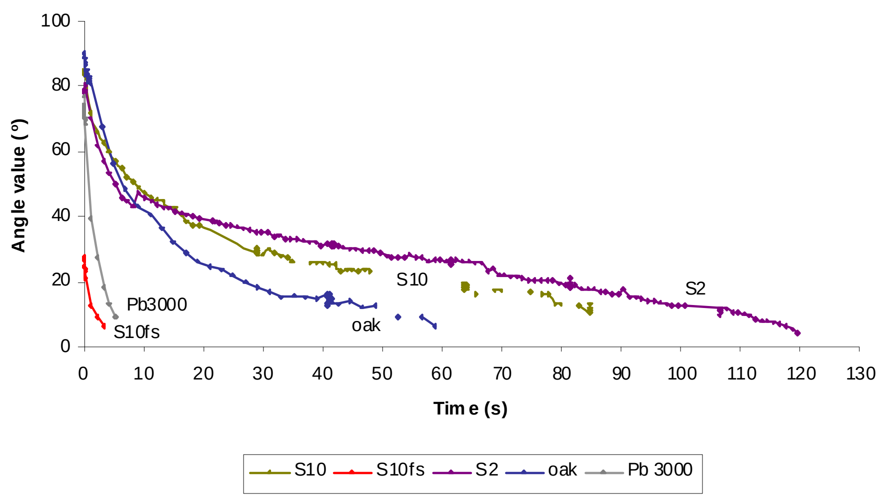

Figure 10: Variation of contact angle in time for oak veneer samples: non-treated (oak), non-treated after six months in soil (S2) and treated with Pb 3000 nanosuspensions: S10, S10fs (before burying in the soil), Pb 3000 (unmodified lignin)

CONCLUSION

The use of the epoxidation reaction made it possible to obtain nanodispersions based on commercial Protobind lignins, which were characterized in terms of dimensional distributions. The nanosuspensions resulting from lignin epoxidation were used for the treatment of poplar and oak veneer to improve wood resistance to biodegradation. The results obtained by evaluating the mass loss and wetting angle against water showed that the tested lignin derivatives ensured the biostability of wood. Comparisons of the data recorded have led to the conclusion that the derivatives obtained behaved differently, depending on the lignin sample and wood species used for substrate. Thus, the derivative synthesized from Pb3000 was more efficient in the case of poplar wood, while the product resulting from Pb1000 epoxidation was more convenient for oak veneer protection.

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