STUDIES CONCERNING THE BIOLOGICAL STABILITY OF SOME COMPOSITE MATERIALS IN THE PRESENCE OF SOME BIOCIDES

STUDII PRIVIND STABILITATEA BIOLOGICĂ A UNOR MATERIALE COMPOZITE ÎN PREZENȚA UNOR BIOCIZI

UNGUREANU ELENA[1], *V. I. POPA*[1],
VIORICA IACOB[2], *E. ULEA*[2]
[1] Technical University "Gheorghe Asachi", Iasi
[2] University of Agricultural Sciences and Veterinary Medicine
"Ion Ionescu de la Brad"Iasi

Abstract. *This work has the purpose of highlighting some possibilities of testing the quality of some biocide systems on the basis of natural products with applications in the protection of the lignocellulose materials represented by test pieces made of fir and beech wood. These have been used both in their untreated state and treated on their surface through brushing both ways. The products tested for the treatment have been used in various types of concentration and they are both of organic origin (unmodified/modified straw lignin, furan resin) and inorganic origin (copper chloride and tetraminocopper hydroxide). Testing the bio-protection and implicitly the biodegradation level has been carried out in several versions, chosen according to the classes of standard biological risk concerning the biological attack. The evaluation of the quality of the studied biocide systems has been achieved by analyzing the resistance of the wooden products studied to the attack of some biological agents). As a result of these tests, it was noticed that the efficiency of the treatment applied on the wooden material depends on the nature of the product used.*

***Rezumat**. Lucrarea îşi propune evidenţierea unor posibilităţi de testare a calităţii unor sisteme de biocizi pe bază de produse naturale cu aplicaţii în protecţia materialelor celoligninice, reprezentate de epruvete de lemn de brad şi fag. Acestea s-au utilizat atât în stare netratată cât şi tratate la suprafaţă prin pensulare în dublu sens. Produsele testate pentru tratament s-au utilizat în concentraţii diferite şi sunt atât de natura organică: lignina din paie nemodificată/modificată,răşina furanică, cât şi de natură anorganică: clorură cuprică şi hidroxid tetraaminocupric. Testarea gradului de bioprotecţie şi implicit a celui de biodegradare s-a analizat în mai multe variante, alese în funcţie de clasele de risc biologic standard privind atacul biologic. Aprecierea calităţii sistemelor biocide luate în lucru s-a realizat prin analiza rezistenţei produselor de lemn studiate la atacul unor agenţi biologici. În urma acestor teste, s-a constatat că eficienţa tratamentului aplicat pe suprafaţa materialului lemnos depinde de natura produsului utilizat.*

Through its definition, the term "composite" is attributed to a complex system, made of several materials of various types. The lignocellulose materials are mainly made of cellulose, lignin and hemicelluloses, natural polymers that

represent more reactive groups capable of taking part in reactions of modification. The research that has been made across the years point out the fact that lignocellulose can be modified by means of microorganisms and of the enzymatic systems involved in biodegradation (15).

The composite structures imposed themselves thanks to the superior performances towards individual materials and the possibility of modeling the properties according to the domain of use (1). To this purpose, the wood as composite material is assessed both as a model structure and under the aspect of its use in various domains as a regenerating, recyclable and ecological product (compatible with the environment). Wood is a composite biological material and thus it is inevitably exposed to deterioration, in some cases its biodegradability being a shortcoming and for this reason they are studying various possibilities of bio-stability are being studied at the moment.

In order to control and adjust the biodegradation process of the lignocellulose composites, various bio-protection methods have been prepared for them , using various modern and traditional techniques, actually developed as techniques of "preserving" the wood (chemical modification, chemical treatment, surface treatment or in-depth treatment with resins, polymers and polymerizable substances, impregnation with salt and other substances, inclusion in composite materials (other materials), protection, gluing) (2, 8, 14, 23, 24).

Having in view the toxicity of the classic biocide agents, there can be noticed nowadays the tendency of obtaining resistance to the attack of microorganisms with regard to systems based on the properties of some natural products, such as for example lignins and the aromatic products (10,13).

The chemical compounds of wood (polysaccharides and lignin) can be characterized by different biological stability. Thus, among these, lignin is the material which is resistant to the action of microorganisms, whereas polysaccharides are characterized by reduced stability (16). Having in view the natural characteristics of lignin, the present work carries out a comparative study of the influence that lignin shows in the process of bio stability, along with the furan resins and chemical agents such as the copper chloride and the tetraminocopper hydroxide (cuproxam) For this reason the present work intends to adopt two processes that are in interdependent reciprocity, the process of bio protection and that of bio degradation of the lignocellulose materials respectively. More than that, some methods of testing and investigating the bio degradation of some composite lignocellulose materials have formed the subjet of some previous studies. (23, 24).

MATERIAL AND METHODS

For this study the following materials have been used:

- test pieces made of fir wood having the size 7,5X3,0x1,5) cm and the equilibrium relative humidity U_r=13,63% and test pieces made of beech wood having the size (8,5x4,3x1,5) cm and the equilibrium relative humidity U_r=14,74%;

- unmodified straw lignin coming from the company Granit Recherche developpement and straw lignin modified through hydroximetilation (3,17,19, 23) (table 1);
- Biorez furan resin coming from the company Trans Furans Chemicals 36%;
- Copper chloride;
- Tetraminocopper hydroxide (cuproxam)
- Ammonia solution 0,1 N

Table 1.

The characteristics of the unmodified (L1) and modified (L1H4) straw lignin

Characteristics	**L_1**	**Characteristics**	**L_1H_4**
Relative humidity,%	5.00	Relative humidity,%	5.85
Ash,%	2.30	Ash,%	0.64
pH in suspension	2.70	pH in suspension	3.50
p-OH	1.70	Rap. OH Al/OH Ar A 2930/A1510	0.84
Carboxyl groups	3.80	Carbonyl groups	0.73
Manganese,%	0.7	Rap.CH2O/L1 (W/W)	0.2583
Nitrogen,%	1	Phenol OH A 1345/A1510	0.69
Uronic acid,%	0	alcohol OH (moles/C9)	0.30
Solubility in acids, %	1	total OH (moles/C9)	0.99

The fir and beech test pieces have undergone the surface treatment trough brushing both ways (in the direction of fibers, perpendicularly (transversally) on these and in the end again in the direction of fibers with unmodified/modified straw lignin, rendered soluble in ammonia 0,1 N and with furan resin solution 36%, copper chloride and cuproxam. The biocides have been used with the following concentration values: 1, 3 and 5 %. The impregnation of the wood test-pieces was carried out in a period of time between 5-10 minutes, after which these were dried under air atmosphere and room temperature conditions for 24 hours. After achieving these operations, the composites have undergone different bio stability tests, taking into account the classes of risk concerning the biological attack on the bio test of wood. The treated fir and beech test-pieces were placed on the soil surface under natural conditions in a stationary unit from the farm “Vasile Adamachi” from USAMV, Iasi. The stationary unit is placed near an area covered with woody vegetation, in order to obtain the optimal conditions for natural infections. The observations have been done every 14 days, collecting the material on which the emersion of the degradation areas could be noticed. The materials have been transported to the laboratory in sterile bags, and there they have undergone the mycetological test.

In order to determine correctly the micromycetes that attach to the wood, the fieldwork samples have been brought to the laboratory and after they have been put in

Petri containers on humid filter paper, they have undergone the thermostatation. After the attachment of the micromycetes has been noticed, these have been mashed on the agar medium Czapek, medium where the micromycetes have to develop in order to determine correctly the genus and species referred to.

RESULTS AND DISCUSSIONS

As a result of the samples analysis, the appearance of the following micromycetes has been noticed:

PENICILLIUM BREVI-COMPACTUM-Dierckx in Soc. Scien. Brux. XXV, p.88 (1901); Thom, The Penicllia, p.295-296 (1930); J.Gilman, A Manual of Soil Fungi, p.255 (1957); Raper and Thom, p.407-409, fig. 106,107(1968); Domsch end Gams, Pilze aus Agrarböden, p.98 (1970)

The fungus can be found on *Fagus silvatica L.* wood treated with $CuCl_2$, Cuam and resins, which is a new host in Romania for these mycetes.

PENICILLIUM FUNICULOSUM- Syn.: *Penicillium pinophilum* Hedgcock.- Thom, U.S. Dept. Agr.,Bur. Anim. Ind., Bul. 118, p.69, fig.27(1910);Thom, The Penicllia, p.464-465, fig.77(1930); Gilman, A Manual of Soil Fungi, p.280(1957); Raper, Thom and Dorothy Fennell, A Manual of Penicillia, p.616, fig.616, fig. 159(1968).

The colony of the micromycete on *Abies alba Mill* wood treated with $CuCl_2$ and Cuam, resin and modified lignin is hairy, green with numerous hyaline conidiophores, with smooth walls, typically bivertical, of 100-300 μm. Gilman mentions it from different American states and in Romania it is mentioned by Misirliu Elibabeta et collab. , from Alpine soils 1964, On paper by Ana Hulea, Piticas Gh 1970, Papacostea P. and collab., from the podsol soils in the Apuseni Mountains-1076 and by Iacob Viorica from The soil of vegetable greenhouses in 2003. In Romania, *Abies alba Mill.* is a new host for this mycete.

ALTERNARIA GEOPHILA- Daszewska, Etudé sur la désagrégation de la cellulose dans la terre de bruyére et la turbe, Bul. Soc. Bot. Geneva II, 4 p. 294(1912); Gilman, A Manual of Soil Fungi, p. 348(1957).

The fungus can develop on *Fagus Silvatica L.* wood treated with $CuCl_2$, placed on the surface of the soil for several months under ordinary climatic conditions. Gilman mentions the fungus from the Swiss and Egyptian soils. The *Alternaria geophila Dasz* fungus is new in Romania on the Fagus silvatica L wood, which seems to be a good host.

STACHYBOTRYS ALTERNANS - Bonorden, Handb., p.117(1851); Sacc., Fungi ital.,del., tab. 898 et Syll. Fung., IV, p.269(1886); Lindau, Rab., Kr. Fl. (Ed. II) VIII, p.628(1910); Migula, Kr. Fl. Bd. III, Pilze 4 Teil, 2 Ab., p. 236, taf. CXXVII, fig. 3-5 (1934); Gilman, A Manual of Soil Fungi, p. 321 (1957). The *Fagus silvatica L.* wood treated with Cu Cl_2, lignins and furan resins placed on soil for several months is invaded by the mycelium of the blackish-brown fungus. Gilmann mentions the fungus in the USA and Puerto Rico soils. In Romania it was found in soil as saprophyte fungus by E. Docea and G Melica in 1953, Revolceanu and I Alteras in 1958, 1959, 1960, by

C. Sandu-Ville- on cotton-wadding in 1961, by Th. Chifu – in soil in 1971 and by Viorica Iacob in 1991 on *Vitis vinifera L.* In Romania *Fagus silvatica L.* is a new host of this micromycete.

CHAETOMIUM FUNICOLA - Cooke, Britsh Fungi, p. 176(1873); Cooke W.B. and Shaw C.G.,Western Fungi, III, Mycol. XXXII/9, p.512(1952); Gilman, A Manual of Soil Fungi, p. 177, Plate III,(1957); C.Sandu-Ville, Ciuperci *Pyrenomycetes - Sphaeriales* din România, p.228(1971).

The *Fagus silvatica L.* treated with resins and copper solutions placed on soil for several months presents little black dots represented by the fungus top. Gilman mentions the micromycete in the Canadian, Californian and German soils and in Romania, C. Sandu-Ville mentions its appearance on wheat in 1969 and in 1971, and E. Ulea mentions it in 1991 on vine.

HUMICOLA GRISEA - Syn.: *Monotospora daleae* Mason- Traaen, Nyt. Mag. Naturvid., 52, p 34 (1914); Gilman, A Manual of Soil fungi, p. 326 (1957); Ellis, Dematiaceous Hyphomycetes, p. 60, Fig. 29. B (1971).

The micromycete develops on the surface of the *Fagus Silvatica L.* wood treated with lignins and resins and on *Abies alba* wood treated with cu CuCl2 solution colonies, white at the beginning then, in grey nuances. It is mentiones in the soils of England (after Gilman) and in Romania it was signaled by Viorica Iacob in 1973 on vegetal remains on the wheat and corn monocultures, and by Ioachimescu - Dinulescu Marilena in 1978, as a degradation factor for the wood in mines. The beech and the fir tree are new hosts for this micromycete in Romania.

FUSIDIUM VIRIDE- Grove, Journ of Bot.,1955, p.164 (18545); Sacc. Syll. Fung. IV, p. 261(1886); Gilman, A manual of Soil Fungi, p. 207(1957).

The isolated fungus on *Abies alba Mill.*wood treated with modified and unmodified lignin forms on the Czapek agar medium a very fine filamentous thallus from where the conidiophores can be destroyed with difficulty.

Also a *FUSARIUM* species from the fir wood was isolated on the Czapek agar medium [4-7, 9, 11, 18, 20].

CONCLUSIONS

The fir and beech test pieces have undergone the attack of some fungi responsible for the process of degradation of the lignocellulose materials. The samples treated were visually and microscopically examined in order to establish the level of development of the fungus mycelium. It was noticed that the fungi species which develops on the lignocellulose material depends on the nature of the chemical substance and its concentration when used.

As a consequence of the studies made, it has been noticed that on the *Fagus silvatica L.* and *Abies alba Mill* has types of micromycetes have appeared, among which the *Alternaria geophila* Dasz. is new for the Romanian microflora, and for the other micromycetes described , the beech and the fir tree are new hosts for our country. More micromycetes have been found on the beech test pieces than on the fir ones.

The results obtained could be subsequently developed for the improvement of the biocide effects of the treatments with modified/unmodified lignin, thus opening the way, through the modification with copper ions, toward the introduction of biocide systems compatible with the environment.

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