National Research Council of Italy

CNR-IVALSA
TREES AND TIMBER INSTITUTE

Exploiting properties of innovative lignocellulosic nanocomposites

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UNIVERSITA DEGLI STUDI DI PARMA
DIPARTIMENTO DI CHIMICA

Summary

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In this presentation are exposed research activities came out from the collaboration between University of Parma and CNR IVALSA, Laboratory of Preservation and Biodegradation about nanocomposites for wood preservation:

1. *Polyamidoamines (PAA) functionalized with siloxane fragments*

2. *Modification of wood by sol-gel (via alkoxysilanes) in situ.*

3. *Functionalization of crystalline nanocellulose (CNC) with metals and siloxanes*

Facilities of wood preservation and biodegradation laboratory

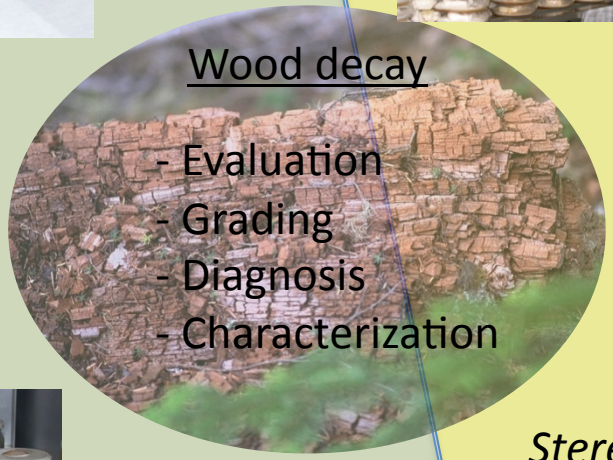
Laboratory cultures

Hylotrupes bajulus

Trichoferus holosericeus
(= Hesperophanes cinereus)

Lyctus brunneus

Certified fungal strains: brown rot and white rot funghi



Equipment

2 controlled T°/RH rooms

Vacuum-Pressure-Temp pilot plant

Stereomicroscope

X-ray apparatus

Vertical laminar flow cabinet

Sterilizing autoclave

1. *Polyamidoamines (PAA) functionalized with siloxane fragments as wood preservatives*

NANOSOLWOOD project. *2012 – 2013*

Partnership with Renner Italia S.p.A., University of Modena and Reggio Emilia, University of Parma and University of Piacenza.

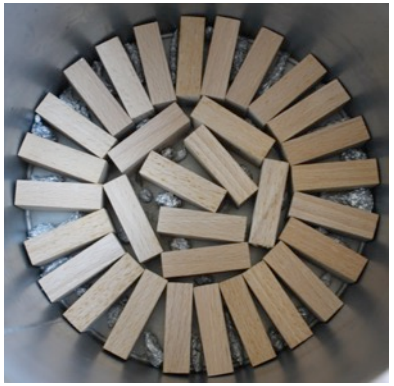
"Innovative treatments for consolidation and preservation of wood through hybrid organic-inorganic nanosols"

Specific skills within the project

Impregnation of solid wood samples (EN 113:2006)

Leaching (EN 84:1998)

Accelerated and standard fungal decay test (EN 113:2006)



POLYAMIDOAMINES (PAA)

1. Polyamidoamines (**PAA**) are obtained by the reaction between N,N-methylene-bis-acrylamide (**MBA**) and ethanolamine **(EtA**).

2. **PAA** can be functionalized with 3-aminopropyltriethoxysilane **(APTES**), through hydrolysis and condensation reaction (sol-gel process) *in situ* into wood block samples.

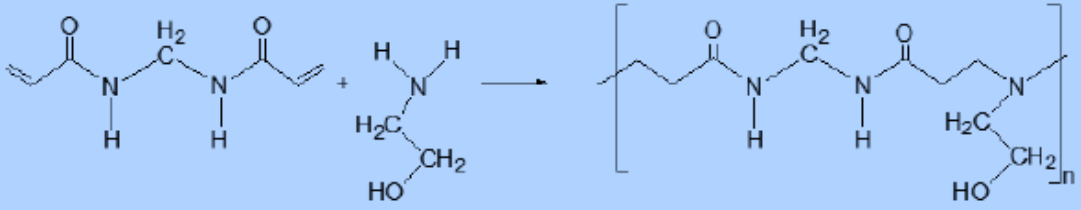


Fig. B.10 - Reaction scheme of polyaddition of N,N'-methylenebisacrylamide (MBA) and ethanolamine (EtA).

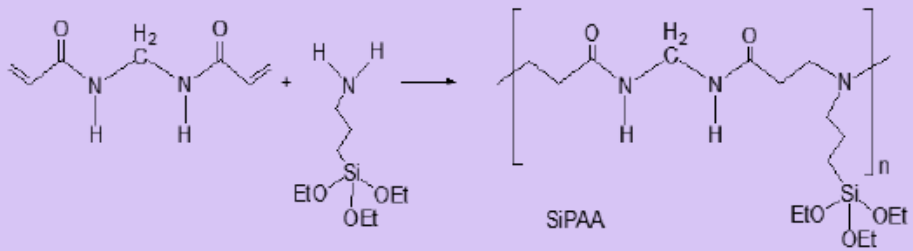


Fig. B.11 - Reaction scheme of polyaddition of N,N'-methylenebisacrylamide and 3-aminopropyltriethoxysilane.

PAAs for wood preservative purposes

Formulations:

Formulation A, MBA : EtA molar ratio 1:1

Formulation B, MBA : APTES molar ratio 1:1

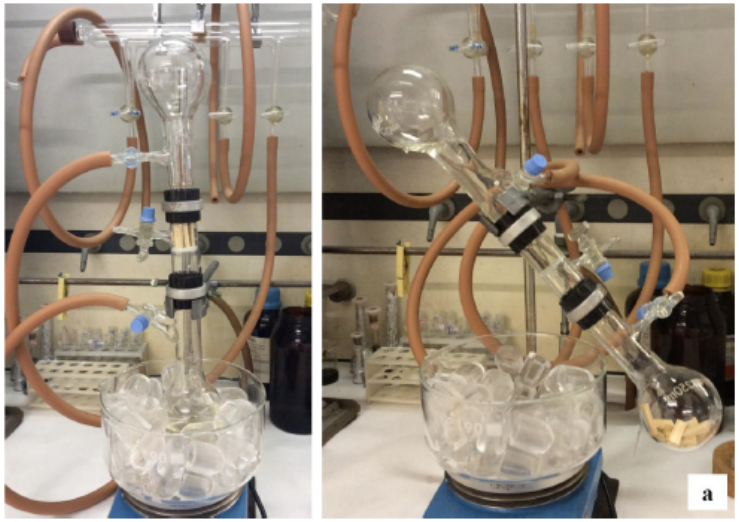
Formulation C, MBA : EtA : APTES, molar ratio 1: 0,5: 0,5

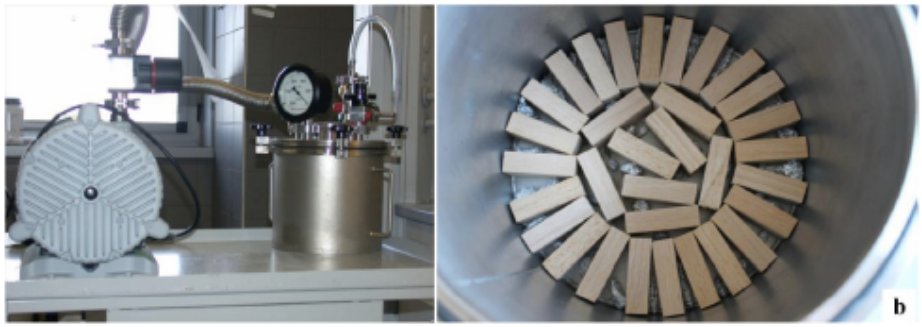
Solvent: water: ethanol 30:70

Preparation.

The reagents of respective formulations were dissolved in solvent then maintained under stirring until that the suspension became clear.

Impregnation



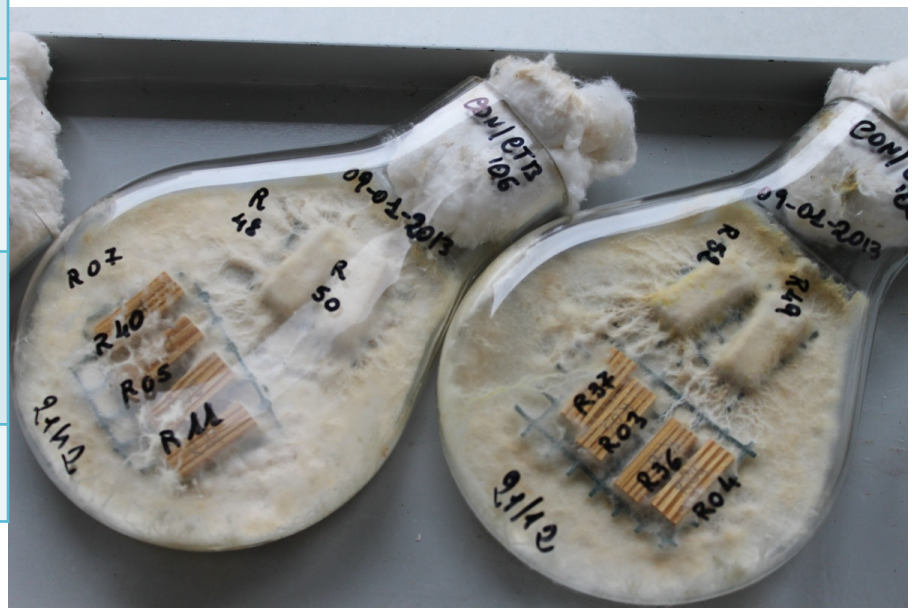


Result of fungal decay test

Dimension of wood mini-blocks:
30 x 10 x 5 mm^3

Formulation	Replicates (n)	Mass Loss (%) Mean (sd)	MC (%) Mean (sd)
A MBA:EtA 1:1 unleached	9	- 1,37 (2,4)	37,0 (5,16)
A MBA:EtA 1:1 leached	4	10,3 (15,7)	52,6 (8,2)
B MBA:APTES 1:1 unleached	9	0,8 (3,5)	33,1 (6,2)
B MBA:APTES 1:1 leached	4	-3,6 (0,4)	71,6 (7,5)
C MBA:EtA:APTES 1:0,5:0,5 leached	4	0,3 (0,6)	73,8 (24,0)
Virulence control	5	33,3 (1,9)	70,9 (3,0)

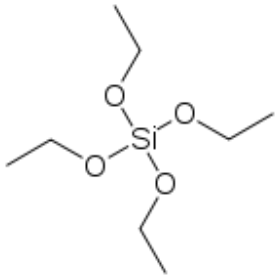
- Mini-block test: Kolle flask, in each one 4 treated and 2 reference controls.
- Duration of test : 8 weeks
- Fungus: *C. puteana*



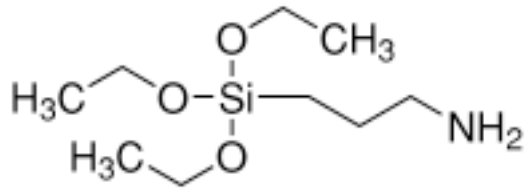
2. *Modification of wood by sol-gel (via alkoxysilanes) for preservation purposes*

Aim:

Evaluation of efficacy against fungal and insect decay of a wood modification based on hybrid inorganic-organic sol-gel systems that can incorporate copper or boric acid, in relation to a outdoor end use of wood.



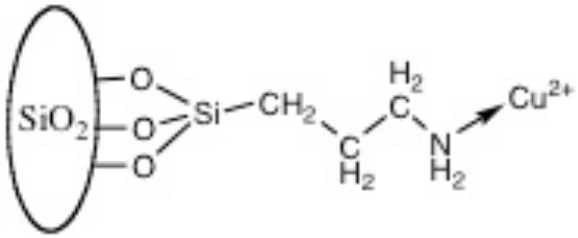
Tretraethoxysilane (TEOS)



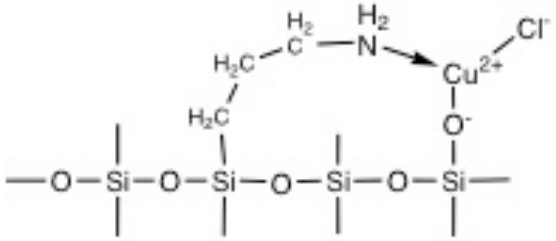
3-Aminopropyltriethoxysilane (APTES)

Interaction of active compounds (as biocides) with siloxane materials

- Copper

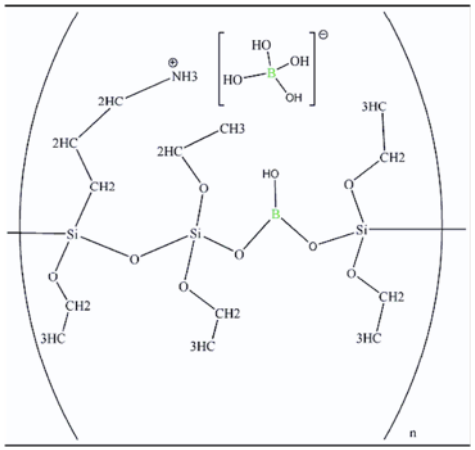


Copper cation anchored by coordinative interaction with amino groups



Grafting of copper to the functionalized silica gel into the wood

- Boron



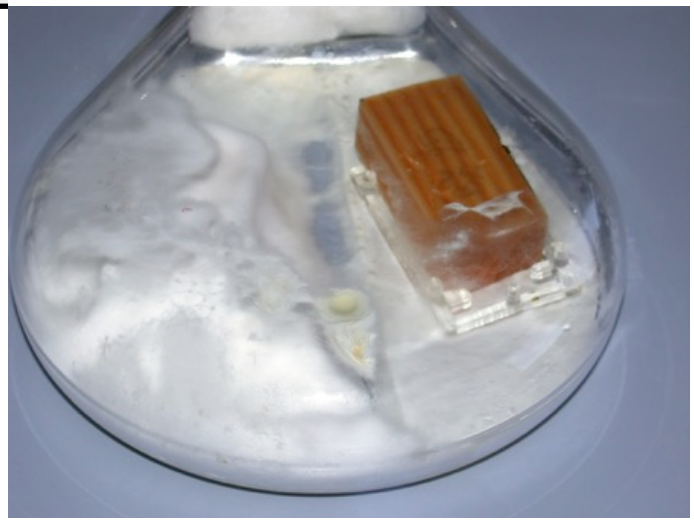
- Interaction with silanol group (borosilicate)
- Ionic interaction with the amino group

Efficacy against fungal decay

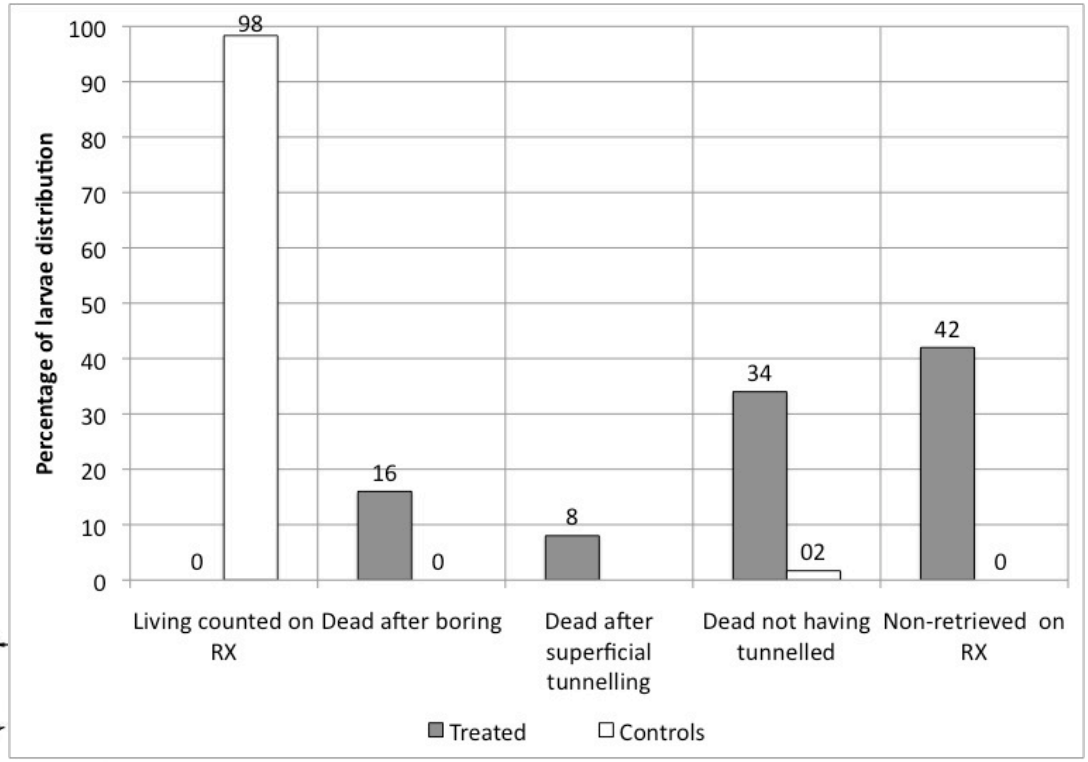
	Standard (16 weeks)	
	Mean mass loss % ***(sd)***	**N**
TEOS APTES AND BORON		
Coniophora puteana	-1.7 (0.5)	8
Poria placenta	-3.5 (0.9)	8
Trametes versicolor	0.4 (0.3)	8
TEOS APTES AND COPPER		
Coniophora puteana	3.4 (3.7)	8
Poria placenta	**42.0 (9.6)**	8
Trametes versicolor	0.0 (0.1)	8

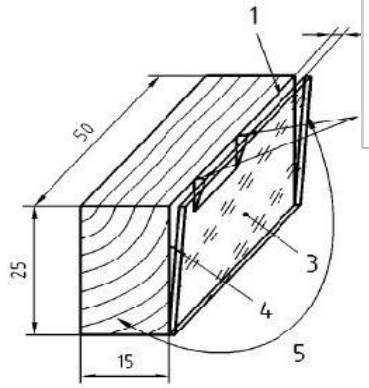
-Negative values depend on the correction factors utilized

- TA/Boron is effective against all fungi
- *Poria placenta* is the critical fungus against treatment with copper
- Standard tests give more severe and homogeneous results than accelerated tests

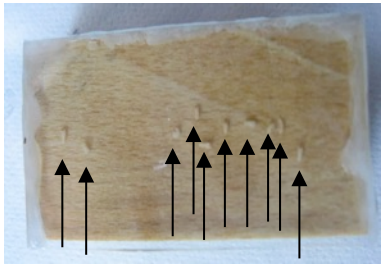


Efficacy against insects: *Hylotrupes bajulus*





Size of specimens for insect attack test (European Standard EN46-1)



Specimen with exposed larvae

Functionalization of crystalline nanocellulose for wood preservative purposes

1. **PDMS**

- 150 ml of CNC (1.2%) with 150 ml of PDMS II (1.5%) (with the ratio of CNC : PDMS, 1:1) pH:8.87

2. **$Cu(OH)_2$**

- 300 ml of CNC with 0.03 g of $Cu(OH)_2$

10 min under sonication

3. **ZnO**

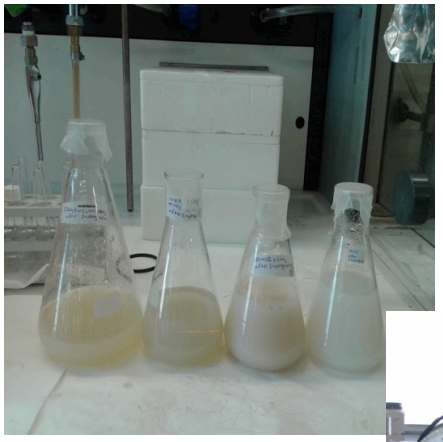
- 200 ml of CNC (1.2%) with 0.04 g of NaHCO3 with 57 ml of ZnO (3.5:1) pH:8.13

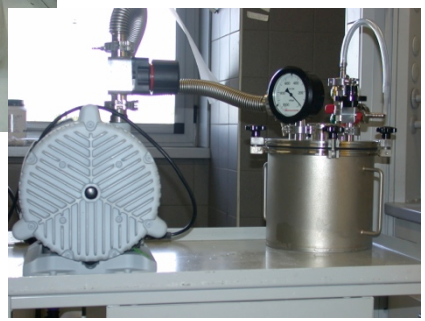
3.*Functionalization of crystalline nanocellulose for wood preservative purposes*

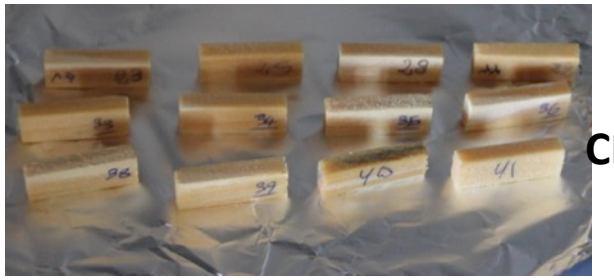
4. Ag nanoparticles

- 60 ml CNC (1.2%) with 30 ml $AgNO_3$ (1 mM) and 8.9 ml $NaBH_4$ (2mM) with stirring in warm condition and covered protected from UV light with Al paper

Crystalline nanocellulose functionalized for preservation of wood (poplar)

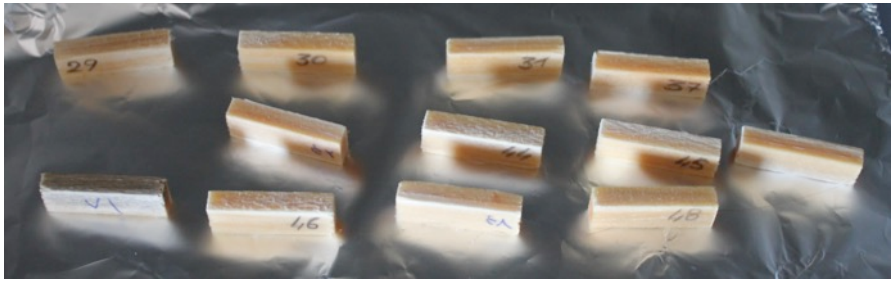






CNC PDMS

CNC Cu



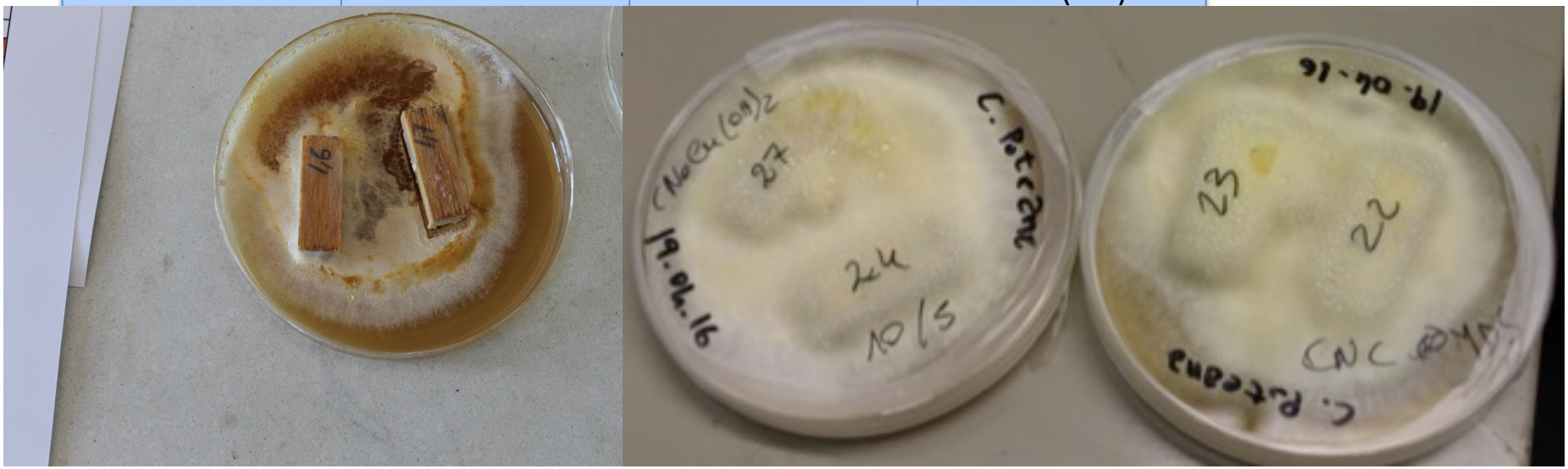
CNC Ag

CNC

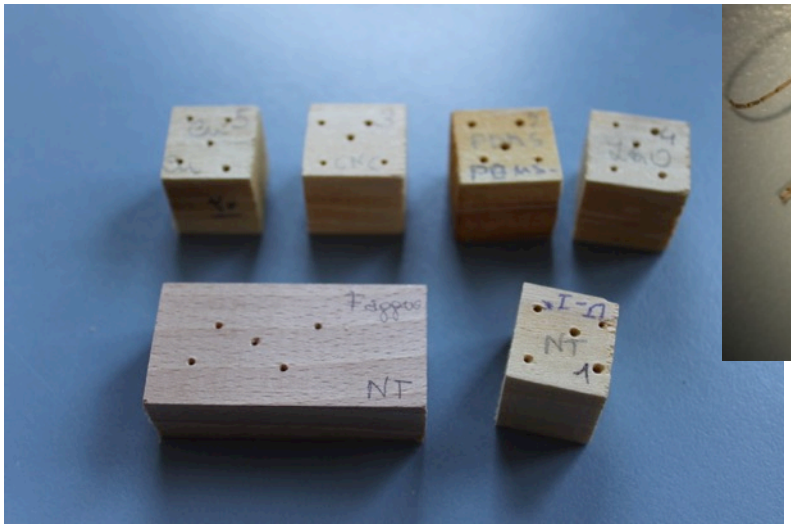
Fungal decay test

Treatment (N)	Fungus	MC (%)	ML (%) (sd)
CNC	*C. puteana*	198.5	34,5 (17)
	T. versicolor	189.9	27,6 (7.3)
CNC/PDMS	*C. puteana*	136.8	19.2 (18.1)
	T. versicolor	204.9	31.8 (10.1)
CNC/CU(OH)2	*T. versicolor*	174.5	23.6 (7.2)
CNC/Ag	*C. puteana*	96.8	52.6 (0.3)
	T. versicolor	220.9	37.2(6.4)
Untreated poplar wood	*C. puteana*	143.6	1.21(1.2)
	T. versicolor	183.5	37.2(6.4)

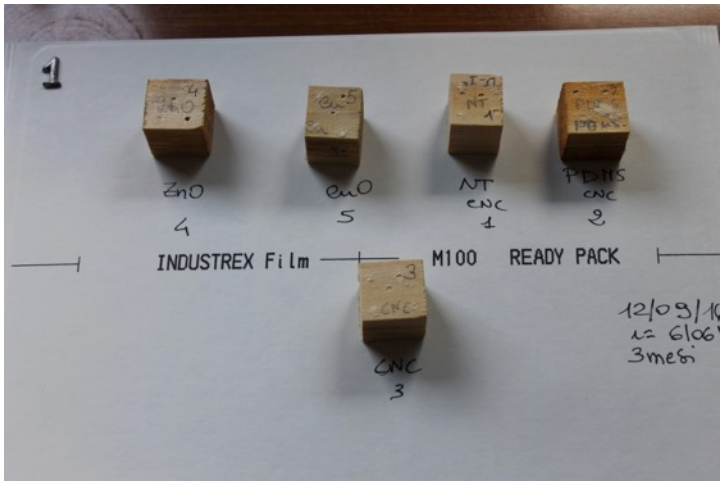
CNC without or with different functionalizations is not efficacy against fungal decay on wood .

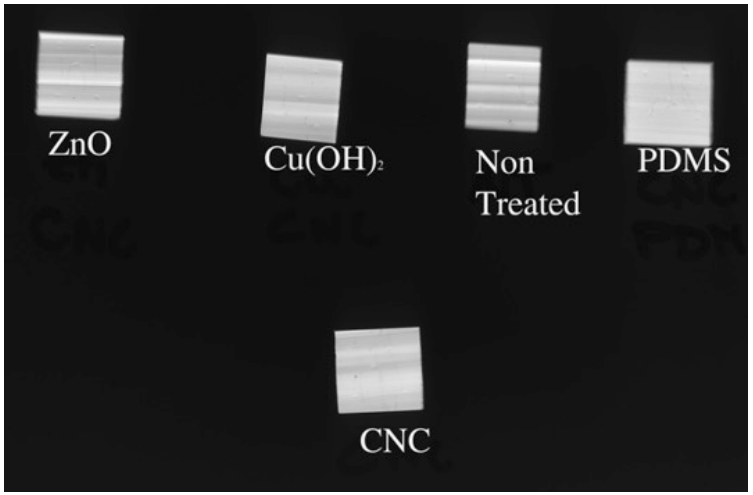


Crystalline nanocellulose for preservation of wood (poplar): mini-block test against insect *T. holosericeus*

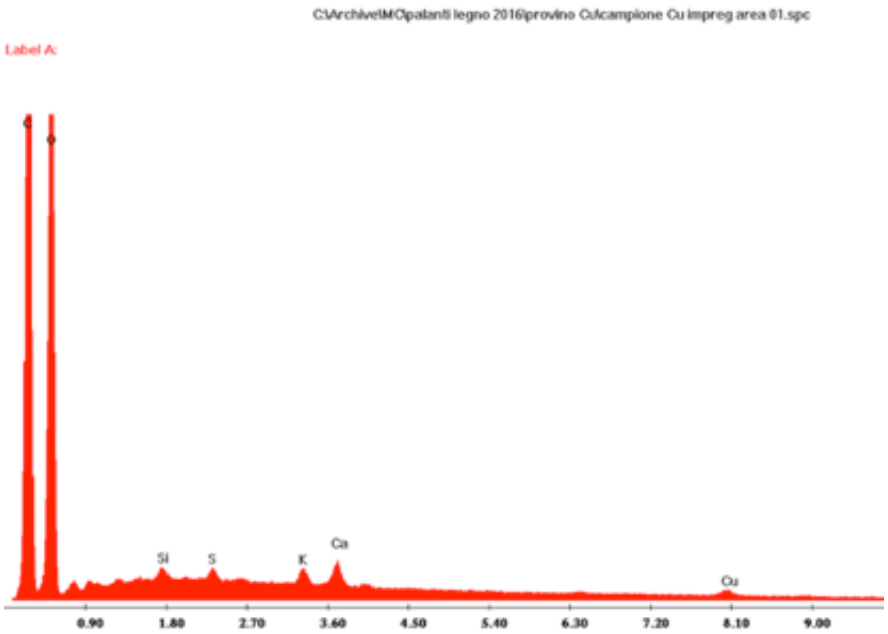


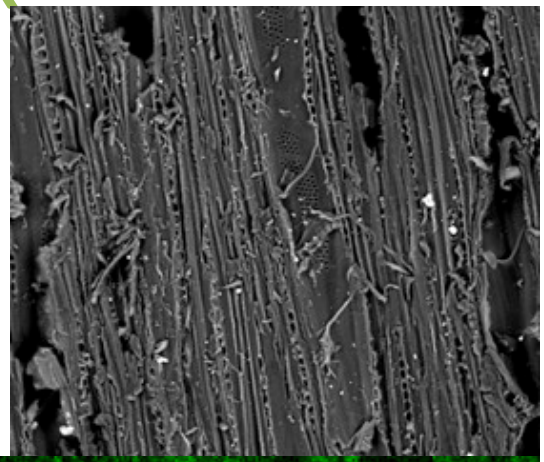
Treatment	Tunnel	Survived larvae
CNC	4	1
CNC/PDMS	6	0
CNC/CU(OH)2	4	1
Untreated poplar	4	0

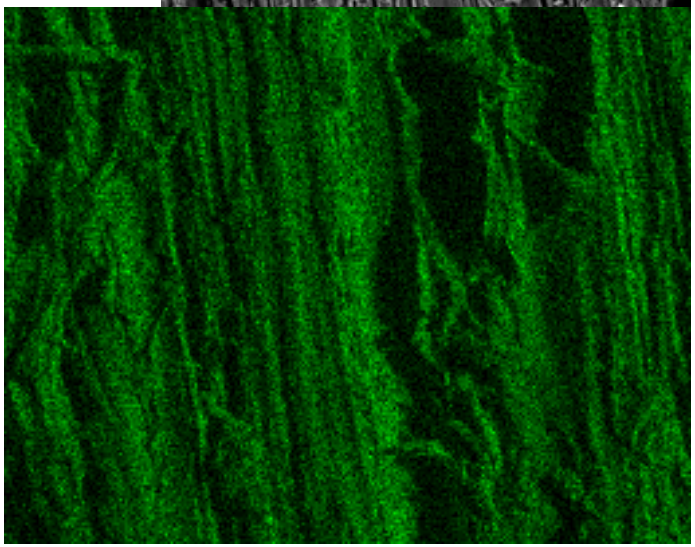




ESEM on CNC functionalized Cu(OH)$_2$ impregnated on poplar wood block



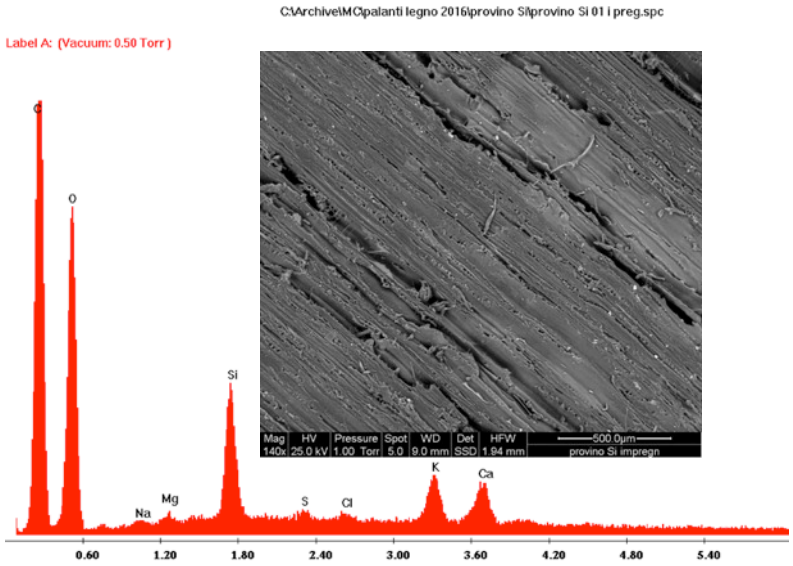




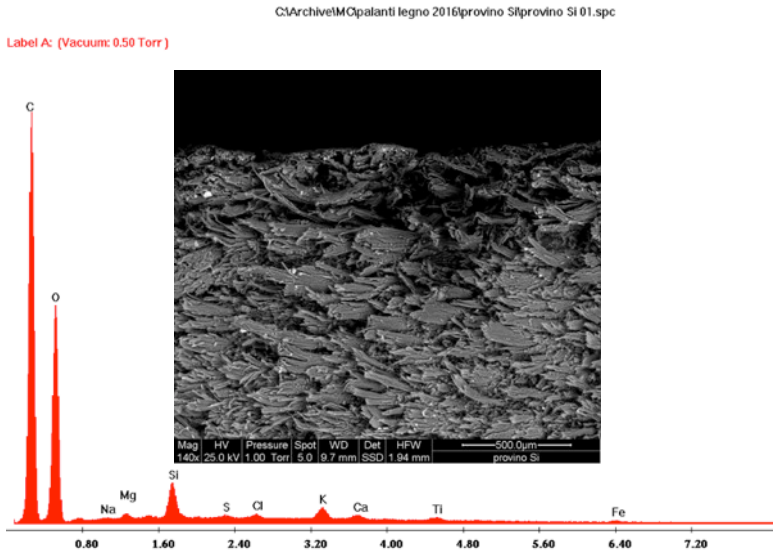
External longitudinal face of wood block

Maria Cristina Salvatici *CEME-Centro di Microscopie Elettroniche, Area della Ricerca Fi*

CNC functionalized with PDMS impregnated on poplar wood mini block

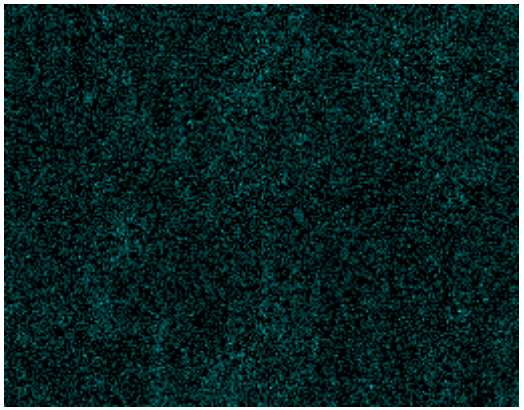


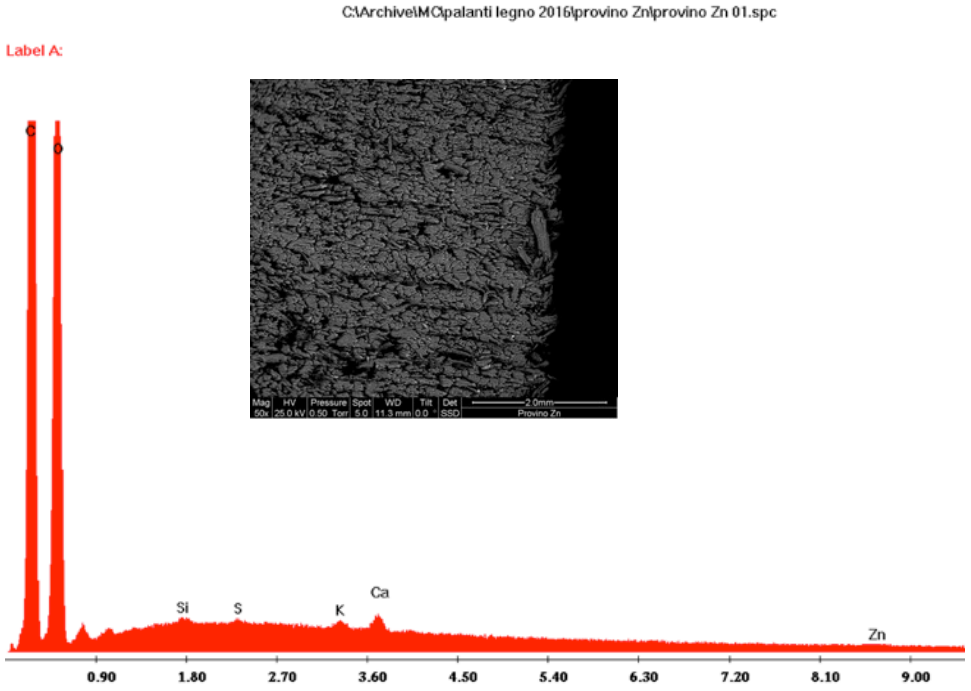
Longitudinal external face



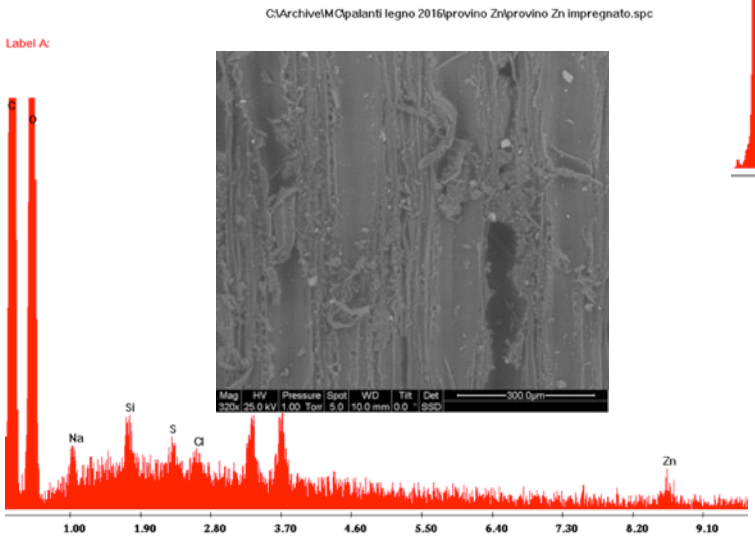
Transversal face
few micron in depth

CNC functionalized with ZnO impregnated on poplar wood mini block





Transversal face
few micron in depth



Longitudinal external face

CNC for consolidation of decayed wood

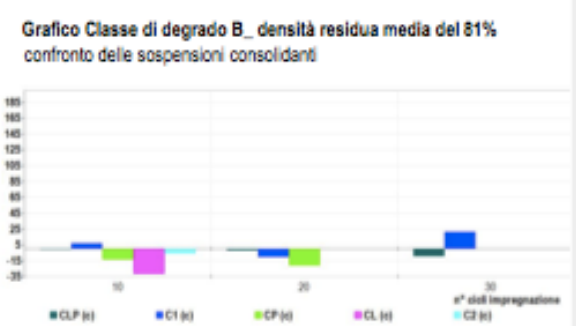


Tabella classe di degrado A

consolidante	n° cicli	Incremento E %	consolidante	n° cicli	Incremento E %
CLP	10	51%	CP	10	50%
CLP	20	77%	CP	20	43%
CLP	30	141%	CL	10	93%
C1	10	160%			
C1	20	198%			
C1	30	160%			

Tabella classe di degrado B

consolidante	n° cicli	Incremento E %	consolidante	n° cicli	Incremento E %
CLP	10	1%	CP	10	7%
CLP	20	13%	CP	20	31%
CLP	30	32%	CL	10	32%
C1	10	50%	C2	10	-5%
C1	20	58%			
C1	30	45%			

Tabella classe di degrado C

consolidante	n° cicli	Incremento E %	consolidante	n° cicli	Incremento E %
CLP	10	-1%	CP	10	-14%
CLP	20	-2%	CP	20	-21%
CLP	30	-10%	CL	10	-31%
C1	10	7%	C2	10	-6%
C1	20	-10%			
C1	30	22%			

Composizione delle sospensioni consolidanti :

C1 : nanocellulosaC2 : nanocellulosa

CP : nanocellulosa e Pdms

CL : nanocellulosa e nanolignina

CLP : nanocelllulosa , nanolignina e Pdms

Work performed by Roberta Basile (Master student of University of Palermo) in Laboratory of wood chemistry of CNR IVALSA under supervision of Benedetto Pizzo (*for more information see the poster session*)

Conclusions

During the last 6 years University of Parma and CNR IVALSA collaborated through different projects for realizing innovative products for wood preservation and consolidation.
Results of this collaboration are international patent on PAAs formulations with company RENNER spa and a lot of international peer review papers.

Unfortunately, the functionalized crystalline nanocellulose did not show good efficacy against fungal and insect decay, probably due to difficult to obtain concentrate formulations starting from crystal nanocellulose for impregnating the wood blocks.
Further investigations with these compounds, CNC/Ag, CNC/ZnO, CNC/$Cu(OH)_2$, will carry out in the next future.
Better results were obtained in the consolidation of decayed wood especially with CNC alone (master thesis of Roberta Basile).