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GROWTH INHIBITION OF MOULDS ON WOOD SURFACES IN PRESENCE OF NANO-ZINC OXIDE AND ITS COMBINATIONS WITH POLYACRYLATE AND ESSENTIAL OILS

Ladislav Reinprecht, Zuzana Vidholdová
Technical University of Zvolen, Faculty of Wood Sciences and Technology
Zvolen, Slovak Republic

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ABSTRACT

The paper deals about an anti-mould efficiency of nano-zinc oxide applied into wood alone (0.1%, 0.33%, 1% and 3% ZnO) or in combination with polyacrylate (5% Paraloid B-72) and essential oils (1% and 3% clove, oregano or thyme oil). Treatment of lime tree and maple samples 50×10×5 mm (L×R×T) with these chemicals was performed by one-step or two-step dipping at 20 °C/1 h. The anti-mould efficiency of used chemicals was determined by the standard STN 49 0604 – evaluating effect of chemicals against growth of four moulds (mixture of *Alternaria alternata*, *Aspergillus niger*, *Penicillium brevicompactum* and *Chaetomium globosum*) in the 7th 14th, 21st and 28th day. The anti-mould efficiency of ZnO nanoparticles was relatively poor, however, it was evidently improved in presence of clove and oregano oils, mainly in the first 7 days of the mould test.

KEYWORDS: Nano-zinc oxide, polyacrylate, essential oils, moulding.

INTRODUCTION

Nanotechnologies are new technologies which are also used for wood treatment with the aim to increase its: (1) photostability (e.g. by nano-titanium dioxide TiO_2 and nano-zinc oxide ZnO), (2) resistance to fire (e.g. by nano-silicon dioxide SiO_2 and TiO_2), and (3) resistance to biological pests (e.g. by nanoparticles of silver Ag and its oxide Ag_2O, nano-zinc oxide ZnO, nano-zinc borate $Zn(BO_2)_2$, nano-copper Cu and its oxide CuO, or nano-titanium dioxide TiO_2). The application of different nanoparticles for wood treatment is associated with their potential impacts on human health and the environment (Gupta et al. 2015, Montanari and Gatti 2016).

Biological efficiency of nanoparticles was mentioned in more works, e.g. of Clausen et al.

2010, Bak et al. 2012, Akhtari and Arefkhani 2013, Lykidis et al. 2013, Stanković et al. 2013, Mantanis et al. 2014, Marzbani and Mohammadnia-Afrouzi 2014, or Reinprecht et al. 2015, 2016. Wood protection against moulds, decaying fungi and insects can be performed with pure nanoparticles, as well as with their combination with other substances having biocide, hydrophobic or other protection effects. In this situation the mutual interaction among all substances used for wood treatment is a very important. To the potential substances for combinative using with nanoparticles belong, for example: (1) polyacrylates traditionally used for hydrophobic surface treatment of wooden products and also for restoration of wooden artefacts (e.g. Unger et al. 2001), and (2) some essential oils suitable for increasing of wood bio-resistance (e.g. Neuschlová et al. 2005, Chittenden and Singh 2011, Pánek et al. 2014).

Acrylates transported into wood in a form of polymer solutions are distributed only in lumens of wood cells and their anti-fungal effect is minimal (Reinprecht et al. 2001). Therefore for conservation of damaged historical artefacts permanently exposed in a humid environment (suitable for moulds and decaying fungi) is recommended combination of acrylates with stable bioactive compounds, e.g. hetorocycles (Tiralová and Reinprecht 2004) or nano-metals (Trăistaru et al. 2012).

Most of essential oils are health-friendly substances (Chittenden and Singh 2011). On the other hand, their sufficient anti-mould and anti-decay efficiency is a relatively small and for wood protection they have to be used in higher concentrations. Their disadvantage is also a higher volatility, so they cannot be applied for a long-term protection of wood at higher temperatures (Batish et al. 2008).

The aim of this work was to search effects of one polyacrylate and three essential oils on the anti-mould efficiency of nano-zinc oxide used for wood protection.

MATERIAL AND METHODS

Wood

For the experiment were used samples 50×10×5 mm (L×R×T) of lime tree wood (*Tilia cordata* Mill.; ρ_0 = 483–497–516 kg·m^{-3}) and maple wood (*Acer pseudoplatanus* L.; ρ_0 = 518–588–653 kg.m^{-3}), in which were not biological damages, knots or other growth inhomogeneity. Samples were sterilized at a temperature of 103 ± 2°C/4 h, and also (after treatment with chemicals) with the 30 W germicidal lamp (Chirana, Slovakia) from a distance of 1 m at a temperature of 22 ± 2°C/0.5 h.

Nano-zinc oxide

Nano-zinc oxide (ZnO), obtained from Sigma-Aldrich: Merck KGaA, Germany, had particles of 50 nm.

Polyacrylate

Paraloid B-72, obtained from The Dow Chemical Company, USA, is polyacrylate copolymer of ethylmethacrylate and methylacrylate. It has an excellent elasticity and a high weathering stability, and therefore it is often used for conservation of wooden artefacts (Unger et al. 2001).

Essential oils

Three pure essential oils of pharmacopoeia quality, obtained from Nobilis Tilia s.r.o., Czech Republic (Tab. 1), were used in the experiment.

Tab. 1: Essential oils for treatment of wood samples.

Common name	Scientific name	Major effective components
Clove	*Syzygium aromaticum*	Eugenol (82%), Caryophyllene (16.5%)
Oregano	*Origanum vulgare*	Carvacrol (71.8%), Thymol (5%), Gamma-Terpinene (4.5%)
Thyme	*Thymus vulgaris*	Thymol (41.3%), p-Cymol (22.6%), Gamma-Terpinene (7.7%), Carvacrol (2.9%)

Treatment of wood

Samples of lime tree and maple woods were treated with solutions or micro dispersions of selected chemicals (sets I. – VI.) using dipping technology at atmospheric pressure (20°C/1 h of each step):

I. ZnO (0.1, 0.33, 1 or 3 % ethanol micro dispersion),
II. polyacrylate (5 % toluene solution of Paraloid B-72),
III. in first step polyacrylate (II.), and in second step ZnO (I.) after evaporation of the toluene solvent,
IV. in first step ZnO (I.), and in second step polyacrylate (II.) after evaporation of the ethanol solvent,
V. essential oil (1 or 3% ethanol solution of clove, oregano or thyme oil),
VI. mixture of ZnO (I.) and essential oil (V.).

Retention of applied solutions or micro dispersions into samples ranged: (1) for lime tree wood /I., II., III., IV./ from 103 to 128 $kg \cdot m^{-3}$, and (2) for maple wood /I., V., VI./ from 137 to 187 $kg \cdot m^{-3}$.

Mould test

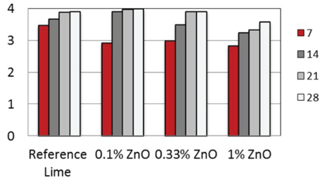
Mixture of four moulds – microscopic fungi: *Alternaria alternata*, *Aspergillus niger*, *Penicillium brevicompactum* and *Chaetomium globosum* – was used for attacking of the top surfaces of wood samples embedded in Petri dishes on Czapek-Dox agar. Mould attacks lasted 28 days at 28 ± 2°C, in accordance with the standard STN 49 0604 (1980). The growth activity of moulds (GAM) on the top surfaces of samples was evaluated in the 7^{th}, 14^{th}, 21^{st} and 28^{th} day by these criteria: 0 = no growth on surfaces, 1 = growth ≤ 10%, 2 = growth ≤ 25%; 3 = growth ≤ 50%; 4 = growth ≤ 50%.

RESULTS AND DISCUSSION

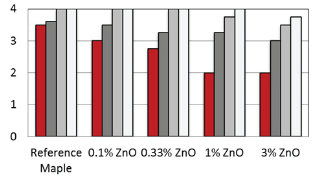
Particles of nano-zinc oxide (ZnO) only party inhibited the growth activity of moulds (GAM) on wood samples (Figs. 1a and 1b).

Practically none effect against moulds had polyacrylate Paraloid B-72 (Fig. 1c). In its presence a partial inhibition effect of ZnO against moulds changed only minimally (Figs. 1a and 1c). Paraloid B-72 proves to be ineffective also against the brown-rot fungus *Coniophora puteana* and the white-rot fungus *Trametes versicolor* (Andres and Mańkowski 2011, Reinprecht et al. 2015).

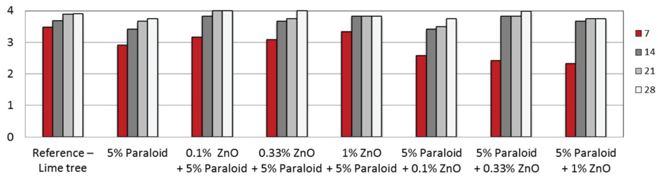
a) Nano-ZnO in lime tree wood (set I.)



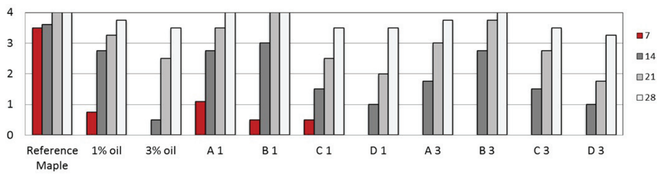
b) Nano-ZnO in maple wood (set I.)



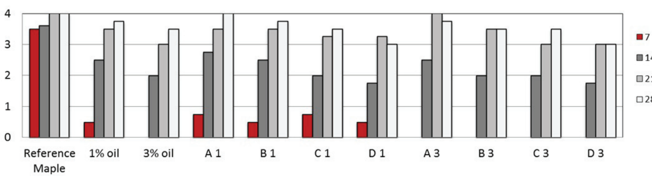
c) Nano-ZnO and polyacrylate Paraloid B-72 in lime tree wood (sets II., III. and IV.)



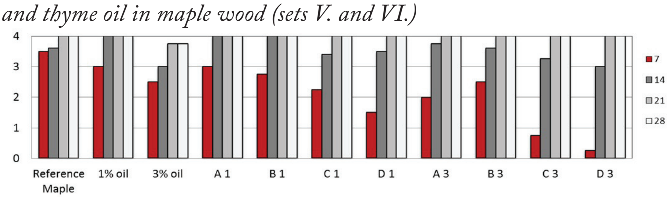
d) Nano-ZnO and clove oil in maple wood (sets V. and VI.)



e) Nano-ZnO and oregano oil in maple wood (sets V. and VI.)



f) Nano-ZnO and thyme oil in maple wood (sets V. and VI.)



Notes to the Figs. 1d, 1e and 1f:

1 % oil = 1 % clove, oregano, or thyme essential oil

3 % oil = 3 % clove, oregano, or thyme essential oil

A1 = 0.1 % ZnO + 1 % essential oil,	A3 = 0.1 % ZnO + 3 % essential oil,
B1 = 0.33 % ZnO + 1 % essential oil,	B3 = 0.33 % ZnO + 3 % essential oil,
C1 = 1 % ZnO + 1 % essential oil,	C3 = 1 % ZnO + 3 % essential oil,
D1 = 3 % ZnO + 1 % essential oil,	D3 = 3 % ZnO + 3 % essential oil.

Fig. 1: The GAM on the top surfaces of wood samples from 7th to 28th day.

On the other hand, clove and oregano oils used alone, or in combination with ZnO, evidently improved resistance of wood against moulds, mainly in the first days of the test (Figs. 1d and 1e, Tab. 2). A good anti-mould efficiency of oregano oil presented also Paster et al. (1995). From three used essential oils, only thyme oil had an evidently smaller anti-mould efficiency (Fig. 1f, Tab. 2). A minimal efficiency of thyme oil against the mould *Aspergillus niger* – often acting on foods – documented also Kumar et al. (2007).

Tab. 2: Correlations between: (1) the concentration of nano-zinc oxide (c_{ZnO} from 0 to 3 %) in mixtures with essential oils, and (2) the growth activity of moulds (GAM from 0 to 4) on the surfaces of maple wood in the 7th and 28th day of mould test.

7th day		
1% Essential oil		
Clove	$GAM = 0.83 - 0.29.c_{ZnO}$	$R^2 = 0.75$
Oregano	$GAM = 0.63 - 0.20.c_{ZnO}$	$R^2 = 0.85$
Thyme	$GAM = 2.95 - 0.50.c_{ZnO}$	$R^2 = 0.97$
3% Essential oil		
Clove	GAM = 0	
Oregano	GAM = 0	
Thyme	$GAM = 2.26 - 0.74.c_{ZnO}$	$R^2 = 0.78$
28th day		
1% Essential oil		
Clove	$GAM = 3.88 - 0.14.c_{ZnO}$	$R^2 = 0.51$
Oregano	$GAM = 3.86 - 0.29.c_{ZnO}$	$R^2 = 0.92$
Thyme	GAM = 4	
3% Essential oil		
Clove	$GAM = 3.74 - 0.16.c_{ZnO}$	$R^2 = 0.50$
Oregano	$GAM = 3.70 - 0.23.c_{ZnO}$	$R^2 = 0.85$
Thyme	$GAM = 3.92 - 0.02.c_{ZnO}$	$R^2 = 0.16$

Coming out from more scientific papers, which are mentioned for example in work of Pánek et al. 2014, the best anti-fungal efficiency have those essential oils which contain: (1) the phenolic compounds, such as eugenol (e.g. clove oil), carvacrol (e.g. oregano and savory oils) and also thymol (e.g. thyme oil), and (2) the oxygenated compounds, such as elemol and cinamaldehyde (e.g. cinnamon oil). However, it should be emphasized, that their anti-fungal efficiency is not seldom a specific, depending on the species of fungal organism, environmental conditions, etc.

CONCLUSIONS

- Nano-zinc oxide nanoparticles only a partly inhibited the growth activity of moulds (GAM) on wood surfaces.
- The anti-mould efficiency of ZnO nanoparticles increased in the presence of clove and oregano oils, however, mainly only in the first days of the mould test.
- On the other hand, the presence of polyacrylate or thyme oil in the treating substances for wood protection (with or without ZnO) was ineffective or only minimally effective against activity of moulds.

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Ladislav Reinprecht*, Zuzana Vidholdová
Technical University of Zvolen
Faculty of Wood Sciences and Technology
T. G. Masaryka 24
960 53 Zvolen
Slovak Republic
Phone: 00421-45-5206383
*Corresponding author: reinprecht@tuzvo.sk