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THE EFFECT OF BIOCIDES IN MF AND MUF RESIN ON SURFACE QUALITY OF LAMINATED WOOD-BASED COMPOSITE MATERIALS

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Abstract

This study is aimed to determine whether the addition of ZnO nanoparticles to thermosetting resin have effect on laminated surface resistance to cold liquids (and aggressive chemicals), dry heat and resistance to abrasion.
The addition of ZnO nanoparticles into melamine formaldehyde resin did not change surface resistance to cold liquids. Laminated surfaces resistance to cold liquids remains basically on the initial level. As well as, resistance of laminate surface to dry heat (180°C) also remains unchanged. Values of abrasion resistance decreased after addition of ZnO nanoparticles. Surface coated by paper impregnated with resin modified with 3 % of ZnO nanoparticles, which was the highest amount of ZnO nanoparticles in melamine resin, had abrasion resistance decreased about 25 % compared to initial values.

Key words: *ZnO nanoparticles, surface quality, abrasion*

INTRODUCTION

Currently, many studies discuss about improving surface functionality using nanotechnology. Nanotechnology is a group of disciplines, which deals with creation and use of technologies on atomic level and therefore in nano scale. *FEYNMAN (1960)* in his study *"There´s Plenty Room at The Bottom"* was first who dealt with matter on its nano scale and described a processes by which we could manipulate with atoms and molecules. Improvement of surface functionality can be achieved by nanotechnology in many ways and so-called smart surface treatments can be created. These types of surface treatments may be achieved by adding of small amount of additives and they can improve their functionality or can create a new functionality caused by change of polymer constitution. Examples of smart surface treatments are self-cleaning, hydrophobic, bioactive and antibacterial surface treatments (TESAŘOVÁ *et al*. 2014).

By the current threat of spreading infectious diseases, antimicrobial surface treatment development is an issue. Spreading of diseases happens mostly by contaminated air, by contact with infected people or animals and often by contact with contaminated objects (KANDELBAUER, WIDSTEN 2008). Antimicrobial surface treatment should be able to prevent microbes to grow, thus to prevent their spreading. One of the most frequently mentioned possible additive for providing antimicrobial properties are zinc oxide (ZnO) nanoparticles.

ZnO nanoparticles have a potential to be effective antimicrobial additive (REINPRECHT *et al*. 2015; REINPRECHT *et al*. 2016). Many research studied antimicrobial effect of this

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biocide. ZnO exhibits activity against Gram-positive and Gram-negative bacteria (JIANG *et al*. 2009; JIANG *et al*. 2014; MANZOOR *et al*. 2016; MARTINS *et al*. 2013;WAHAB *et al*. 2010; SIRELKHATIM *et al*. 2015; VANI *et al*. 2011).Effectiveness of ZnO nanoparticles grows with the decreasing particle size (JIANG *et al*. 2009; PALANIKUMAR *et al*. 2012).

All above mentioned papers studied only antimicrobial effectiveness of ZnO nanoparticles in practice. However, none of them studied the effect of this biocide to chemical or mechanical resistance of surface when used.

Papers impregnated and coated with thermosetting resins are commonly used as a decorative and protective laminate for wood composites such as particleboard and medium density fibreboard. Manufacture of paper laminates consists of décor paper impregnation with a mixture of melamine formaldehyde (MF) and urea formaldehyde (UF) resins, afterwards, the resin is cured, impregnated paper is then covered by MF resin and pressed onto wood-based composite (ROBERTS, EVANS 2005). This type of surface treatment is characterized by good water resistance, good high temperature resistance, chemical resistance and scratch and abrasion resistance and for this reason it is often used as furniture surface layer. The goal of our study is to find out whether ZnO nanoparticles as a potential antimicrobial agent have effect on surface chemical or mechanical properties of MF laminates used for wood-based composite materials

MATERIALS AND METHODS

Materials

Commercially produced zinc oxide nanoparticles (<100 nm particle size (DLS); <35 nm average particle size (APS); 50 wt. % in water), which was not surface modified were purchased from Sigma-Aldrich Co. Ltd. Coating décor paper (UNI white 0500, areal weight 90 g.m^{-2}) and MF resin used for impregnation in this study were provided by Bučina DDD, Co. Ltd.

Methods

In the first step, ZnO nanoparticles were added into resin to reach certain concentration. Concentrations of this biocide were 0.1; 0.3; 0.6; 1; 2; 3 wt. %. Then décor paper was impregnated with modified MF resin. Décor paper impregnation was made on mechanical laboratory applier. Average amount of thermosetting resin was 120 g.m^{-2}. Subsequently, impregnated décor paper was cured in a laboratory kiln for 3 minutes at the temperature of 160±3 °C. After the curing process, cured impregnated paper was pressed onto particle board with pressing parameters T=175 °C and p=0,3MPa for 4 min. One week before testing, specimens were conditioned at temperature 23±2 °C and relative humidity 50±5 %. After conditioning, specimen surfaces were tested for resistance to cold liquids and aggressive chemicals, dry heat and abrasion in accordance with STN EN 12720+A1 (*Furniture – Assessment of surface resistance to cold liquids*), STN EN 12722+A1 (*Furniture – Assessment of surface resistance to dry* heat), STN EN 15185 (*Furniture – Assessment of the surface resistance to abrasion*) respectively.

RESULTS

The mean values of resistance to cold liquids and dry heat are shown in Table 1. Mean values of abrasion resistance and proportional reduction of abrasion resistance are shown in

Table 2. Fig. 1 shows proportional values of abrasion resistance and a linear trend in measured data.

Table 1 Resistance to cold liquids and dry heat of surface coated by MF impregnated paper

		ZnO addition[%]					
	Optimal values for untreated resin*	**0.1**	**0.3**	**0.6**	**1**	**2**	**3**
Used liquids	**Resistance degrees (mean values)**						
Ketones	2-3	3	3	3	3	3	3
Acetone	3-5	5	5	5	5	5	5
Alcohol	3-5	5	5	5	4	4	5
Oil	3-5	5	5	5	5	5	5
Water	3-5	5	4	4	4	4	4
Coffee	3-5	4	4	4	3	4	4
Ink	3-5	5	5	5	5	4	4
Tea	3-5	3	4	3	3	4	4
Acetic acid	3-5	5	5	5	5	5	5
Dry heat [180°C]	3-5	3	4	3	3	3	3

5 – without visible changes
4 – slight gloss changes visible only when light source is mirrored and is close to tested surface
3 – slight differences visible from several directions
2 – noticeable differences, without structural (textural) changes
1 – noticeable differences, structure (texture) is changed or surface treatment is completely or partially removed
**optimal values according to producer*

Table 2 Abrasion resistance of surface coated by MF impregnated paper

ZnO addition [%]	Mean number of cycles	SD*	Abrasion resistance values [%]	Δ[%]
0	**240**	17.68	100	-
0.1	**240**	12.94	100	0.00
0.3	**230**	17.68	95.83	-4.17
0.6	**220**	12.94	91.67	-4.17
1	**200**	10.84	83.33	-8.33
2	**190**	12.82	79.17	-4.17
3	**180**	7.07	75.00	-4.17
Overall abrasion resistance reduction				**-25**

** standard deviation from 8 measured samples*

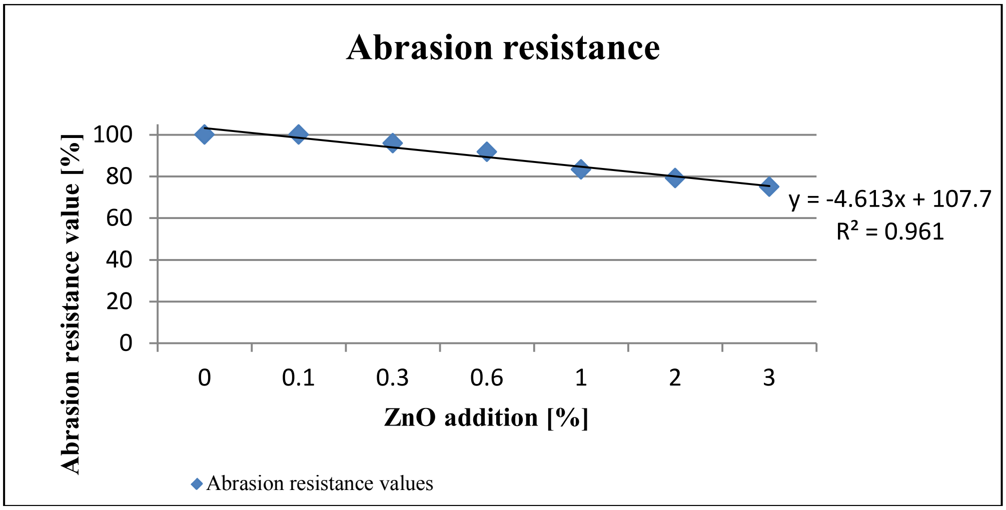

Fig.1 Effect of ZnO on abrasion resistance of impregnated décor paper

DISCUSSION

Resistance of surface coated with MF impregnated décor paper depends on various factors. *NEMLI, USTA (2004)* noticed that abrasion resistance of MF impregnated decor paper depends on amount of saturation (impregnation) the MF resin in the paper. They also noticed better resistance properties of laminates, if paper were produced with MF resin alone (without mixture with UF resin).

According to our study, ZnO nanoparticles did not have effect on final resistance of MF impregnated paper to cold liquids or dry heat. We suppose that it can be explained with no chemical changes in MF resin chemical structure after curing.

In contrast with resistance to cold liquids and dry heat, resistance to abrasion decreased after the addition of ZnO nanoparticles. After the addition of 0.1 wt. % ZnO nanoparticles to MF resin, there was no change in abrasion resistance of laminate. Abrasion resistance decreased to 95.83 % of the initial value after the addition of 0.3 wt. % Zno nanoparticles, but the largest reduction of abrasion resistance occurred with 3 wt. % addition of ZnO nanoparticles. Generally, abrasion resistance decreased about 25 % compared to the initial value. This fact can be explained by presence of ZnO nanoparticles, which were not in chemical bonds with MF resin and therefore, acted as an additional abrasive.

CONCLUSION

People are endangered by various diseases in present days. Diseases spreading mostly happen by contaminated air, by contact with infected people or animals and many times by contact with contaminated objects. Furniture also belongs to the objects, which can be potential disease carrier.

Coating by thermosetting resin impregnated décor paper is frequently used as a furniture surface treatment. This type of surface treatment should meet certain qualitative properties such as good abrasion resistance and resistance to cold liquids and dry heat at certain level. These properties can be reduced or changed by thermosetting resin modification.

Our study shown, that addition of ZnO nanoparticles into MF resin had no effect on the surface resistance of laminate to cold liquids. Values of resistance to cold liquids remain almost on the initial level. Resistance of laminate surfaces to dry heat also remains unchanged. However, values of abrasion resistance decreased with increasing addition of ZnO nanoparticles. Initial point (IP) of unmodified specimen was reached after 240 cycles. After modification of resin by ZnO nanoparticles with 0.6 % IP of specimen was reached after 220 cycles, which represents decreased abrasion resistance about 8 %. Surface coated by paper impregnate with resin modified with 3 % of ZnO nanoparticles reached its IP after 180 cycles, thus abrasion resistance decreased about 25 %.

Additional work is needed to determine the ideal amount of ZnO nanoparticles addition so that laminate surface maintain mechanical and chemical resistance and gain convenient antimicrobial properties.

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REFERENCES

FEYNMAN, R P. *There´s plenty room at the bottom.* In Engineering and Science, 1960, 23 (5). p. 22-36. ISSN 0013-7812

JIANG, W. – MASHAYEKHI, H. – XING, B. *Bacterial toxicity comparison between nano- and micro-scaled oxide particles.* In Environmental Pollution (157), 2009, p. 1619-1625. ISSN 0269-7491

JIANG, Y. – O´NEILL, A. J. – DING, Y. *Zinc oxide nanoparticle-coated films: fabrication, characterization, and antibacterial properties.* In: Journal of Nanoparticle Research (17:180), 2015. DOI: 10.1007/s11051-015-2993-6

MANZOOR, U. – SIDDIQUE, S. – AHMED, R. et al. *Antibacterial, structural and optical characterization of mechano-chemically prepared ZnO nanoparticles.* In: PLoS ONE 11(5), e0154704. DOI: 10.1371/journal.pone0154704

MARTINS, N. C. T. – FREIRE, C. S. R. – NETO, C. P. et al. *Antibacterial paper based on composite coatings of nanofibrillated cellulose and ZnO.* In: Colloids and Surfaces A: Physicochemical and Engineering Aspects (417), 2013, p. 111-119. ISSN 0927-7757

NEMLI, G. – USTA, M. *Influence of some manufacturing factors on the important quality properties of melamine-impregnated papers.* In: Building and Environment (39), 2004, p. 567-570. DOI: 10.1016/j. Buildenv.2003.12.008

PALANIKUMAR, L. – RAMASAMY, S. N. – BALACHANDRAN, C. *Size-dependent antimicrobial response of zinc oxide nanoparticles.* In: IET Nanobiotechnology (8), 2014, p. 111-117. DOI: 10.1049/iet-nbt.2012.0008

ROBERTS, R. J. – EVANS, P. D. *Effect of manufacturing variables on surface quality and distribution of melamine formaldehyde resin in paper laminates.* In: Composites Part A: Applied Science and Manufacturing (36), 2005, p. 95-104. ISSN 1359-835X

REINPRECHT, L. – VIDHOLDOVÁ, Z. – GAŠPAR, F. *Decay inhibition of maple wood with nano-zinc oxide used in combination with essential oils.* In: Acta Facultatis Xylologiae Zvolen (58), 2016, p. 51-58. DOI: 10.17423/afx.2016.58.1.06

REINPRECH, L. – VIDHOLDOVÁ, Z. – KOŽIENKA, M. *Decay inhibition of lime wood with zinc oxide nanoparticles used in combination with acrylic resin.* In: Acta Facultatis Xylologiae Zvolen (57), 2015, p. 43-52.

SIRELKHATIM, A. – MAHMUD, S. – SEENI, A. et al. *Review on zinc oxide nanoparticles: Antibacterial activity and toxicity mechanism.* In: Nano-Micro Letters (7), 2015, p. 219-242. DOI: 10.1007/s40820-015-0040-x

TESAŘOVÁ, D. *Povrchové úpravy dřeva.* Praha: Grada Publishing, 2014. 136 p. ISBN 978-80-247-4715-6

VANI, C. – SERGIN, G. K. – ANNAMALAI, A.*A study on the effect of zinc oxide nanoparticles in staphylococcus aureus.* In: International Journal of Pharma and Bio Sciences (2), 2011, p. 326-335. ISSN 0975-6299

WAHAB, R. – MISHRA, A. – YUN, S.I. et al. *Antibacterial activity of ZnO nanoparticles prepared via non-hydrolitic solution route.* In: Applied Microbiology and Biotechnology (87), 2010, p. 1917-1925. DOI: 10.1007/s00253-010-2692-2