Annals of Warsaw University of Life Sciences - SGGW
Forestry and Wood Technology № 91, 2015: 225-228
(Ann. WULS - SGGW, For. and Wood Technol. 91, 2015)

Propolis and organosilanes in wood protection. Part II: AAS and EA analyses

[1]MAGDALENA WOŹNIAK, [1]IZABELA RATAJCZAK, [1]IWONA RISSMANN, [2]BARTŁOMIEJ MAZELA
[1]University of Life Sciences in Poznan, Department of Chemistry, Wojska Polskiego 75, PL-60625 Poznan, Poland
[2]University of Life Sciences in Poznan, Institute of Chemical Wood Technology, Wojska Polskiego 38/42, PL-60637 Poznan, Poland

Abstract: *Propolis and organosilanes in wood protection. Part II: AAS and EA analyses.* The paper presents results of chemical analysis of Scots pine wood treated with a formulation based on ethanolic extract of propolis (EEP) and organosilicon compounds (methyltrimethoxysilane – MTMOS, vinyltrimethoxysilane – VTMOS). The concentration of Ca, Mg, K, Fe, Si, C, O, H, N in wood samples after impregnation and after the exposure to *C. puteana* were shown. The results of biological and chemical analyses indicate that mixture of ethanolic extract of propolis and silicon compounds could be used as a potential natural and eco-friendly wood protective agent.

Keywords: propolis, Scots pine, elemental analysis EA, Atomic Absorption Spectrometry AAS, organosilanes, propolis

INTRODUCTION

Propolis indicates very complex composition, whose depends on many factors. It usually contains resin, waxes, aromatic acids, flavonoids, pollen, vitamins and macro- and microelements e.g: Ca, Mg, Fe, F, Cu and Zn (Castaldo, Capasso 2002; Gong et al. 2012). Propolis extacts possess a lot of biological activities such as: antifungal and antibacterial which there are the most popular and extensively investigated among beneficial actions of this natural material (Kujumgiev et al. 1999). Propolis has a lot of different application e.g: in food industry, medicine, optoelectronic and as well as in wood protection (Castaldo, Capasso 2002; Drapak et al. 2006). Budija et al. (2008) investigated the possibility of the use of propolis extract for the finishing of wood, showing that this substance could be used as a component in natural wood finishes.

Organosilicon compounds exhibit very high hydrophobicity caused by the presence of organic mainly methyl groups. Silicon compounds are applied in plastic, papers, building and textile industry and in wood protection. Dimensional stability, fire resistance, hydrophobicity, weather resistance and many others wood properties are improved by the applications of organosilanes (Donath et al. 2006; Mai, Militz 2004; Sebe, Brook 2001).

The aim of this study was to determine the properties of wood treated with a formulation consisted of propolis and organosilicon compounds (methyltrimethoxysilane – MTMOS, vinyltrimethoxysilane – VTMOS). In this part of the paper there are present results of chemical analysis of wood after impregnation and after the exposure to *C. puteana*.

MATERIALS AND METHODS

Chemicals

The formulation used in this study consisted of 30% ethanolic extract of propolis (EEP), 8% MTMOS (methyltrimethoxysilane) $CH_3Si(OCH_3)_3$ (Sigma Aldrich) and 2% VTMOS (vinyltrimethoxysilane) $CH_2CHSi(OCH_3)_3$ (Sigma Aldrich).

Preparation of ethanolic propolis extract

Raw propolis was cut into small pieces and extracted with a 10-fold volume of 70% ethanol under shaking conditions. The extraction was carried out in the darkness and ambient

temperature for 5 days. The final extract of propolis was concentrated on a rotary evaporator under the reduced pressure conditions at 40°C to constant weight. The final concentration (30%) of alcoholic extract was obtained by dissolution of suitable amount of residue in 70% ethanol.

Atomic Absorption Spectrometry (AAS)

Representative samples of 0.5 g wood powder were mineralized in the Marsexpress CEM International microwave mineralization system. Concentrations of Ca, Mg, K, Fe, Si and Cu in treated wood samples and in treated wood samples after the exposure to *C. puteana* were determined by flame atomic absorption spectrometry (FAAS) using the Spectra 200 AA spectrometer by Varian. Analytical curves were prepared on the basis of a series of freshly prepared standard obtained from standard solution of analyzed elements. The final results were mean values of three simultaneous measurements.

Elementary analysis (EA)

Contents of carbon, nitrogen, hydrogen and oxygen were determined using the Elemental Analyzer Flash 2000 Series. Instrument calibration was performed with the BBOT (2,5-bis-(5-tert-butyl-benzoxazol-2-yl)thiophene) standard for CHN analysis and with benzoic acid for oxygen determination, using linear fit as the calibration method.

RESULTS AND DISCUSSION

Macro- and microelements are components of raw propolis and its ethanolic extracts [Kędzia 2009; Bonvehi, Bermejo 2013]. The content of Ca, Mg, K, Fe, Cu and Si in wood samples after treatment with tested formulation and after exposure to *C. puteana* are presented in Table 1. Contents of analyzed elements in treated wood were higher or similar to those in untreated wood. Silicon concentrations were detected in treated wood samples impregnated by vacuum and soaking method at 65.02 and 48.61 mg · kg^{-1}, respectively. Silicon content confirmed high reactivity of wood components with the protecting system.

Table 1. The content of Ca, Mg, K, Fe, Cu, Si in wood samples after treatment and after exposure to *C. puteana.*

Samples	Ca	Mg	K	Fe	Cu	Si
			[mg · kg^{-1}]			
Scots pine	646.51 ± 5.93	171.94 ± 1.91	380.28 ± 1.79	1.09 ± 0.32	11.88 ± 0.05	6.93 ± 0.25
EEP VMI	938.12 ± 7.62	266.75 ± 23.09	462.44 ± 2.16	1.55 ± 1.58	11.04 ± 0.09	27.09 ± 6.72
EEP + VTMOS + MTMOS VMI	945.84 ± 24.85	205.59 ± 36.33	381.64 ± 1.20	7.58 ± 0.08	11.25 ± 0.05	65.02 ± 0.12
EEP+ VTMOS + MTMOS SMI	1036.46 ± 10.92	315.53 ± 1.62	386.66 ± 2.28	2.37 ± 0.85	10.66 ± 0.03	48.61 ± 0.57
The results after exposure to *C. puteana*						
EEP VMI	918.57 ± 4.52	210.79 ± 5.30	489.37 ± 7.72	5.05 ± 0.54	11.25 ± 0.12	4.73 ± 0.37
EEP + VTMOS + MTMOS VMI	1033.42 ± 29.43	235.34 ± 4.25	393.76 ± 5.15	16.69 ± 0.97	11.41 ± 0.05	55.25 ± 2.78
EEP + VTMOS + MTMOS SMI	787.18 ± 41.11	246.82 ± 2.12	392.45 ± 2.63	15.19 ± 0.21	12.22 ± 0.02	45.80 ± 1.05

VMI – the vacuum impregnation method, SMI – the soaking impregnation method

Concentrations of analyzed elements were comparable in wood samples after treatment and after the exposure to *C. puteana*. The concentrations of silicon in Scots pine samples after exposure to tested fungus were slightly lower than in treated samples. It could be indicate that silanes introduced to wood together with the preparation remain permanently bound with wood both after exposure to the fungus *C. puteana*.

Table 2. The content of NCH O in wood treated and wood after exposure to *C. puteana* [%]

Samples	NITROGEN	CARBON	HYDROGEN	OXYGEN
Scots pine	0.074 ± 0.008	47.389 ± 0.157	6.309 ± 0.097	41.387 ± 0.279
EEP VMI	0.067 ± 0.001	53.533 ± 0.259	6.072 ± 0.008	36.996 ± 0.377
EEP+ VTMOS + MTMOS VMI	0.063 ± 0.003	52.279 ± 0.173	6.164 ± 0.122	36.320 ± 0.794
EEP+ VTMOS + MTMOS SMI	0.088 ± 0.006	48.211 ± 0.074	6.218 ± 0.026	40.510 ± 0.106
The results after exposure to *C. puteana*				
Scots pine	0.358 ± 0.009	49.603 ± 0.040	5.916 ± 0.149	41.758 ± 0.029
EEP VMI	0.071 ± 0.001	54.333 ± 0.120	6.044 ± 0.013	39.294 ± 0.166
EEP + VTMOS + MTMOS VMI	0.055 ± 0.003	52.147 ± 0.058	5.969 ± 0.032	38.390 ± 0.220
EEP+ VTMOS + MTMOS SMI	0.155 ± 0.005	48.810 ± 0.273	6.014 ± 0.112	42.080 ± 0.242

VMI – the vacuum impregnation method, SMI – the soaking impregnation method

Table 2 presents contents of nitrogen, carbon, hydrogen and oxygen in modified wood samples and in samples after exposure to *C. puteana.* The results of elemental analysis of wood samples impregnated by the soaking method were similar to those of untreated wood samples. A similar finding was reported in wood samples after exposure to fungi, which may indicate that vacuum impregnation is a better method for impregnation with the tested formulation.

CONCLUSIONS

The results of chemical and biological analysis presented in both parts of article (Propolis and organosilanes in wood protection. Part I: FTIR analysis and biological tests and Part II: AAS and EA analysis) indicate that tested formulation based on propolis extract and organosilicon compounds could be used as a natural factor for bio-friendly wood protection. The mycological test shown that wood treated with protecting system was resistant against *C. puteana*, in comparison with the untreated samples. Compared to natural Scots pine sapwood, which according to PN-EN 350-2 is classified as class 5 – not durable as regards its resistance to *Basidiomycotina* fungi, pine wood treated with tested formulation, impregnated by vacuum method, can be classified as a class 1 – very durable, while samples impregnated by soaking method can be classified as class 2 – durable. The durability of the chemical bonds between wood and protecting system was confirmed by chemical analyses using FTIR spectroscopy AA spectrometry and elementary analysis.

REFERENCES

1. BONVEHI J.S., BERMEJO F.O., 2013: Element content of propolis collected from different areas of South Spain. Environ Monit Assess 185; 6035-6047
2. BUDIJA F., HUMAR M., KRICEJ B., METRIC M. 2008: Propolis for wood finishing. IRG/WP 08-30464
3. CASTALDO S., CAPASSO F. 2002: Propolis, an old remedy used in modern medicine. Fitoterapia Suppl. ;, S1-S6
4. DONATH S., MILITZ H., MAI C. 2006: Creating water-repellent effects on wood by treatment with silanes. Holzforschung 60; 40-46
5. DRAPAK S.I., BAKHTINOV A.P., GAVRYLYUK S.V., DRAPAK I.T., KOVALYUK Z.D. 2006: Structural and optical characterization of the propolis films. Appl. Surf. Sci. 253; 279-282

6. GONG S., LUO L., GONG W., GAO Y., XIE M. 2012: Multivariate analyses of element concentrations revealed the groupings of propolis from different regions in China. Food Chem. 134; 583-588
7. KĘDZIA B., 2009: Chemical composition of Polish propolis. Part I. The initial period of invastigations. Post Fitoter 1; 39-44
8. KUJUMGIEV A., TSVETKOVA I., SERKEDJIEVA Y., BANKOVA V., CHRISTOV R., POPOV S. 1999: Antibacterial, antifungal and antiviral activity of propolis different geographic origin. J. Ethnopharmacol. 64; 235-240
9. MAI C., MILITZ H. 2004: Modification of wood with silicon compounds. Treatment system based on organic silicon compounds - a review. Wood Sci. Technol. 37: 453-461
10. SÈBE G., BROOK M.A., 2001: Hydrophobization of wood surfaces: covalent grafting of silicone polymers, Wood Sci. Tech. 35; 269-282

Streszczenie: *Propolis i organosilany w ochronie drewna. Część II: Analizy AAS, EA.* W pracy przedstawiono wyniki analizy chemicznej drewna sosny zwyczajnej zaimpregnowanej etanowym ekstraktem propolisu (EEP) oraz ekstraktem propolisowym z dodatkiem dwóch organosilanów – winylotrimetoksysilanem (VTMOS) i metylotriometoksysilanem (MTMOS). Uzyskane wyniki analiz chemicznych (AAS, EA) i FTIR oraz badań biologicznych przedstawionych w części I pracy (*Propolis i organosilany w ochronie drewna. Część I: analiza FTIR i testy biologiczne)*, wskazują na dobre właściwości fungistatyczne oraz możliwość zatrzymania składników badanego preparatu w drewnie.

Acknowledgement
The study was supported by financial resources of the research project: "Superior bio-friendly systems for enhanced wood durability" (No. Pol-Nor/203119/32, DURAWOOD), funded by Norway Grants and the National Centre for Research and Development of Poland (NCRD) as a part of Polish-Norwegian Research Programme and of the research project no. 507.472.40.

Corresponding author:

Izabela Ratajczak
University of Life Sciences in Poznan, Department of Chemistry
Wojska Polskiego 75, PL-60625 Poznan, Poland
e-mail: iza.ratajczak@up.poznan.pl