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HYDROPHOBIC PROPERTIES OF WOOD TRAETED WITH PROPOLIS-SILANE FORMULATIONS

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ABSTRACT

The study presents results of hydrophobic properties examination of Scots pine wood treated with a propolis extract and two propolis-silane formulations determined by contact angle analysis and water uptake test. From contact angles data the surface free energy and its shares as well as the work of adhesion were calculated and described in this paper. Treatment with the ethanolic extracts of propolis (EEP) and the propolis-silane formulations a water repellent property of treated wood when compared to control wood. Addition of silicon compounds to the propolis extract caused decreased of the water uptake and increased of the contact angle value of treated wood. The most effective hydrophobic effect was obtained using the impregnation with the formulation based on EEP and organosilanes: vinyltrimethoxysilane (VTMOS) and tetraethyl orthosilicate (TEOS).

KEYWORDS: propolis extract, silane, contact angle, water uptake, hydrophobicity.

INTRODUCTION

Wood as an organic material is depredated by numerous environmental factors including water, fire or microorganisms which limits its applications. Nowadays, restrictive toxicological requirements (e.g. Biocidal Products Regulations no. 528/2012 of the European Parliament) and increased ecological awareness of consumers, caused that replacement of traditional biocides used in wood protection is critical. The biocides could replacing by new preservatives often based on natural substances harmless to human health and the environment. Propolis is such a natural substance which may be used as a bio-friendly protective agent.

Jones et al. (2011) reported the activity of propolis extract applied to wood against brown rot fungi *Coniophora puteana*, while Budija et al. (2008) examined contact angle of water on wood impregnated with propolis extract and indicated hydrophobic properties of propolis film. Extracts of this natural material have been also used as a constituent of protective agents. Scots pine sapwood protected with formulation consisted of the propolis extract and two silanes: methyltrimethoxysilane and (3-trimethoxysilyl)propyl methacrylate showed resistance against *C. puteana*, in comparison to the untreated wood. Moreover, the fungistatic properties of treated wood were also observed when wood samples were leached, according to the EN 84 standard (Woźniak et al. 2016). The research indicated that wood impregnated with the propolis-silane formulation showed higher resistance against *C. puteana* than wood impregnated only with propolis extract (Woźniak et al. 2015). Ratajczak et al. (2017) proved that wood protection system based on propolis extract, caffeine and silicon compounds inhibited the growth of *C. puteana* on wood samples. The chemical analyses (including atomic absorption spectrometry and Fourier transform infrared spectroscopy) confirmed durability of the chemical bonds between wood and constituents of the propolis-silane formulation (Woźniak et al. 2015).

An interesting area of research investigation is the problem of wettability, free and critical surface energy of the surfaces subjected to protection in the light of adsorbtive theory of adhesion (Kúdela, Liptáková 2006, Petrić 2013, Kúdela 2014).

Based on the theoretical assumptions of the adsorbtive theory of adhesion and the Young-Dupre equation, based on the interaction of the surface forces of the contacting materials the adhesion relations can be determined. In source works it can be find theoretical formulas for determination of surface forces and determination of free surface energy of wood with its dispersive and polar shares (Gray 1961, Kúdela and Liptáková 2006, Kúdela 2014).

Chemical and thermal modification of wood can change its hydrophilic character (Lu and Wu 2006, Petrić et al. 2007, Wang and Piao 2011, Petrić 2013, Guntekin et al. 2017, Kymalainen et al. 2017). The hydrophobization effect can be achieved though wood impregnation with different hydrophobic agents, such as resins, rutil (TiO_2) nanostructures or organosilanes (Bach et al. 2005, Donath et al. 2006, Aaserud et al. 2009, Fuczek et al. 2010, Zheng et al. 2015, Dong et al. 2016, Lourencon et al. 2016). Silicon compounds are commonly used in wood industry. They can be used as classic backers, in solvent applications as well as in waterborne coatings, to achieve beneficial effects in the adhesion of the coating binders and in the improvement of some of the performance characteristics of the finishings (Chen et al. 1997). Silanes increase the resistance of protected wood to fungal attack and improve hydrophobic properties, dimension stability and weather resistance (Sebe and De Jeso 2000, Sebe and Brook 2001, Tingaut et al. 2006, Panov and Terziev 2009, Ghosh et al. 2013).

To the authors' knowledge, properties of wood treated with propolis-silane formulation, except biological resistance have not been described yet. Therefore, the aim of the following study was to determine hydrophobic properties of Scots pine wood treated with the propolis extract and two propolis-silane formulations. The paper presents results of wettability determined by contact angle analysis and water uptake test of treated wood.

MATERIALS AND METHODS

Wood

The investigations were carried out on Scots pine (*Pinus sylvestris* L.) sapwood samples with an average density of 525±85 kg•m^{-3} and a moisture content of 12±1%. All wood samples were without knots and other growth inhomogeneity. The wood samples of 5 x 10 x 100 mm (R x L x T) were used in wettability analysis while the samples dimension for water uptake test were 20 x 20 x 20 mm.

Impregnating formulation

The ethanolic extract of propolis (EEP) at a 15% concentration was purchased from PROP-MAD (Poland). The first of a propolis-silane formulation (EEP-MPTMOS/TEOS) consisted of EEP and organosilanes: 3-(trimethoxysilyl)propyl methacrylate (MPTMOS) and tetraethyl orthosilicate (TEOS) at a 5% concentration. The second formulation (EEP-VTMOS/TEOS) contained EEP and vinyltrimethoxysilane (VTMOS) and tetraethyl orthosilicate (TEOS) at a 5% concentration. The silicon compounds were purchased from Sigma-Aldrich (Germany).

Impregnation method

The wood samples were impregnated using the vacuum method – 15 min under vacuum conditions – 0.8 kPa and 2 hrs under an atmospheric pressure. The wood samples after impregnation were weighted and recorded weight was used to calculate the retention of EEP and examined formulations. The wood samples were conditioned to constant weight at the relative humidity (RH) of 65±5% and the temperature of 20±1°C.

The average retention of EEP for wood samples used in wettability analysis was 105 $kg \cdot m^{-3}$ while for the impregnating formulation EEP-MPTMOS/TEOS it was 165 $kg \cdot m^{-3}$ and for EEP-VTMOS/TEOS – 163 $kg \cdot m^{-3}$. The average retention for wood samples applied in water uptake test was for EEP – 97 $kg \cdot m^{-3}$, EEP-MPTMOS/TEOS – 150 $kg \cdot m^{-3}$ and for EEP-VTMOS/TEOS – 157 $kg \cdot m^{-3}$.

Contact angle measurement

The dynamic contact angle Θ of the untreated and treated wood samples was measured according to the EN-828 standard using a PG-3 goniometer with an integrated camera (Fibro Systems AB, Sweden). Drops of 3.5 μl of redistilled water were placed on the wood tangential surface. The contact angle was determined at 3 selected points of 10 tested wood samples during 300 s and 40 measurements for the untreated and treated wood samples with each formulation were obtained. The all measurements were performed at laboratory conditions RH of 65±5% and the temperature of 20±1°C. The average contact angles were calculated to determine the wettability. From measurements of contact angle, the values of the surface free energy (γ_S) and work of adhesion (W_a) with their dispersive and polar shares were calculated according to equations described in literature (Gray 1961, Kúdela and Liptáková 2006, Kúdela 2014).

Water uptake test

Liquid water uptake was determined by immersed the untreated and treated wood samples in redistilled water in separated containers in the 65% relative moisture content room and at the temperature of 20±1°C for a total of 360 h. The wood samples were taken out periodically from water, wiped with a sheet of absorbent paper, weighted and returned to water. This procedure was repeated after 0.5, 1, 2, 4, 8, 24, 48,72, 96, 120, 144, 192, 240 and 360 h for each wood samples. There were ten replicates per each treatment. The percentage of weight change was used to determine the liquid water uptake of wood, according to equation:

$$\Delta W (\%) = [(W_2 - W_1)/W_1] \times 100 \qquad (\%)$$

where: W_1 – the weight of wood samples before water immersion
W_2 – the weight of wood samples after water immersion.

RESULTS AND DISSCUSION

The course of contact angle Θ in the function of time for the wood surfaces untreated and treated with EEP, EEP-MPTMOS/TEOS and EEP-VTMOS/TEOS is presented on Fig. 1.

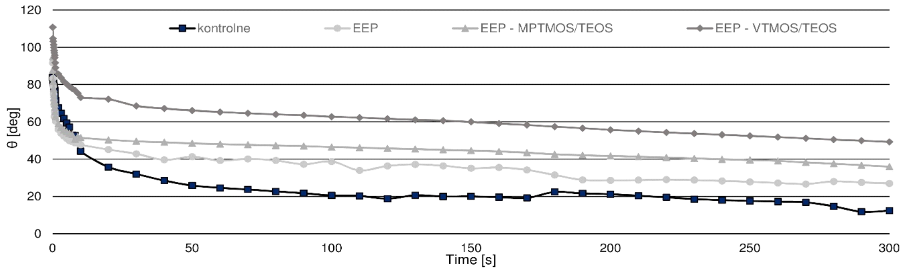

Fig. 1: The course of contact angle (Θ) in the function of time for wood surfaces untreated and treated with propolis-silane formulations.

The treatment of wood with EEP and propolis-silane formulations improve the performance of wood against wettability increasing contact angles of water. The highest value of the contact angle was determined for wood treated with EEP-VTMOS/TEOS formulation. Wood impregnated with EEP-MPTMOS/TEOS and EEP-VTMOS/TEOS formulations exhibited better water repellence than untreated wood and wood impregnated with the propolis extract without addition of silanes. In period of 10-60 s after a water drop was applied on wood surface the contact angle of wood impregnated with EEP was within the range of 47.71-39.23 deg, while for wood protected with EEP-MPTMOS/TEOS it was 51.54-48.08 deg and for wood treated with EEP-VTMOS/TEOS it was 73.07-65.20 deg. The contact angle of the untreated wood samples ranged from 44.24-24.60 deg. These results indicated, that water drop was absorbed into the wood structure after its contact with the untreated wood surface more rapidly than in case of its contact with the protected wood surface.

Literature data indicated that wood impregnated with both propolis extract and silicon compounds improvement its hydrophobicity. Budija et al. (2008) proved that proplis extract applied on wood surfaces with a brush formed a thin film exhibited hydrophobic properties. Moreover, the results described by mentioned authors demonstrated there were any significant differences in values of contact angles depending on the number of propolis layers and drying temperatures (Budija et al. 2008). Also, wood treated with silicon compounds demonstrated higher values of contact angle in comparison to untreated wood, as described by Aaserud et al. (2009) and Wang et al. (2011). Aaserud et al. (2009) indicated that wood treated with ethanolic and water solutions of examined silanes showed values of contact angles above 100 deg, while Wang et al. (2011) described results of contact angles measurements of wood modified with alkoxysilanes by sol-gel process and indicated the water repellent properties of treated wood surfaces. The results characterized by Hochmańska et al. (2014) indicated improvement in the hydrophobic character of wood treated with silane-modified protective systems including systems consisted of natural oils, alkyd resin and silicon compounds: methyltrimetoxysilane, aminoethylaminopropyltrimethoxysilane and glycidoxypropyltrimethoxysilane.

The results obtained in this study and described by other authors suggest that improvement of hydrophobic properties of wood treated with the propolis-silane formulations relate to action of both propolis and silicon compounds.

Based on the value of contact angle, surface free energy (γ_S) and the work of adhesion (Wa) in mJ•m^{-2} were calculated and their polar shares in the function of time (10-60 s) are presented on Fig. 2-3

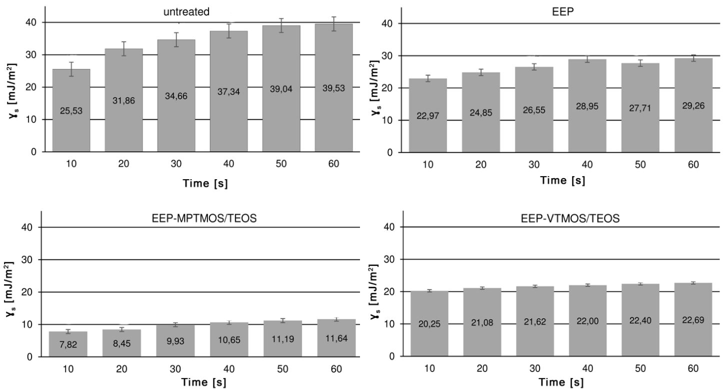

Fig. 2: The course of γ_S in the function of time for wood surface untreated and treated with EEP and propolis-silane formulations.

The surface free energy of the treated wood was lower than that of the untreated wood. Wood impregnation with the propolis extract and the propolis-silane formulations decreased the polar share of the surface free energy and it did not influence on the value of dispersion shares compared with the reference, untreated wood. The dispersion share was similar in all untreated and treated wood samples and was around 30 mJ·m^{-2}.

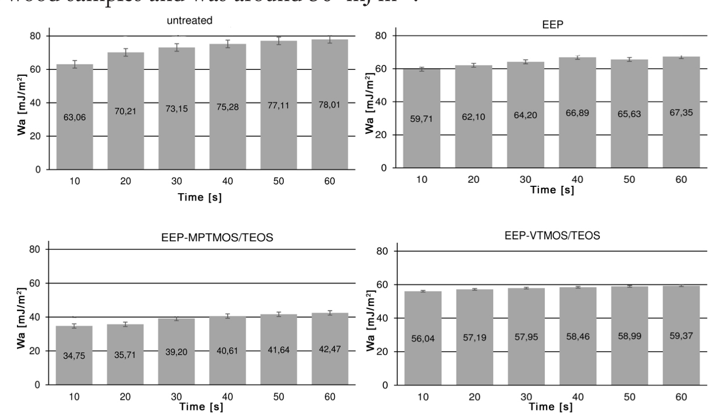

Fig. 3: The course of Wa in the function of time for wood surface untreated and treated with EEP and propolis-silane formulations.

The dispersive share of Wa for the untreated and treated with all variants of formulations wood samples was almost constant and fell within the range of 53-59 mJ·m^{-2}. Wood treatment decreased the polar share for all examined formulations compared with the control samples and caused that the work of adhesion for the treated wood were lower than that for the untreated samples. The lowest values of Wa were observed for wood impregnated with EEP-VTMOS/TEOS.

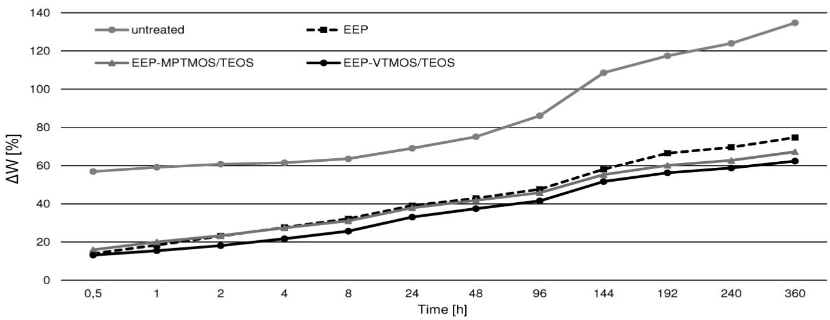

Fig. 4: The water uptake of untreated and treated with EEP and propolis-silane formulations wood samples.

Water absorption of the control and treated wood as a function of time is shown on Fig 4. Wood samples treated with EEP and propolis-silane formulations showed a significant decrease in liquid water uptake compared with the untreated wood samples. Addition of silicon compounds to propolis extract caused slightly decrease of water uptake of the treated wood. Wood treated with EEP-VTMOS/TEOS demonstrated the lowest water uptake among all examined treated wood samples. During the 0.5-4 h time of wood samples immersion, the percentage of weight change of untreated wood samples increased from 56.9% to 61.5%, while that of EEP-treated wood samples increased from 14.0% to 27.7%, EEP-MPTMOS/TEOS-treated wood samples increased in range of 16.0-27.4% and EEP-VTMOS/TEOS-treated wood samples increased from 13.2% to 27.7%. The water uptake by wood treated with EEP, EEP-MPTMOS/TEOS and EEP-VTMOS/TEOS was approximately 45%, 50% and 54% lower that of the untreated control samples, respectively.

Hydrophobic properties of wood treated with different silicon compounds determined by water immersed test are widely described in literature. Panov and Terziev (2009) reported that impregnation with alkoxysilanes improved wood hydrophobicity but there was not clear relationship between the type of silane used in impregnation and water absorption on treated wood. Effect of wood surface hydrophobization caused by silanes examined using water uptake test was also reported by Donath et al. (2006) and Ghosh et al. (2013). Results obtained by Ghosh et al. (2013) indicated that increasing concentration of silicons and length of their chain imparted higher hydrophobicity properties of treated wood. Donath et al. (2006) indicated that impregnation of wood with silanes and siloxanes led to reduce water absorption independent of the functional groups of used silicon compounds.

CONCLUSIONS

Scots pine wood treated with the ethanolic extract of propolis showed improve hydrophobic properties when compared to the untreated wood. Addition of silicon compounds to the propolis extract caused decrease of water uptake and increase of contact angle values of the treated wood. Wood samples impregnated with the EEP-VTMOS/TEOS formulation demonstrated the most effective hydrophobic effect. The increase in the hydrophobic properties of treated wood could be explained by the loss of hydrophilic hydroxyl groups which they could be engaged in bonding with reactive chemical groups coming from silicon compounds and constituents of propolis extract. The chemical interactions between wood and constituents of formulation based on propolis extract and silanes were described in previously authors works. The results present in this paper indicated that the propolis extract and the propolis-silane formulations can be used as an efficient hydrophobic agent for wood protection.

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