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Dimensional stability and hygroscopic properties of waterlogged archaeological wood treated with alkoxysilanes

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ABSTRACT

Archaeological waterlogged elm wood was treated with methyltrimethoxysilane (MTMS) and (3-mercaptopropyl)trimethoxysilane (MPTES), respectively, and anti-shrink efficiency and sorption properties of the impregnated wood samples were determined. The applied impregnants stabilized wood dimensions efficiently enough, i.e. the obtained anti-shrink efficiency was 81 and 98% for MTMS- and MPTES-treated wood, respectively. Both alkoxysilanes can be considered as potential new consolidants. Hygroscopic properties of untreated and impregnated wood were investigated with the DVS experiments. The application of MTMS and MPTES reduced wood equilibrium moisture content (*EMC*) and sorption hysteresis e.g. hysteresis relative change was −83.7 and −73.7% for MTMS- and MPTES-treated wood, respectively. The *EMC* reduction was observed in the whole hygroscopic range and it was primary due to the monolayer capacity decrease to 50 and 30% of the value for untreated wood and observed for adsorption and desorption modes, respectively. The DVS experiments revealed chemical instability of the MTMS-wood system which was neutralized after the cyclic sorption. The possible scenarios of the interaction of both alkoxysilanes with wood structure were discussed.

1. Introduction

Since wood is composed of natural polymers, it deteriorates over time when exposed to any environment. Depending on conditions (such as temperature, humidity, oxygen content), degradation processes can be fast and widespread or very slow and negligible. Due to limited oxygen availability and a high moisture level, waterlogged environment restrict the decaying microbes to anaerobic tunneling and erosion bacteria or soft-rot fungi. This results in decay slowdown and fosters wood preservation even over centuries. Although the appearance (color and surface texture) of excavated waterlogged artifacts is usually almost unchanged, they suffer from some deterioration resulting in chemical and physical changes of wood tissue (e.g. Björdal, 2012; Blanchette, 2010; Capretti et al., 2008; Kim and Singh, 2000). Wood decomposition in water or wet soil involves mainly the loss of carbohydrate components. The resulting voids in wood substance fill with water, keeping the original shape of the object, but making it soft and spongy when pressed. If wood is exposed to drying, it cracks and shrinks, irrecoverably losing its form, integrity, aesthetics and thus the historical value (e.g. Björdal, 2012; Blanchette, 2010). Therefore, once the waterlogged wood has been excavated from the burial environment, it needs a proper conservation treatment to preserve its original form and appearance.

None of the existing conservation methods is fully appropriate as it was already reported, e.g. Braovac and Kutzke (2012), Christensen et al. (2012), Walsh et al. (2017). Hence an extensive study was undertaken to develop new consolidants to preserve valuable artifacts of wooden cultural heritage (Cavallaro et al. 2015, 2017; Christensen et al., 2015; Cipriani et al., 2013; McHale et al. 2016, 2017; Walsh et al. 2014, 2017). The application of organosilicon compounds is one of the possible solutions. These chemicals have been commonly used in a broad range of industries, i.e. for hydrophobization of various materials (e.g. Bai et al., 2016; Christodoulou et al., 2013; Dey and Naughton, 2016; Palanti et al., 2012; Przybylak et al., 2016; Rodriguez et al., 2016) or preservation of wood and wood-based composites (e.g. De Vetter et al., 2009; De Vetter et al., 2010; Mai and Militz, 2004; Wang et al., 2013; Xie et al., 2013). However, only few reported so far on the studies concerning silanes application for conservation of waterlogged wood (Andriulo et al., 2017; Broda and Mazela, 2017; Broda et al. 2017, 2018; Smith, 2002) and there is a lack of more detailed data. Owing to their bifunctional structure, especially organo alkoxysilanes seem to be useful for waterlogged wood treatment. The compounds consist of three hydrolysable alkoxy groups and one functional organic group attached to a silicon atom. In the presence of water molecules, through a series of hydrolysis and condensation reactions (the so-called sol-gel process) alkoxy groups can form covalent bonds between

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neighboring silane monomers and between a silane molecule and hydroxyl groups of wood components, resulting in a highly condensed gel linked to wood polymers (e.g. Kartal et al., 2007, 2009). It was already demonstrated that alkoxysilanes are able to penetrate and bulk the cell wall (e.g. Donath et al., 2004; Mai and Militz, 2004). Owing to the high surface-to-volume ratio their particles are metastable (Mahltig et al., 2008), thus, when applied to wood, they can form a three-dimensional network of polysiloxane and the cell wall polymers within the wooden matrix. This can stabilize wood structure and support its dimensional stability (e.g. Panov and Terziev, 2009; Schneider and Brebner, 1985). An organic group can provide alkoxysilanes some additional functionality, such as hydrophobicity, decay resistance, fire resistance or supplementary site to bond with cell wall polymers (e.g. Brinker and Scherer, 1990; Mai and Militz, 2004; Tshabalala et al., 2003).

The crucial concerns of waterlogged wood protection include not only dimensional stabilization, but also its mechanical properties as well as protection against biotic and abiotic degradation. All the mentioned issues are related to the variation of moisture content in wood (e.g. Rowell, 2012; Xie et al., 2010). Waterlogged wood is usually impregnated with polyethylene glycol (PEG) and the two-stage treatment, i.e. introducing firstly low and subsequently high molecular weight PEG, is the most common one. It was already depicted that in the case of PEG-treated wood an anomalous increase of wood equilibrium moisture content was found for high air relative humidity (e.g. Olek et al., 2016). The problem was explained by high hygroscopicity of low molecular weight PEG (Majka et al., 2017). The influence of alkoxysilanes impregnation on the hygroscopic properties of waterlogged wood was practically not analyzed in detail.

The aim of the research was to verify usability of two alkoxysilanes differing in the type of an organic functional group for waterlogged wood conservation. Their effectiveness was evaluated by determining wood dimensional stability upon treatment and drying. Moreover, changes in wood hygroscopic properties were evaluated by the analysis of sorption behavior of untreated and treated wood using a Dynamic Vapor Sorption apparatus. The secondary objective was to explain the influence of various organofunctional groups of the applied alkoxysilanes on wood hygroscopic properties.

2. Materials and methods

2.1. Archaeological wood

Archaeological waterlogged elm wood (*Ulmus* spp.) was used in the research. The log was taken from the bottom of the Lednica Lake (the Wielkopolska Region, Poland). Almost completely buried under a layer of mud, it was found in the vicinity of the remains of the medieval “Poznań” bridge. Soft and spongy wood structure indicated a high level of its degradation. It was confirmed by the results of physical and chemical analyses: the determined cellulose content was as low as 5%, wood basic density was 156 kg/m^3, and the calculated loss of wood substance was ca. 60% (Broda and Mazela, 2017). Such a severely degraded elm log was an appropriate material for testing the effectiveness of the new conservation methods.

The research was performed on the elm heartwood specimens with a size of 20 · 20 · 10 mm (tangential, radial and longitudinal direction, respectively). Five replicates were used for each treatment variation.

2.2. Alkoxysilanes impregnation

Due to their potential stabilizing and hydrophobic properties, two different alkoxysilanes were used to impregnate the waterlogged wood, i.e. methyltrimethoxysilane (MTMS) provided by Sigma-Aldrich and (3-mercaptopropyl)trimethoxysilane (MPTES) specially synthesized for the purposed of the study. Therefore, the wood samples were divided into two sets which were treated with 50% solution of the particular silane in ethanol using the vacuum-pressure method. Impregnation was carried out by applying a vacuum of 0.09 MPa for 0.5 h and a subsequent pressure of 1 MPa for 6 h, repeated six times. In order to increase the effectiveness of the treatment, the material was dehydrated with 96% ethanol for 4 weeks prior to the impregnation.

The samples were air-dried for 2 weeks following the treatment. They were weighted before and after treatment and alkoxysilane uptake was calculated according to the formula (e.g. Jeremic et al., 2007):

$$U = \frac{m_t - m_u}{m_u}\cdot 100 \tag{1}$$

where: U – impregnant uptake (%), m_t – mass of oven-dried treated wood (g), m_u – mass of oven-dried untreated wood (g).

2.3. Dimensional stability assessment

Volumetric shrinkage (S) of untreated and treated wood was calculated according to the following equation:

$$S = \frac{V_0 - V_1}{V_0}\cdot 100 \tag{2}$$

where V_0 (%) – initial volume of a samples, i.e. for the maximum moisture content in waterlogged conditions, V_1 (%) – final volume of a sample, i.e. after air-drying for untreated wood and after treatment and drying for impregnated wood (sample volume was calculated on the basis of the measurements of the sample length in three anatomical direction with the use of a digital caliper - five measurements at equal distances from each other on the entire length of the sample). It enabled the estimation of dimensional stability of treated wood by determining the volumetric anti-shrink efficiency (ASE) after drying:

$$ASE = \frac{S_u - S_t}{S_u}\cdot 100 \tag{3}$$

where S_u (%) – volumetric shrinkage of untreated (control) wood, S_t (%) – volumetric shrinkage of impregnated wood. As suggested by Grattan et al. (1980), the ASE values of at least 75% can be considered as sufficient for conservation practice. The criterion was used in the study to estimate the effectiveness of the applied silanes.

2.4. Sorption experiments

In order to determine the effects of MTMS and MPTES impregnation on waterlogged elm wood, the hygroscopic properties of the material were studied. The sorption experiments were made at a temperature of 25 °C using the Dynamic Vapor Sorption apparatus (DVS Advantage 2 from Surface Measurement Systems, London, UK). The samples of the thickness of ca. 0.5 mm in the tangential direction and the dimensions of 15 mm and 4 mm in the radial and longitudinal directions, respectively, were obtained from untreated and impregnated material and then used for the sorption experiments. The samples were firstly stored over phosphorus pentoxide in order to approach the dry state. The values of the equilibrium moisture content were registered for the adsorption and desorption mode for untreated as well as MTMS and MPTES treated wood. It has been assumed that hygroscopic equilibrium at a given relative humidity was obtained when a change of the mass was less than 0.002% per minute for at least 10 min (Majka et al., 2017).

2.5. Sorption isotherms modeling

The obtained adsorption and desorption isotherms were modeled with the three-parameter GAB model, which enabled the interpretation of its parameters and description of water sorption mechanisms. The GAB model was applied in the following form (e.g. Basu et al., 2006; Esteban et al., 2010):