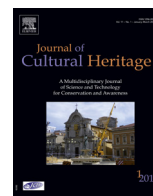




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Original article

Application of methyltrimethoxysilane to increase dimensional stability of waterlogged wood

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ABSTRACT

Conservation of historic wooden monuments, especially regarding waterlogged archaeological wood, is a complex, long-term, multi-stage and also a quite difficult process. The main problem is poor dimensional stability of such artefacts due to a high degree of wood tissue degradation and its significant saturation with water. Exposing wood to a natural drying process causes its shrinkage, cracking and irreversible deformation due to collapse. Therefore, the first stage of maintenance of waterlogged wooden objects is to replace the water filling cell lumina and cell walls with an appropriate consolidation agent that will protect wood against shrinkage, collapse and loss of shape. Silanes have so far been used mainly as additives for wood preservatives and coatings, increasing wood hydrophobicity or decreasing its hygroscopicity. Some silanes show resistance to biotic degradation. As confirmed in scientific reports, their ability to improve dimensional stability of contemporary wood makes them a potential agent for stabilisation of archaeological wood. The aim of the research was to determine the influence of methyltrimethoxysilane (MTMOS) treatment on the dimensional stability of waterlogged elm wood excavated from the Lednica Lake in the Wielkopolska Region. Freshly taken from the lake and still completely saturated with water, elm wood samples were treated with ethanol solution of 50% MTMOS by the vacuum-pressure impregnation method. Pre- and post-treatment dimensions of wood samples were measured and anti-shrink efficiency (ASE) was calculated. ASE values of elm wood treated with MTMOS varied from 69.4% to 94.5%, depending on the state of wood degradation. In case of reference wood samples treated with polyethylene glycol, ASE ranged between 96.1% and 100%. Taking into account the improvement of wood dimensional stability obtained, the aesthetic end result of the treatment and its properties of hydrophobicity and anti-fungal activity, the silane MTMOS can be considered as a potential agent for conservation of waterlogged wood and seems to be worth further study.

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1. Introduction

Serious degradation of wood excavated from lakes, rivers, marine sites, wet soil or peat bogs, results from long exposure to various biotic and abiotic factors. This process starts with leaching water-soluble substances, such as carbohydrates, mineral salts or tannins. Then, cell wall decomposition begins through cellulose hydrolysis caused by bacteria or fungi. Even the middle lamella containing lignin, that has remained after the first step of wood degradation and supports wood structure, decomposes over time. Consequently, bonds between wood components loosen up and intercellular spaces extend. Wood becomes more porous and extremely permeable for water [1,2]. Its structure resembles

a sponge, and thus absorbs huge amounts of water. Although the main components of wood are degraded and its cell walls are weakened, the lignin remains of the middle lamella together with the absorbed water enable wooden objects to keep their shape and dimensions of as long as they remain wet. However, the absorbed water evaporates after exposure to air. The emerging capillary tension and the increase of surface tension forces of the evaporating water cause collapse of the weakened cell walls [3]. Wood shrinks, cracks and loses its shape and dimensions [1]. If the wooden object is a valuable historic monument, it requires particularly effective preservation. In the first step of waterlogged wood conservation, the water filling the wood structure must be replaced with an appropriate chemical compound that will protect the wooden object against shrinkage and deformation.

At present, the most popular conservation agent is polyethylene glycol (PEG) which is freely soluble in alcohols (ethanol, methanol, isopropanol) as well as in water. PEG is commercially available in a range of molecular weights from 300–600 (liquids),

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through 1000–1500 (semi-liquids), to 3250–6000 (wax-like substances). Low molecular PEG is applicable for conservation of better preserved waterlogged wood while high molecular PEG is more appropriate for more decayed wooden objects. PEG can penetrate wood tissue, replace water molecules and reinforce its structure, thus improving its dimensional stability [4,5]. Unfortunately, it is not a perfect agent for wood conservation due to its considerable disadvantages [6]. In external conditions, subject to temperature or humidity changes, PEG leaches from wood, resulting in irreversible shrinkage and cracking [7]. Moreover, the chemical reactivity of this component with other substances can cause fast wood degradation [8], which makes it unsuitable for wood conservation. It has been shown by Almkvist [9] and Sandström et al. [10], that metal and sulphur compounds, which are often present in waterlogged wooden artefacts (e.g. ships), can be involved in oxidative reactions causing depolymerisation of not only the wood components, but also preservation agents like PEG. Such reactions generate various low molecular organic acids (formic, glycolic, oxalic), causing further wood degradation. Therefore, there is a need to find new effective substances for safe preservation of wooden cultural heritage.

Alkoxysilanes, used mainly as additives for wood preservatives [11,12], seem to be an attractive alternative to the conventional PEG. These organosilicons are classified as bifunctional compounds that contain both an organic functional Y group and readily hydrolysable X groups. Owing to this unique structure, they are extremely versatile substances which may react with diverse compounds, creating chemical bonds between the Y groups and an organic material, and within X groups. Due to the presence of reactive groups silanes form stable Si-O-C and Si-O-Si bonds with the wood surface, reducing its hydrophilicity and thus eliminating the undesirable features of timber [13,14]. Alkoxysilanes can hydrolyse and condense in an aqueous medium, which, in combination with good hydrophobic and antifungal properties, makes them a potentially effective substance for waterlogged archaeological wood conservation, as indicated in recent studies [15,16]. Water contained in waterlogged wood would allow the alkoxysilanes to hydrolyse and chemically bind to wood components, embedding in cell walls and thus preventing their collapse. This way, wood should keep its original shape and dimensions. Moreover, the chemical binding of silanes with wood would prevent their leaching out, thus making the protection of archaeological wood more effective and permanent.

The aim of the research was to determine the influence of methyltrimethoxysilane (MTMOS) treatment on the dimensional stability of waterlogged wood. The object of the study was a waterlogged elm log excavated from the bottom of the Lednica Lake in the Wielkopolska Region, which was found near the remains of a medieval “Poznań” bridge, dating back to the 10th to 11th centuries. The bridge connected the shore of the Ostrów Lednicki island (the seat of the first rulers of Poland) with the road leading into the city of Poznań [17]. Polyethylene glycol 400 (PEG 400) was used as a reference due to its common application in waterlogged wood conservation. Finding an effective agent for archaeological waterlogged wood conservation will allow preservation of such historic treasures for future generations.

2. Materials and methods

2.1. Materials

A waterlogged elm (*Ulmus* sp. L.) log was cut into 1-cm-thick slices. No sapwood was found on the log. The slices were subdivided into three heartwood zones, differing in the level of wood degradation: outer (E1), middle (E2) and inner (E3) (Fig. 1). Small square

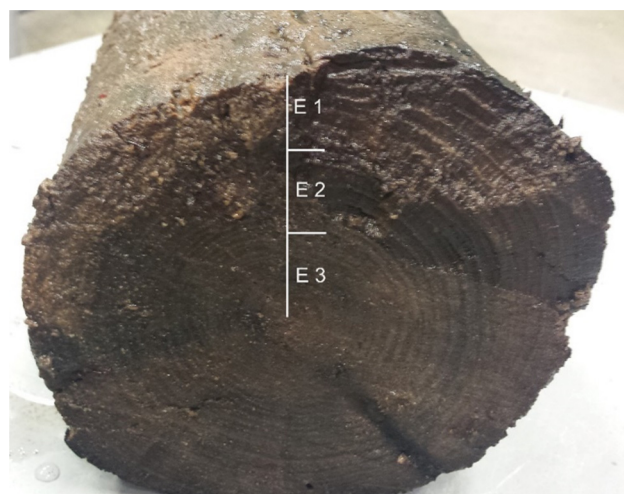


Fig. 1. Cross-section of waterlogged elm log divided into three zones. E1: outer heartwood; E2: middle heartwood; E3: inner heartwood.

samples (20 × 20 × 10 mm, radial × tangential × longitudinal direction) were cut out from each zone.

Methyltrimethoxysilane (MTMOS) was used as a potential stabilisation agent for waterlogged wood treatment. (PEG 400) was used as a reference conservation agent due to its usefulness in conservation of wood at different level of degradation.

2.2. Methods

2.2.1. Chemical analysis

In order to evaluate the state of degradation of waterlogged elm wood, the percentage content of main wood components (cellulose [C], holocellulose [H], lignin [L] and extractives) was determined by chemical analysis. Cellulose content was measured according to the Seifert procedure by using acetylacetone-dioxanehydrochloric acid [18]. Holocellulose content was determined according to the procedure described by Browning [18] using an acid solution of sodium chlorite. Lignin content was measured according to the TAPPI standard [19]. Solvent extractive components and ash were measured according to TAPPI standards [20,21] respectively. Two layers, outer and inner heartwood of the elm log were analysed separately.

2.2.2. Physical wood properties

Physical parameters such as density and moisture content allow evaluation of the state of degradation of waterlogged wood [22]. However, it must be kept in mind that correct evaluation of the state of preservation of waterlogged wood cannot be based only on one type of measurement. As shown by Macchioni [23,24], collapse and high ash content in wood samples can interfere with the measurement of waterlogged wood physical properties, giving an untrue image of the state of wood preservation. Therefore, other analyses (as microscopy or chemical analysis) should be performed.

Maximum moisture content and conventional density of waterlogged elm wood were determined, and the loss of wood substance (LWS) was calculated on the basis of the results obtained [25]. LWS is a conventional value which allows estimating the amount of the wood substance that has remained in archaeological samples, and, by extension, is very useful for determining extent of wood degradation.

The maximum moisture content of wood (MC_{max}) was determined by wood mass measurement for samples were repeatedly saturated with water under pressure of 50 hPa and then oven-dried

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