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Research Paper

Distribution and penetration of tung oil in wood studied by magnetic resonance microscopy

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ABSTRACT

Water repellents, as environmentally-friendly treatments, are gaining popularity as non-biocidal solutions for wood protection. Drying oils, in addition to waxes and organosilicon compounds, are one of the most important water repellents for wood. Tung oil has so far been proven to be one of the best performing oils for wood protection. However, tung oil, similarly as other oils, does not penetrate deeply into wood, due to its high viscosity. In order to improve the penetration of oil into wood, a vacuum-pressure procedure has to be applied. The species used in this study are important in Central Europe: sweet chestnut heartwood (*Castanea sativa*), European larch heartwood (*Larix decidua*), Scots pine heartwood and sapwood (*Pinus sylvestris*) and Norway spruce (*Picea abies*). Oil uptake depends on the applied impregnation method and on the wood species used. Retention of tung oil was higher after an impregnation process than with the immersion procedure. Magnetic resonance imaging (MRI) was applied to elucidate the influence of wood species on oil penetration and distribution in wood after treatment. High spatial resolution MR imaging is highly sensitive to changes of liquids in wood and is therefore also very appropriate for monitoring oil penetration. Furthermore, with a good signal to noise ratio of MR images, the method can also discern among specimens with different patterns of oil distribution, as well as between areas of early-wood and late-wood.

1. Introduction

Increased environmental concerns in recent years have resulted in renewed interest in non-biocidal solutions for wood preservation. These techniques include proper selection of wood species, wood modification, proper planning of construction details and the application of various hydrophobic treatments (Palanti et al., 2011; Thybring, 2013). Their mode of action is based on reducing the rate of water uptake into the capillaries. These hydrophobic treatments usually only slow down water penetration without fully preventing it, so they are not meant to be used where there is ground contact. If the wood moisture content is kept low enough, fungal decay is no longer possible (Goethals and Stevens, 1994; Lesar and Humar, 2010). After a long period of soaking in water, wood treated with water repellents usually retains similar amounts of water and swells to the same extent as untreated wood (Thybring, 2013). However, most wood in use of class 2 (above ground, covered) and class 3 (above ground, uncovered) EN (2013) is exposed to weathering for limited periods only, hence water repellents perform well in such conditions. One of the most important requirements for water repellents applied outdoors is that they should not seal the surface of the wood. A surface film makes water diffusion possible, which enables drying of the wood after precipitation (Williams and Feist, 1999). One of the most important water repellents used in wood preservation other than waxes (wax emulsions) (Lesar and Humar, 2011) and organosilicon compounds (De Vetter et al., 2009) is drying oils (Schultz et al., 2007). Tung oil is a drying oil obtained by pressing seeds from the nut of the tung tree (*Vernicia fordii; V. montana*). As a drying oil, tung oil dries when exposed to air, forming a transparent film. Tung oils consist of the following fatty acids: palmitic acid (5.5%), oleic acid (4.0%), linoleic acid (8.5%) and alpha-eleostearic acid (82.0%) (Anon, 2016). Its water-repellent efficacy has been proven in several laboratory and field trials (Humar and Lesar, 2013). We have proven its excellent water repellence even after severe aging and weathering procedures (Žlahtič and Humar, 2016). Data from these studies clearly show that the performance of drying oils depends on the amount of applied oil, i.e., treatment procedures. As reported for several other preservative systems, penetration and retention do not depend on the treatment procedure only but also on the wood species used (Banks, 1970; Siau, 1984; Kumar and Morrell, 1989). Refractory wood species are rarely used for wood impregnation procedures, since target retention and

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penetration is difficult to achieve. Permeability is influenced by a variety of factors, including sapwood-heartwood ratio, density, presence of bordered pits, tyloses, size of vessels and tracheids and pits and resin canals, as well as pre-treatment such as drying or hydrothermal treatment of wood (Flynn, 1995; Durmaz et al., 2015). It can be presumed, that the importance of the natural products isolated from various industrial crops will increase in the developed countries, as end users are avoiding the toxic biocides, and are using alternatives of natural origin instead. Even more, these alternatives have to be produced with industrial techniques with the lowest environmental impact.

There are different pathways how water moves through the wood. In dried wood, during impregnation liquids takes various pathways (Zimmer et al., 2014). In axial direction impregnation solution moves through the tracheids (conifers) or vessels (hardwoods), that are connected with pits. At conifers bordered pits connects the tracheids. However, the anatomical assembly of bordered pits permits the maintenance of a xylary water column, while preventing the spread of air through embolized tracheids (Maschek et al., 2013). This mechanisms enables survival of the trees but on the other hand causes problems during impregnation. Hence, the number, size and aspiration state of the bordered pits greatly influence the treatability of coniferous sapwood (Stamm, 1947; Militz, 1993; Zimmer et al., 2014). Small diameter latewood tracheids as well as the portion of unaspirated pits in the latewood fraction positively influence treatability (Sedighi-Gilani et al., 2012). On the other hand it should be considered, that axial planes in the wood are limited, thus flow of the preservative solutions in radial and tangential direction is even more important. In radial direction, fluid transport occurs through the rays. For example, in Scots pine, the ray system consist of ray tracheids and ray parenchyma (Wagenführ, 1996).

This paper elucidates the influence of wood species and treatment method on tung oil retention and permeability of selected wood species. Permeability is a key wood parameter important for impregnation or drying processes. The magnetic resonance imaging (MRI) method was used to analyse oil uptake *in situ*. MRI is a non-destructive, non-invasive and non-contact technique already being successfully applied in wood science (Bucur, 2003a, 2003b; Merela et al., 2005; Oven et al., 2011) and with other porous materials (Moreaux and Dereppe, 1994; Demeure et al., 1994). Wood is an ideal material for MRI studies, due to its high moisture content when green and its hygroscopic character when in use (Oven et al., 2011). In the case of dry wood, as for example in our study, the moisture content of wood was kept so low that there was no free water and only tung oil can be seen on the MR images due to the protons in a liquid state inside the oil. The prime objective of this study was to determine the suitability of the method of MRI, and to prove the influence of wood species and treatment method on tung oil retention, penetration and distribution. The aim of this study was to employ the 3D MRM technique to visualize the oil distribution and penetration in various wood species and to make a correlation between oil retention and the MRI signal. This method was used because, in addition to the total amount of oil, it can also detect the spatial oil distribution in the wood sample. MRM refers to very high resolution MRI imaging, with resolution down to nanometre scale. Resolution of the classical MRI is typically about one mm^3.

2. Materials and methods

2.1. Material

The present study was performed on economical important wood species in Central Europe that are frequently used in class 2 and 3 applications. In order to improve their outdoor performance, they are frequently treated with various oils, like linseed and tung oil. The magnetic resonance imaging (MRI) method was used to analyse oil uptake in situ. The following materials were utilised: chestnut heartwood (*Castanea sativa*), European larch heartwood (*Larix decidua*), Scots pine heartwood and sapwood (*Pinus sylvestris*) and Norway spruce (*Picea abies*) wood. Specimens were defect-free, without visible signs of decay or blue staining, as prescribed in standard EN (2006). The materials were classified into various treatability classes as prescribed in standard EN (2015). Sweet chestnut heartwood (class 4), spruce heartwood (class 3-4), larch heartwood (class 4) and scots pine heartwood (class 3-4) belong to the group of the wood species that are extremely difficult to treat. Only scots pine sapwood has been classified as an easily treated material (class 1). This selection of the materials offers us observation of the oil penetration to wood species with various anatomical characteristic (softwoods vs hardwoods; sapwood vs heartwood; permeable vs impermeable; ring porous wood).

The dimensions of the samples used for tensiometer experiments were 5.0 cm × 1.5 cm × 2.5 cm (longitudinal × radial × tangential). The dimensions of the specimens used for MRM scanning were initially 7 cm × 1.2 cm × 1.2 cm (longitudinal × radial × tangential). These specimens were treated with tung oil (Samson, Kamnik, Slovenia) and then sawn into five smaller specimens, as indicated on Fig. 1. The dimensions of the specimens used in the MRM study were limited by the size of the RF coil.

Selected samples were treated with tung oil (Humar and Lesar, 2013) to improve the hydrophobic properties of the wood. Half of the specimens used for MR imaging were impregnated with oil and the other half were immersed in oil for 1 min. Impregnation was performed according to the full cell process, i.e., 30 min vacuum (80 mbar), 120 min pressure (8 bar), 15 min vacuum (80 mbar) and 20 min soaking. The remains after both treatments were wiped off with paper towel. Uptake of the oil was determined gravimetrically. It is believed that after drying slightly lower amount of oils remained in the wood because of volatile compounds that afterwards evaporate from the wood. After impregnation, samples were dried for 4 weeks at room temperature (20 °C; RH = 60%).

2.2. Uptake of tung oil and water on tensiometer

The longitudinal direction is the most prominent pathway for liquid penetration; it was therefore elucidated with tensiometer analysis. The cross section surfaces of the specimens were exposed to oil for 200 s, to determine tung oil uptake in the longitudinal direction. The measurements were carried out at room temperature (≅20 °C) and RH of 60 ± 5% on a Tensiometer K100MK2 device (Krüss, Germany) according to a modified EN 1609 standard (1997). Specimens were positioned so that the wood cross section surface was in contact with the test liquid and their masses were subsequently measured continuously every 2 s for 200 s. The velocity before contact was 6 mm/min, the sensitivity of contact was 0.005 g and the depth of immersion was set at 1 mm. Depending on the final weight and cross section surface of the immersed sample, the uptakes of tung oil in grams per square centimetre were calculated. For comparison, samples were also immersed in water according to the same procedure.

2.3. High-resolution magnetic resonance imaging

MRM experiments were performed on a TecMag Redstone (USA) MRI spectrometer with a superconducting 9.4 T magnet (Jastec, Japan). The specimens were imaged in a 20-mm diameter RF coil. To obtain the oil distribution along the longitudinal, tangential and radial directions, 1D MRM was used with the following parameters: field of view (FOV) of 20 mm, echo time (TE) of 1.6 ms, repetition