



Wood-water relationship and micro-chemical properties of huminated archaeological European elm (*Ulmus laevis* P.)

Amir Ghavidel¹ · Shennan Wang² · Miklós Bak³ · Lauri Rautkari² · Reza Hosseinpourpia^{4,5}

Received: 8 January 2025 / Accepted: 23 July 2025
© The Author(s) 2025

Abstract

Archaeological wood requires effective conservation to prevent further degradation, and traditional modifications such as polyethylene glycol (PEG) have limitations, including hygroscopicity and chemical degradation over time. To explore alternative modification, this study was conducted to investigate the suitability of humins, crosslinked with different concentrations of succinic acid (SA), to protect archaeological elm wood from the Agapia Monastery against water and to determine the modification mechanism. Key parameters such as dimensional stability, moisture sorption isotherms, and determination of accessible hydroxy groups as a function of humination modification were analyzed using dynamic vapor sorption (DVS). The modification mechanism was studied by microstructural and chemical properties evaluation by Confocal-Raman spectroscopy and scanning electron microscopy (SEM). Results indicated that humins, particularly crosslinked with SA, significantly improved the water-related properties of wood and its dimensional stability. The humination also reduced the accessibility of the hydroxy group, thus decreasing the equilibrium moisture content (EMC) of huminated elm at relative humidities (RHs) ranging from 0 to 95%. While SEM images revealed structural changes in the modified wood, Confocal-Raman spectroscopy confirmed the successful allocation of humins into the cell walls. This study demonstrates that humins are promising materials for archaeological wood conservation, providing improvements in both chemical and physical properties.

Introduction

Since the time of the first hominids, wood has been utilized as a source of shelter, tools, and weapons. Wood deteriorates over time when exposed to any environment since it is made up of natural polymers. Degradation processes can be quick and

Extended author information available on the last page of the article

broad or extremely slow and minimal, depending on variables (such as temperature, humidity, and oxygen concentration) (Braovac and Kutzke 2012; Ghavidel et al. 2020, 2021b; Gjelstrup Björdal 2012). Archaeological wooden artifacts require immediate conservation treatment to maintain their integrity and avoid permanent destruction (Broda et al. 2021b; Ghavidel et al. 2021a).

The conservation of archaeological wood presents distinct challenges depending on its state of preservation, which is primarily divided into waterlogged and dry conditions. For waterlogged archaeological wood, the main objective is to prevent irreversible shrinkage and cellular collapse during drying. Currently, polyethylene glycol (PEG) is the most common chemical used for this purpose, acting as a bulking agent that replaces water within the degraded wood structure. However, despite its effectiveness as a primary consolidant for waterlogged wood, PEG treatment has certain long-term drawbacks. The PEG modification enhances the hygroscopicity of wood, resulting in severe swelling at high relative humidity, which can cause irreversible damage such as cracking (Broda et al. 2021a, b; Popescu and Broda 2021). Furthermore, PEG is known to have a plasticizing impact on the wood and can be prone to high leachability and degradation into acidic by-products, which in turn can cause further chemical degradation of the artifact over time (Almkvist and Persson 2008; Hocker et al. 2012; Wagner et al. 2016).

In search of alternatives, recent research has focused on developing new treatment materials to replace traditional chemicals like PEG. Organosilicon compounds have shown promise for wood conservation. For instance, Popescu and Broda (2021) compared the effects of alkoxysilanes and siloxane on the stabilization of waterlogged archaeological elm wood. They found that alkoxysilanes stabilize wood by bulking the cell walls and chemically altering the wood, while siloxane primarily fills the cell lumina. (Broda et al. 2019, 2020) demonstrated the effectiveness of organosilicon compounds in minimizing moisture absorption, enhancing anti-shrinkage properties, and reducing biological degradation. Similarly, Ghavidel et al. (2021) reported that tetraethyl orthosilicate (TEOS) modification significantly delayed the sorption time to reach equilibrium moisture content (EMC) in dry archaeological oak wood, reducing its hygroscopicity.

Humins are heterogeneous and polydisperse macromolecules made up mostly of furanic rings with primary functional groups such as aldehydes, carboxylic acids, and hydroxyls (Constant et al. 2017; Filiciotto et al. 2018; Ghavidel and Hosseinpourpia 2024; Sangregorio et al. 2018; van Zandvoort et al. 2013). During lignocellulosic biomass processing, humins often form as by-products, particularly under acidic conditions (van Zandvoort et al. 2013). The structure of humins is known to be affected by reaction time, temperature, feedstock structure, and concentration (Hoang et al. 2013). Several studies have demonstrated the potential of humination as an effective modification technique to enhance wood properties. Humination of Scots pine microveneers considerably improved their photodegradation resistance and mechanical stability after exposure to artificial weathering tests (Ghavidel and Hosseinpourpia 2024). Sangregorio and co-workers (2020) reported that the reaction between humins and wood polymers increased the tensile strength and dimensional stability of pinewood veneers. They also showed that humins-treated wood exhibited longer ignition times, a slower heat release rate, and reduced CO formation compared

to furfurylated wood, making it a promising alternative for enhancing fire resistance. Humins were also utilized in combination with polyfurfuryl alcohol (PFA) to form composite materials, which were further reinforced with cellulose fibers, enhancing both tensile strength and reducing brittleness (Pin et al. 2014). This approach has proven particularly useful for developing high-performance, sustainable building materials with enhanced resistance to degradation (Mija et al. 2017). Very recently, Ghavidel and colleagues (2025) reported that the humination modification in the presence of citric and succinic acids considerably enhanced the material properties of Scots pine sapwood. The authors stated that the dimensional stability and static and dynamic bending properties, as well as resistance to white and brown rot fungi, were significantly higher in the huminated samples than in the unmodified ones. They suggested placing the humination modification in a semiactive category as its interaction with the wood cells may include both lumen filling and chemical bonds within the cell wall. However, further accurate methods like micro-chemical analyses are required to draw more comprehensive conclusions. In addition, even though different chemicals, like those based on silicon and glycol, have been utilized for the conservation of archaeological wood, the application of wood modification methods for the protection of archaeological wood is limited. In contrast, the conservation of dry archaeological wood, the focus of this study, presents a different set of challenges. The primary goals are to consolidate fragile material, improve the hydrophobic character against fluctuation of ambient conditions, and protect it from future degradation. Therefore, this work aimed to study the protection effect and the modification mechanism of humination process by evaluating the wood-water relationship and microstructural properties of huminated archaeological elm crosslinked with succinic acid. The micro-chemical properties of huminated samples were analyzed by means of scanning electron microscopy and Confocal-Raman spectroscopy.

Materials and methods

Raw materials and sample preparations

The archaeological elm sample was sourced from a structural support beam of an old house within the monastic village of Agapia Monastery (Romanian: Mănăstirea Agapia), a Romanian Orthodox nunnery located 9 km west of Târgu Neamt, in the commune of Agapia, Neamt County. The monastery complex itself dates back to its construction between 1641 and 1643. The beam was collected during the renovation of the historic building. Visually, the wood structure was severely damaged due to biological degradation, and no chemical preservatives had been previously applied.

From this beam, a bulk sample was transported to the laboratory. At the time of the experiments, its equilibrium moisture content was approximately 11%. To prepare the experimental specimens, the weathered outer surfaces of the bulk sample were carefully removed. From the interior, undamaged portion, a series of small specimens with dimensions of $10 \times 10 \times 15 \text{ mm}^3$ ($R \times T \times L$) were cut.

A total of 32 specimens were prepared and divided into four experimental groups: a control group without modification (C), a group modified with humins (H), and two

groups modified with humins crosslinked with either 1% (HSA-1%) or 3% (HSA-3%) succinic acid (SA). Each group contained 8 replicates. Prior to modification, all prepared specimens were oven-dried at 103 °C for 24 h to determine their initial dry mass.

Humins were kindly provided by Avantium Renewable Polymers B.V. (Amsterdam, the Netherlands). Due to the high viscosity of humins, initial steps were taken to reduce their viscidness. Primary, humins were heated at 60 °C for 60 min, then the pre-heated humins were added to the distilled water at a mass ratio of 1:1 and stirred at 60 °C for an additional 60 min using a mechanical stirrer. Then, the mixture was mixed at 2000 rpm for 10 min using an ultra-turrax (IKA T18D, Germany) at room temperature. The mixture was then held at room temperature for 3 h to collect the soluble humins. The dissolved humins with a solid content of 30% were then used for the impregnation of wood. Succinic acid (Sigma Aldrich; purity: $\geq 99\%$) was used as a crosslinker and applied at 1% and 3% (W/W_{solid humins}).

Dried elm wood samples were impregnated with different humins solutions as a: humins (H), b: humins-1% succinic acid (HAS-1%), and c: humins-3% succinic acid (HAS-3%) under vacuum (370 mbar) for 4 h at 25 °C. After impregnation, the samples were held in room condition for 24 h to allow further penetration. The excess solutions from the surfaces were then cleaned up with tissue paper, and the samples were located in the oven at 30 °C. The temperature gradually increased by 30 °C every 24 h until 103 °C and then exposed to 120 °C for 10 h. This procedure was designed to prevent physical damage to the fragile wood and to ensure proper chemical reactions. The weight% gain (WPG) of the samples was calculated according to Ghavidel and Hosseinpourpia (2024), prior to the leaching test following EN 84 (1997).

Dimensional stability

The dimensional stability was determined by calculating the volumetric changes of the six dried samples after impression in water at 25 °C for three cycles. The cell wall bulking, maximum swelling ($\text{swell}_{\text{max}}$), and anti-swelling efficiency (ASE) of modified samples were then assessed after the third cycle following the methods explained previously by Xiao et al. (2012). The ASE and $\text{swell}_{\text{max}}$ were calculated for the samples after the leaching process.

Water vapor sorption analysis

Water vapor sorption behavior of the control and modified archaeological elm wood samples was analyzed by the automated dynamic vapor sorption (DVS) equipment (Q5000 SA, TA instruments). As described previously (Ghavidel et al. 2020), from each of these selected specimens about 20 mg of samples cut to approximately 2 mm length were exposed to relative humidity (RH) increment and decrement from 0, 5, 15, 25, 35, 45, 55, 65, 75, 85, and 95% RH, then reverted to 0% RH at a constant dm/dt of 0.001% for 10 min. The equilibrium moisture content (EMC) was calculated based on the mass at each given RH to the dried mass recorded at 0% RH.

Hydroxy group accessibility

Hydroxy accessibility was gravimetrically measured from thin wood samples with an automated sorption balance (DVS Advantage ET, Surface Measurement Systems, UK) with 0.1 μg accuracy. Prior to measurement, sample with a dry weight of 10–15 mg was soaked in D_2O in an air-tight container for one week. D_2O was replaced three times during the soaking to ensure all the accessible hydroxys were deuterated. During the measurements, the N_2 flow was kept at 200 sccm and the target temperature was 25 $^\circ\text{C}$. Automated sorption balance measurement consisted of a four-step sequence (Fig. 1): (I) expose pre-deuterated wood samples to D_2O vapor at 95% target RH for 12 h; (II) drying under N_2 flow for 24 h; (III) exposure to H_2O vapor at 95% target RH for 12 h; (IV) drying under N_2 flow for 24 h. Figure 1 shows the changes in mass (mg) of one wood sample (02) as a function of time (h).

The equation for calculating hydroxy accessibility OH_{acc} (Kyyrö et al. 2021):

$$\text{OH}_{\text{acc}} = 1000 \times (m_{\text{OD}} - m_{\text{OH}}) / (\Delta M \times m_{\text{OH}})$$

where m_{OD} and m_{OH} are the mass of wood samples and the end on OD and OH steps, and ΔM is the atomic mass difference between deuterium and protium (1.006 g mol^{-1}).

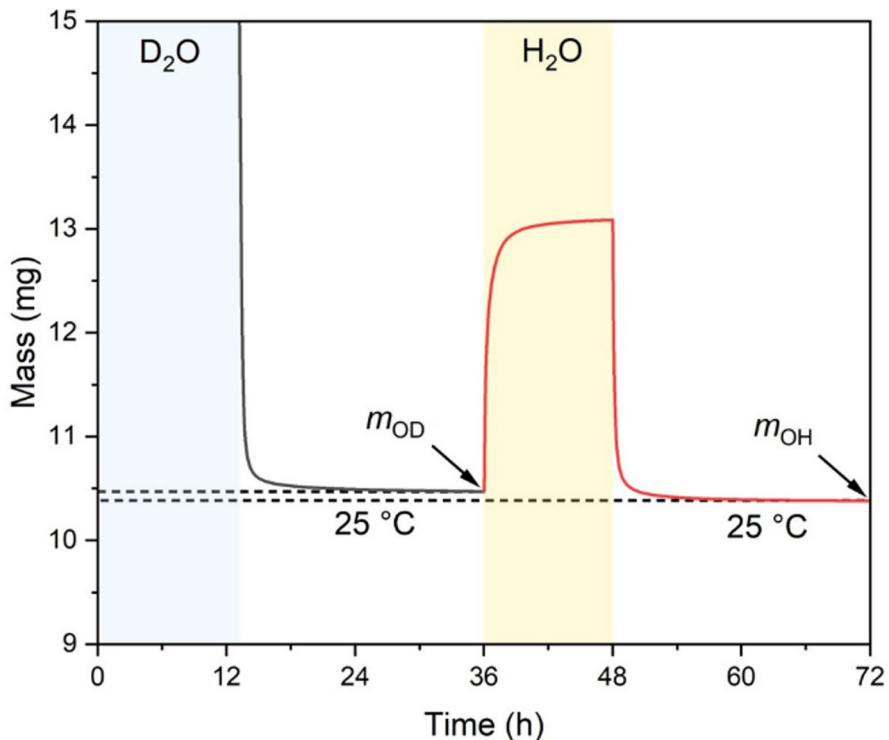


Fig. 1 Changes in mass (mg) of control wood sample as a function of time

Confocal Raman analysis

Cross sections with a thickness of ca. 40 μm were prepared with a rotary microtome (Nahita ZFP011, Auxilab, Spain). The sections were placed on glass slides in a droplet of deionized water, covered with a quartz coverslip (1 mm thickness), and sealed with nail polish. Images were collected with a confocal Raman microscope (Renishaw InVia Qontor) equipped with a 785 nm laser and a Centrus 05TJ55 CCD detector behind an 830 lines/mm grating. The measurements were conducted within the spectral range between 400 and 1800 cm^{-1} using an integration time of 0.3 s and a 50 $\times$ objective. Raman images of fiber cells were measured with 220 lines per image and 220 points per line at a step size of 0.3 μm .

Scanning electron microscopy

10 $\times$ 10 $\times$ 10 mm³-sized samples of archaeological elm wood were used for both unmodified and modified samples. Before imaging, the surface was sliced using a razor blade. No sputter coater was used to coat the surfaces of the samples. SEM imaging was conducted using a Hitachi S-3400 N type of equipment with a vacuum of 70 Pa and an accelerating voltage of 10 kV. One sample from each group was used for SEM imaging, and several images were taken from different areas of each sample.

Statistical analysis

To determine the statistical differences between the dimensional stability of modified and control samples, a one-way analysis of variance (ANOVA) was performed using the IBM SPSS statistical software, version 26 (IBM Corporation, New York, USA). Duncan's multiple-range test was also used to analyze the significant differences between the samples at a 0.05 significance level.

Results and discussions

Changes in dimensional stability

Figure 2 shows the weight and dimensional changes of archaeological elm samples after humination. The weights of the samples were obviously increased after humination (Fig. 2a). The presence of crosslinker significantly increased the WPG values as compared to the solely huminated samples, although the differences in WPG values of samples modified with HSA-1% and HSA-3% were statistically insignificant (ANOVA, $\alpha=0.05$). This increase is attributed to the chemical role of SA in fixing the humins within the wood structure. A similar trend was observed after the leaching test, even though a strong discharge of humins with about 40% occurred in almost all samples. The dimensional changes of huminated wood were evaluated by means of maximum swelling, Anti-swelling efficiency, and bulking (Fig. 2b–d). The $\text{swell}_{\text{max}}$ indicates the ability of wood cells to reach their maximum expansion margin. Figure 2b, illustrated that the humination considerably decreased the $\text{swell}_{\text{max}}$

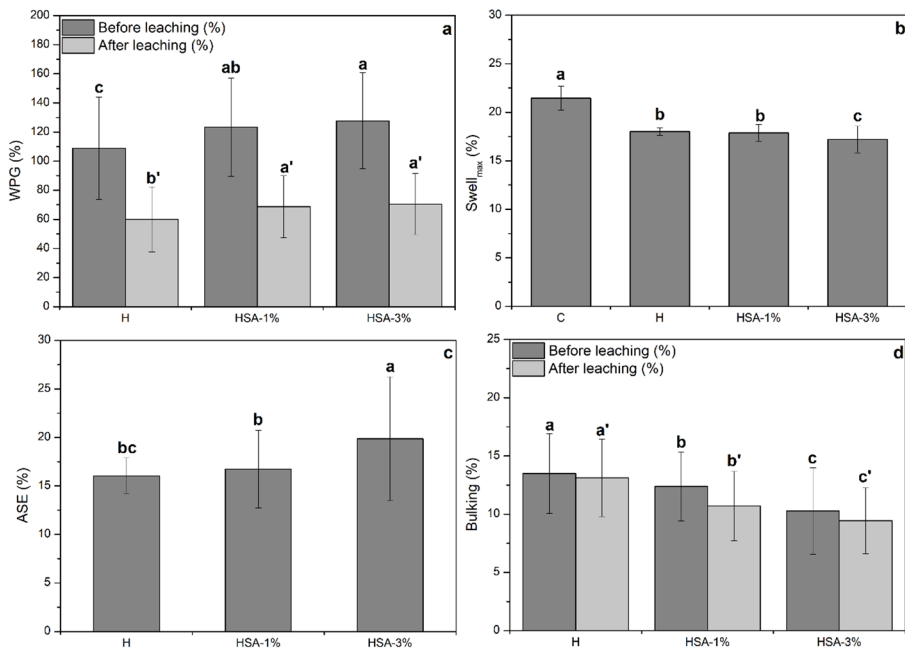


Fig. 2 WPG (a), maximum swelling (b), ASE (c), and bulking (d) of unmodified and huminated archaeological elm wood. Different superscript letters indicate a significant difference between the samples with varying solutions of humination at $p < 0.05$ level

in archaeological samples from 21.4% in unmodified archaeological elm to 17.8%, 18.0%, and 17.1% in H, HSA-1%, and HSA-3% modified samples, respectively. The anti-swelling efficiency (ASE), as a resistance reflector of wood cell walls to swell, increased from 16.1% in solely huminated samples to 16.7% in HSA-1% and 19.8% in HSA-3% (Fig. 2c). The significant improvement in dimensional stability, as demonstrated by the high ASE values, is a critical outcome for the conservation of dry archaeological wood. This type of wood is often structurally compromised, with weakened cell walls and pre-existing micro-cracks from centuries of aging and degradation. When such fragile wood absorbs ambient moisture during periods of high relative humidity, it swells. This swelling generates significant internal stresses within the delicate wood structure. In a degraded matrix, these stresses can easily lead to the propagation of existing cracks and the formation of new ones, causing irreversible physical damage. The repeated cycles of swelling and shrinking due to natural environmental fluctuations induce a form of mechanical fatigue, which progressively weakens the object over time (Broda et al. 2021a). Therefore, a treatment that effectively reduces swelling is highly desirable because it minimizes the wood's dimensional response to humidity changes. By stabilizing the wood, the humination treatment helps to preserve the physical integrity of the artifact and protect it from this primary mode of long-term deterioration. The cell wall bulking was apparently increased by humination (Fig. 2d), showing the incorporation of the humins solution in the wood cell walls. The highest cell wall bulking value of 13.5% was obtained in the solely huminated sample, followed by 12.4% in HSA-1% and 10.3% in HSA-3%.

Although the bulking was slightly decreased after leaching, the trend was similar to the unleached samples. The decrement of bulking value with increasing the cross-linker level from 1 to 3% might be attributed to the formation of more crosslinked structure through esterification reaction between carboxyl groups of SA and available hydroxy groups in humins and also wood cell wall (Sangregorio et al. 2019), which resulted in reducing the ability of cell wall for physical expansion.

Moisture sorption behavior

The sorption isotherms and hysteresis of archaeological elm samples as a function of humins modifications were shown in Fig. 3a, b. The EMC values of humined samples were considerably lower than the unmodified samples throughout the entire RHs. EMC at 95% RH decreased from 23.7% in unmodified samples to 15.4%, 7.3%, and 8.7% in the samples respectively modified with H, HSA-1%, and HSA-3%. (Esteban et al. 2010), and (Guo et al. 2018) reported previously that when the hemicelluloses in archaeological wood degraded, it also resulted in a decrease in the crystallinity index of cellulose and the length of the crystalline regions, which led to the appearance of new sorption sites. It is thus assumed that the higher EMC value of archaeological wood is related to its degraded structure and increased porosity from long-term environmental exposure. The cleavage of cell wall polymers creates more accessible hydroxy groups and voids, making it prone to adsorbing and desorbing moisture, which leads to greater dimensional changes, posing preservation challenges (Ghavidel et al. 2020, 2021a, b). The huminated samples in the presence of a crosslinker (SA) showed more straight adsorption lines with invisible upward bends at around 60–70% RH. The EMC value of HSA-3% at 95% RH was slightly higher than the HSA-1%, which can be due to a slight degradation of the cell wall matrices at the higher concentration of succinic acid. Similar result was reported previously in wood modified with proton acid at high temperatures (Hosseinpourpia et al. 2017).

The sorption hysteresis of archaeological elm samples was considerably reduced by humination modification (Fig. 3b). Sorption hysteresis explains the physical differences that occur in the wood matrix during the relaxation process to adsorb or desorb water molecules (Hosseinpourpia et al. 2017). Hosseinpourpia and co-workers (2020)

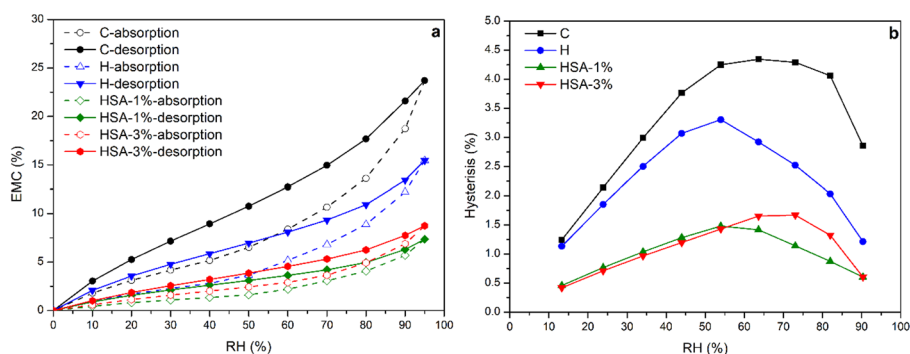


Fig. 3 Moisture sorption isotherms (a) and hysteresis (b) of unmodified and modified archaeological elm at a given RH level

previously discussed that the extent of these physical differences is highly affected by the stiffness of the cell wall matrices after different modification processes. It is assumed that the hysteresis reduction in the resin-modified wood is related to the filling of the cell wall pores due to the bulking, which freezes the cell wall in a pre-swollen state, and thus limits the dynamics of the cell walls to response to the RH changes (Hosseinpourpia et al. 2020). The sorption hysteresis was increased by increasing the RH in the solely huminated sample until 55% RH and then drastically decreased. The huminated samples in the presence of crosslinker (HSA-1% and HSA-3%), however, resulted in a more pronounced reduction in hysteresis. This might be due to the combination of bulking effect and reduction in the flexibility of the cell wall, presumably by the formation of a rigid crosslinked structure with cell wall polymers. Similar behavior was reported previously in wood modified with formaldehyde (Himmel and Mai 2015). SA contains carboxyl groups ($-\text{COOH}$), which can contribute to promoting the crosslinking reaction of humins with the hydroxy groups ($-\text{OH}$) of cell wall polymers through an esterification reaction.

Hydroxy accessibility

The control and HSA-3% wood samples were first exposed to D_2O vapor at 95% relative humidity (RH), and then dried under a dry N_2 flow to remove any excess moisture. After that, the samples were re-exposed to H_2O vapor at the same humidity level (95% RH) to restore protons and were dried again. The difference in mass between the initial and final drying phases helped determine how many OH groups were accessible to water vapor, which reflected the level of deuteration that occurred during the process. As shown in Table 1, the hydroxy accessibility of HSA-3% dropped considerably compared to the unmodified control samples, as a rather direct consequence of the chemical interaction between the treatment and the wood polymers. As Ghavidel and Hosseinpourpia (2024) noted, both SA and humins can interact with hemicellulose and cellulose, reducing the availability of hydroxy groups, but they have a lesser effect on lignin.

Hydroxy accessibility is a key factor in how wood absorbs moisture, as the presence of these groups determines how the wood interacts with water. Huminations that reduce hydroxy accessibility, like chemical modifications or heat huminations, can make the wood less hygroscopic, which enhances its dimensional stability. For instance, processes like hot water extraction and acetylation reduce hydroxy accessibility by either removing or altering hemicellulose. This reduction in hydroxy groups leads to lower moisture content and minimizes the dimensional changes the wood undergoes when exposed to different humidity levels (Altgen et al. 2018; Kyyrö et al. 2021).

Table 1 Hydroxyl accessibility of control and modified archaeological elm wood samples

Sample	OH accessibility (mmol g^{-1})*
Control	8.54 (± 0.02)
HSA-3%	7.08 (± 0.97)

*The data is an average of two measurements

Micro-chemical analysis

The micro-chemical properties of archaeological elm wood before and after humination was performed by SEM and Confocal-Raman spectroscopy. The SEM images of the cross-section of the samples are demonstrated in Figs. 4 and 5 with 500X and 100X magnifications, respectively. Before the humination the natural pores such as vessels were well visible while, after humination of wood samples, the volume of void spaces in the latewood structure and some of the lumens in the earlywood structure were completely filled by humins (red arrows) indicating the high interaction with the wood cells. Figures 4 and 5 (blue arrows in figures c and d) illustrate that a bulk deposition gives the treated wood a denser and more consolidated appearance, an effect that becomes more pronounced with increasing crosslinker concentration. The SEM graphs confirmed the obvious changes in the microstructure of archaeological elm after humination modification.

A closer examination of the SEM images reveals some degree of cell deformation in the treated specimens. This phenomenon is likely a result of the thermal curing process and the thermal stress applied to the treated wood (Boonstra et al. 2006).

In confocal Raman spectroscopy imaging, numerous Raman spectra are obtained from the sample, creating a map where each pixel represents a distinct spectrum. The control and modified samples with different concentrations of SA were mapped and the average spectra were extracted from the cell walls region. The spectra displayed

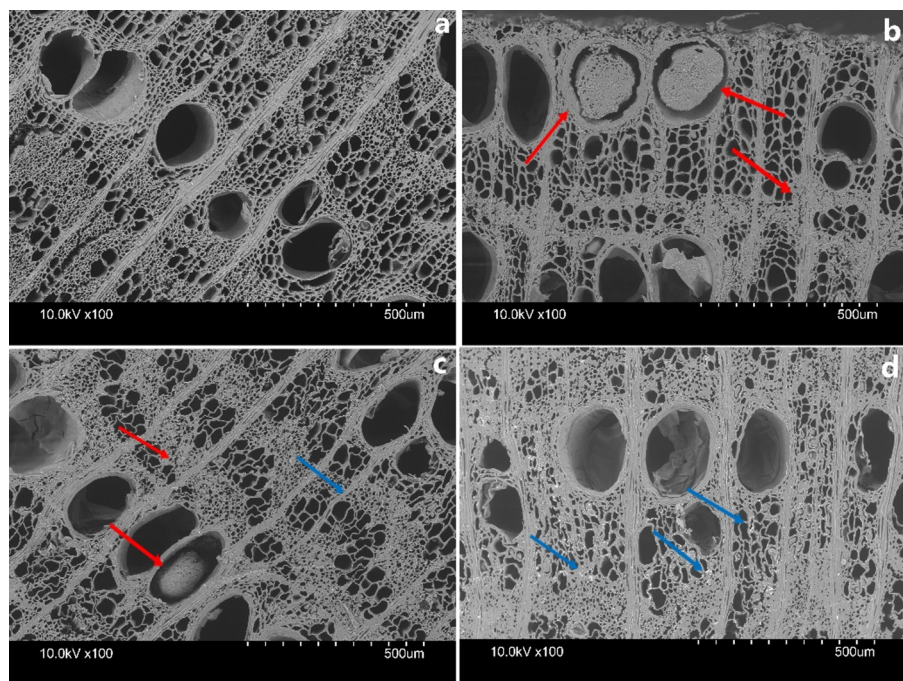


Fig. 4 Scanning electron microscopy (SEM) micrographs from cross-sections at 100-times magnification of unmodified (a), H (b), HSA-1% (c) and HSA-3% (d) archaeological elm wood. Arrows indicate the presence of humins (red arrows) and SA (blue arrows) (color figure online)

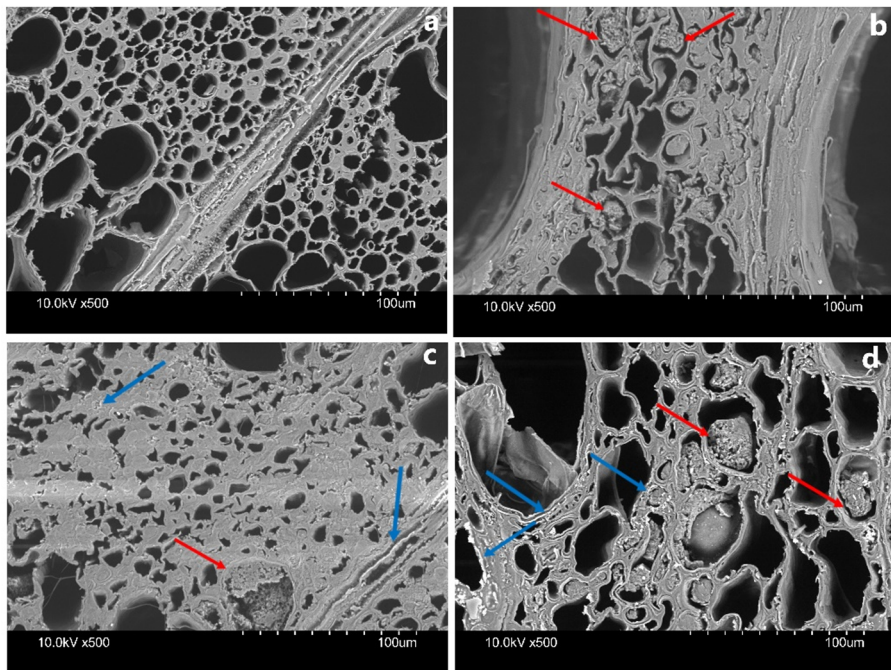


Fig. 5 Scanning electron microscopy (SEM) micrographs from cross-sections at 500-times magnification of unmodified (a), H (b), HSA-1% (c) and HSA-3% (d) archaeological elm wood. Arrows indicate the presence of humins (red arrows) and SA (blue arrows) (color figure online)

characteristic features of wood, highlighting contributions from cellulose and lignin (Fig. 6). However, in modified samples with humins and SA, a peak at 1520 cm^{-1} was found which belongs to the $\text{C}=\text{C}$ in the furan ring (Ghavidel and Hosseinpourpia 2024; Kim et al. 2011). Besides, another peak at 1560 cm^{-1} in modified samples with humins and crosslinker was shown. This peak can be related to the double bond in the furfural structure of humins (Kim et al. 2011). The presence of a furan peak in the Raman spectra of wood indicates the formation or introduction of furanic compounds, which are associated with humins. This observation suggests that the humins successfully penetrated into the cell walls of wood, particularly under conditions where humins are introduced. The detection of this peak is a clear sign to confirm that the humins have chemically interacted with the wood matrix, embedding themselves within the cell walls and potentially altering the physical and chemical properties of wood. The presence of humins in the cell walls by presenting the peak at 1520 cm^{-1} is shown in the Raman mapping image (Fig. 7).

The results indicate that humination modification demonstrated a semi-active mechanism where small humin molecules infiltrated the wood cell walls. The confocal Raman results indicate that infiltration of wood cell walls with humin, most probably the ones with the lower molecular weights, while larger molecules predominantly accumulated in the middle lamellae, as demonstrated by SEM imaging. Confocal Raman spectroscopy indicates that. This dual distribution mechanism, combining physical lumen-filling with chemical cell wall modification, distinguishes the humin-

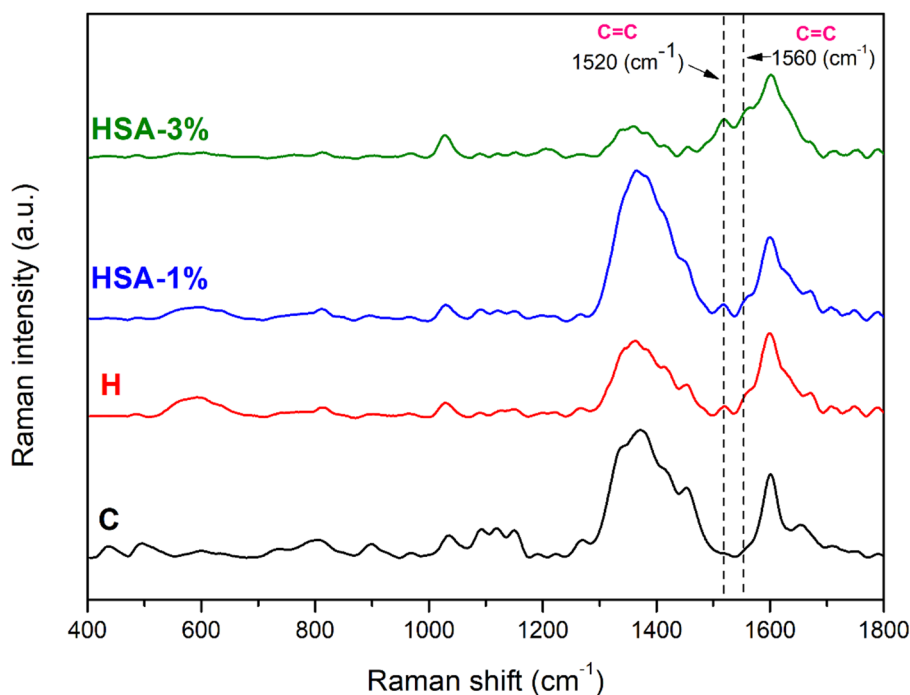


Fig. 6 Raman spectra of archaeological elm wood modified with humins and succinic acid

based approach from conventional conservation treatments. Unlike PEG, which acts primarily as a passive, hygroscopic bulking agent relying on weaker physical interactions (Jeremic et al. 2007), the humin-SA system forms a stable, hydrophobic, and covalently crosslinked network. Furthermore, while silicon-based consolidants create a rigid inorganic scaffold (Broda et al. 2019), the method of humin-SA achieves a more intimate chemical integration by forming direct ester bonds between the organic humin polymer and the cell wall components of wood. This active, chemically grafted modification therefore represents a potentially more durable strategy for consolidating and stabilizing dry archaeological wood compared to traditional methods. The addition of SA as a crosslinker significantly promoted the curing process by promoting esterification reactions between the carboxyl groups in humins and the hydroxy groups of wood polymers (Ghavidel et al. 2025), which enhanced the rigidity of the cell walls and further stabilizing the humin in the wood structure (Ghavidel et al. 2025). This was evident in the enhanced ASE and reduced EMC values of the huminated samples crosslinked with SA, which occurred by reducing the possibility of water being accommodated in the cell walls through hindered swelling ability (Ghavidel et al. 2025).

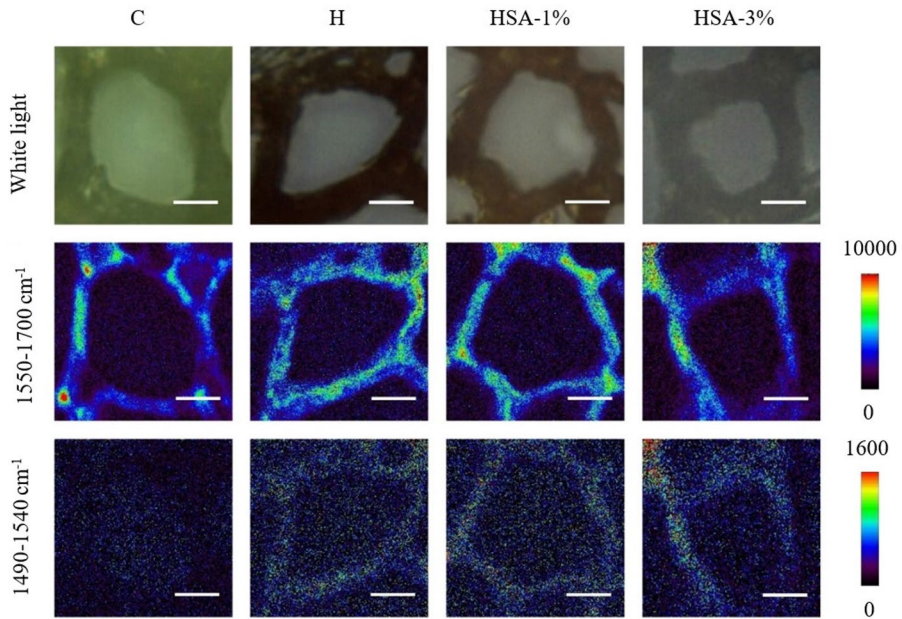


Fig. 7 Raman mapping images on the cross sections of control and modified archeological elm wood samples

Conclusion

The humination modification significantly enhanced the hydrophobicity of archaeological elm wood by improving dimensional stability and reducing moisture adsorption and desorption. The addition of succinic acid (SA) as a crosslinker amplified the effectiveness of the humination process, with higher SA concentrations promoting the formation of a more crosslinked structure. The observed improvements in anti-swelling efficiency (ASE) and equilibrium moisture content (EMC) reduction underscore the potential of humins as a viable conservation material. Micro-chemical analyses, including Raman spectroscopy and SEM imaging, confirmed the successful integration of humins into the wood cell walls and lumina, highlighting their role in improving wood-water relationships. These results suggest that humination, as a semi-active modification, enhances wood properties through a combination of physical incorporation and chemical bonding. While the crosslinking reaction with SA increases stabilization, the process retains the flexibility typical of semi-active modifications, distinguishing it from fully active methods like acetylation or furfurylation. The findings demonstrate that humination modification is a promising alternative to traditional conservation methods such as polyethylene glycol (PEG), offering improved resistance to moisture-induced degradation while maintaining the structural integrity of archaeological wood.

Acknowledgements The authors acknowledge Avantium Renewable Polymers B.V. (Amsterdam, the Netherlands) for providing the humins. Reza Hosseinpourpia acknowledges the support from the Knowl-

edge Foundation through the project ‘Competitive timber structures - Resource efficiency and climate benefits along the wood value chain through engineering design’ (grant number 20230005).

Author contributions A.G., Data curation, Formal analysis, Investigation, Writing– original draft, Writing– review and editing. S.W., Formal analysis, Writing– review and editing. M.B., Formal analysis, Writing– review and editing. L.R., Writing– review and editing. R.H., Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing– original draft, Writing– review and editing. All authors reviewed the manuscript.

Funding Open access funding provided by Linnaeus University. This article is funded by Knowledge Foundation (20230005).

Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Almkvist G, Persson I (2008) Degradation of polyethylene glycol and hemicellulose in the Vasa. 62:64–70. <https://doi.org/10.1515/HF.2008.009>
- Altgen M, Willems W, Hosseinpourpaj R, Rautkari L (2018) Hydroxyl accessibility and dimensional changes of Scots pine sapwood affected by alterations in the cell wall ultrastructure during heat-treatment. *Polym Degrad Stab* 152:244–252. <https://doi.org/10.1016/j.polymdegradstab.2018.05.005>
- Boonstra MJ, Rijdsdijk JF, Sander C, Kegel E, Tjeerdsma B, Militz H, Van Acker J, Stevens M (2006) Microstructural and physical aspects of heat treated wood. PART 1. Softwoods. *Maderas Cienc Tecnol* 8:193–208. <https://doi.org/10.4067/S0718-221X2006000300006>
- Braovac S, Kutzke H (2012) The presence of sulfuric acid in alum-conserved wood– Origin and consequences. *J. Cult. Herit. Wood Sci Conserv* 13:S203–S208. <https://doi.org/10.1016/j.culher.2012.02.002>
- Broda M, Mazela B, Dutkiewicz A (2019) Organosilicon compounds with various active groups as consolidants for the preservation of waterlogged archaeological wood. *J Cult Herit Mod Contemp Art* 35:123–128. <https://doi.org/10.1016/j.culher.2018.06.006>
- Broda M, Dąbek I, Dutkiewicz A, Dutkiewicz M, Popescu C-M, Mazela B, Maciejewski H (2020) Organosilicons of different molecular size and chemical structure as consolidants for waterlogged archaeological wood– a new reversible and retreatable method. *Sci Rep* 10:2188. <https://doi.org/10.1038/s41598-020-59240-8>
- Broda M, Curling SF, Frankowski M (2021a) The effect of the drying method on the cell wall structure and sorption properties of waterlogged archaeological wood. *Wood Sci Technol* 55:971–989. <https://doi.org/10.1007/s00226-021-01294-6>
- Broda M, Spear MJ, Curling SF, Ormondroyd GA (2021b) The viscoelastic behaviour of waterlogged archaeological wood treated with Methyltrimethoxysilane. *Materials* 14:5150. <https://doi.org/10.3390/ma14185150>

- Constant S, Lancefield CS, Weckhuysen BM, Bruijninx PCA (2017) Quantification and classification of carbonyls in industrial Humins and lignins by 19F NMR. *ACS Sustain Chem Eng* 5:965–972. <https://doi.org/10.1021/acssuschemeng.6b02292>
- EN 84 (1997) Wood preservatives - Accelerated aging of treated wood prior to biological testing-Leaching procedure. European Committee for Standardization, Brussels, Belgium
- Esteban LG, de Palacios P, García Fernández F, García-Amorena I (2010) Effects of burial of *Quercus* spp. Wood aged 5910 ± 250 BP on sorption and thermodynamic properties. *Int Biodeterior Biodegrad* 64:371–377. <https://doi.org/10.1016/j.ibiod.2010.01.010>
- Filiciotto L, Balu AM, Van der Waal JC, Luque R (2018) Catalytic insights into the production of biomass-derived side products methyl levulinate, furfural and humins. *Catal. Today, Selected Contributions to the Symposium on Catalysts & Catalytic Technologies for Conversion of Biomass & Its Derivatives* (252nd ACS Meeting and Exposition, Philadelphia, PA) 302:2–15. <https://doi.org/10.1016/j.cattod.2017.03.008>
- Ghavidel A, Hosseinpourpia R (2024) Photodegradation stability of huminated European pine (*Pinus sylvestris* L.) microveneers. *Holzforschung* 78:283–292. <https://doi.org/10.1515/hf-2024-0006>
- Ghavidel A, Hosseinpourpia R, Militz H, Vasilache V, Sandu I (2020) Characterization of archaeological European white elm (*Ulmus laevis* P.) and black Poplar (*Populus Nigra* L). *Forests* 11:1329. <https://doi.org/10.3390/f1121329>
- Ghavidel A, Bak M, Hofmann T, Vasilache V, Sandu I (2021a) Evaluation of some wood-water relations and chemometric characteristics of recent oak and archaeological oak wood (*Quercus robur*) with archaeometric value. *J Cult Herit* 51:21–28. <https://doi.org/10.1016/j.culher.2021.06.011>
- Ghavidel A, Hosseinpourpia R, Gelbrich J, Bak M, Sandu I (2021b) Microstructural and chemical characteristics of archaeological white elm (*Ulmus laevis* P.) and Poplar (*Populus* spp). *Appl Sci* 11:10271. <https://doi.org/10.3390/app112110271>
- Ghavidel A, Eceiza A, Xie X, Hosseinpourpia R (2025) Humination modification: a green approach to improve the material properties of Scots pine (*Pinus sylvestris* L.) sapwood. *ACS Omega* 10(3):2996–3005. <https://doi.org/10.1021/acsomega.4c09540>
- Gjelstrup Björndal C (2012) Microbial degradation of waterlogged archaeological wood. *J Cult Herit Wood Sci Conserv* 13:S118–S122. <https://doi.org/10.1016/j.culher.2012.02.003>
- Guo J, Zhou H, Stevanic JS, Dong M, Yu M, Salmén L, Yin Y (2018) Effects of ageing on the cell wall and its hygroscopicity of wood in ancient timber construction. *Wood Sci Technol* 52:131–147. <https://doi.org/10.1007/s00226-017-0956-z>
- Himmel S, Mai C (2015) Effects of acetylation and formalization on the dynamic water vapor sorption behavior of wood. *Holzforschung* 69:633–643. <https://doi.org/10.1515/hf-2014-0161>
- Hoang TMC, Lefferts L, Seshan K (2013) Valorization of Humin-Based byproducts from biomass Processing—A. *Route Sustainable Hydrogen ChemSusChem* 6:1651–1658. <https://doi.org/10.1002/cssc.201300446>
- Hocker E, Almkvist G, Sahlstedt M (2012) The *Vasa* experience with polyethylene glycol: a conservator's perspective. *J Cult Herit Wood Sci Conserv* 13:S175–S182. <https://doi.org/10.1016/j.culher.2012.01.017>
- Hosseinpourpia R, Adamopoulos S, Holstein N, Mai C (2017) Dynamic vapour sorption and water-related properties of thermally modified Scots pine (*Pinus sylvestris* L.) wood pre-treated with proton acid. *Polym Degrad Stab* 138:161–168. <https://doi.org/10.1016/j.polymdegradstab.2017.03.009>
- Hosseinpourpia R, Adamopoulos S, Walther T, Naydenov V (2020) Hydrophobic formulations based on tall oil distillation products for High-Density fiberboards. *Materials* 13:4025. <https://doi.org/10.3390/ma13184025>
- Jeremic D, Cooper P, Brodersen P (2007) Penetration of poly(ethylene glycol) into wood cell walls of red pine 61:272–278. <https://doi.org/10.1515/HF.2007.068>
- Kim T, Assary RS, Curtiss LA, Marshall CL, Stair PC (2011) Vibrational properties of levulinic acid and Furan derivatives: Raman spectroscopy and theoretical calculations. *J Raman Spectrosc* 42:2069–2076. <https://doi.org/10.1002/jrs.2951>
- Kyyrö S, Altgen M, Seppäläinen H, Belt T, Rautkari L (2021) Effect of drying on the hydroxyl accessibility and sorption properties of pressurized hot water extracted wood. *Wood Sci Technol* 55:1203–1220. <https://doi.org/10.1007/s00226-021-01307-4>
- Mija A, van der Waal JC, Pin J-M, Guigo N, de Jong E (2017) Humins as promising material for producing sustainable carbohydrate-derived Building materials. *Constr Build Mater* 139:594–601. <https://doi.org/10.1016/j.conbuildmat.2016.11.019>

- Pin J-M, Guigo N, Mija A, Vincent L, Sbirrazzuoli N, van der Waal JC, de Jong E (2014) Valorization of biorefinery Side-Stream products: combination of Humins with polyfurfuryl alcohol for composite elaboration. *ACS Sustain Chem Eng* 2:2182–2190. <https://doi.org/10.1021/sc5003769>
- Popescu C-M, Broda M (2021) Interactions between different organosilicons and archaeological water-logged wood evaluated by infrared spectroscopy. *Forests* 12:268. <https://doi.org/10.3390/f12030268>
- Sangregorio A, Guigo N, van der Waal JC, Sbirrazzuoli N (2018) Humins from biorefineries as thermo-reactive macromolecular systems. *Chemsuschem* 11:4246–4255. <https://doi.org/10.1002/cssc.201802066>
- Sangregorio A, Guigo N, de Jong E, Sbirrazzuoli N (2019) Kinetics and chemorheological analysis of Cross-Linking reactions in Humins. *Polymers* 11:1804. <https://doi.org/10.3390/polym11111804>
- Sangregorio A, Muralidhara A, Guigo N, Thygesen LG, Marlair G, Angelici C, de Jong E, Sbirrazzuoli N (2020) Humin based resin for wood modification and property improvement. *Green Chem* 22:2786–2798. <https://doi.org/10.1039/C9GC03620B>
- van Zandvoort I, Wang Y, Rasrendra CB, van Eck ERH, Bruijninx PCA, Heeres HJ, Weckhuysen BM (2013) Formation, molecular structure, and morphology of Humins in biomass conversion: influence of feedstock and processing conditions. *Chemsuschem* 6:1745–1758. <https://doi.org/10.1002/cssc.201300332>
- Wagner L, Almkvist G, Bader TK, Bjurhager I, Rautkari L, Gamstedt EK (2016) The influence of chemical degradation and polyethylene glycol on moisture-dependent cell wall properties of archeological wooden objects: a case study of the Vasa shipwreck. *Wood Sci Technol* 50:1103–1123. <https://doi.org/10.1007/s00226-016-0861-x>
- Xiao Z, Xie Y, Adamopoulos S, Mai C (2012) Effects of chemical modification with glutaraldehyde on the weathering performance of Scots pine sapwood. *Wood Sci Technol* 46:749–767. <https://doi.org/10.1007/s00226-011-0441-z>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Authors and Affiliations

Amir Ghavidel¹ · Shennan Wang² · Miklós Bak³ · Lauri Rautkari² · Reza Hosseinpourpia^{4,5}

✉ Reza Hosseinpourpia
reza.hosseinpourpia@lnu.se

¹ School of Engineering, University of Northern British Columbia, 499 George St., Prince George, BC V2L1R7, Canada

² Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Espoo 02150, Finland

³ Faculty of Wood Engineering and Creative Industries, University of Sopron, Sopron, Hungary

⁴ Department of Forestry and Wood Technology, Linnaeus University, Lückligs Plats 1, Växjö 351 95, Sweden

⁵ College of Forest Resources and Environmental Science, Michigan Technological University, Houghton, MI 49931, USA