

Conference paper

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Hybrid nanocomposites made of diol-modified silanes and nanostructured calcium hydroxide. Applications to Alum-treated wood

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Abstract: The alum-treated Viking Age archaeological wooden objects from the Oseberg find have undergone extensive chemical deterioration due to the original conservation treatment, based on alum salts ($KAl(SO_4)_2 \cdot 12H_2O$), done in the early 1900s. Today, the artifacts are highly acidic ($pH \leq 2$) and fragile; in some cases wood has almost completely lost its structural integrity. Research on conservation methods for these finds is currently underway. In the present study, organic/inorganic multi-functional ‘hybrid systems’ – using propylene glycol modified TEOS and alkaline nanoparticles ($Ca(OH)_2$) – have been engineered to deacidify and consolidate alum-treated wood in a single step. The advantage of using silicon monomer and nano-materials as a starting point resides in their ease of penetration into the wood structure, where silicon monomers subsequently undergo polymerization. Treated samples were investigated using thermal analysis (DTG), X-Ray Diffraction (XRD), infrared spectroscopy (ATR-FTIR), SEM/EDX and Gas Chromatography Mass Spectroscopy (GC-MS). Results suggest that in addition to consolidating the wood, alkoxy silanes could act as a bridging agent between remaining lignin and calcium hydroxide nanoparticles.

Keywords: alkaline nanoparticles; alum salt; archaeological wood; hybrid systems; in situ polymerization; Oseberg finds; pH control; POC-16.

Introduction

Archeological wood is not only threatened by biological degradation. Chemical processes, initiated by environmental conditions or by chemical compounds present in the wood, may also cause decay processes. Norway owns one of the world’s most important archeological finds: the Oseberg find. Unfortunately, a large part of the wooden objects is threatened by an ongoing deterioration process caused by a conservation treatment known as the “alum treatment”, which was applied in the early 20th century. The waterlogged wooden

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fragments were immersed in concentrated solutions of alum (potassium aluminum sulfate) heated to 90 °C. Before reconstruction into whole objects, fragments were impregnated with linseed oil, and then pieced together using metal screws, pins, fills and modern wood. Fragments which were not reconstructed into objects are in the museum stores and may or may not contain linseed oil.

From the treatments it was envisioned that the salt would penetrate into the waterlogged wood, replacing the existing water. Upon cooling, the recrystallized alum would have supported the wood structure. However, alum did not penetrate in depth, leaving the inner core unconserved. This resulted in mechanical stress during drying, leading to the formation of inner cracks and voids.

In 2014, the Museum of Cultural History launched the project “Saving Oseberg” with the aim of developing methods to preserve these unique, fragile artifacts. One of the most threatening factors was found to be the very high acidity of the wood ($\text{pH} \leq 2$) [1]. The source of the acidity originated from the alum-treatment itself: heating of the alum solution generated sulfuric acid, which was subsequently absorbed by the wood. This initiated the hydrolysis of the remaining cellulose and caused extensive oxidation of the lignin structure, which eventually resulted in the loss of wood structural integrity [2].

Re-treatment of the objects requires a twofold effect: the reduction of acidity and the strengthening of wood. Due to the high fragility of the objects, it is of paramount importance to minimize the number of applications and reduce the risk of irreversible damage.

We reported in a previous study the use of calcium hydroxide nanoparticles dispersed in isopropanol in order to increase the pH of alum-treated wood samples [3]. Moreover, silica sols, hybridized with lignin, have been previously investigated by Telysheva et al. [4], and used to increase the mechanical strength of wood.

Our previous experiments carried out on this wood used hybrid systems made of TEOS (tetraethyl orthosilicate) and calcium hydroxide nanoparticles in order to deacidify and consolidate alum-treated wood in a single step. However, these systems gelled after only few hours of treatment, thus preventing complete impregnation. This rapid gelation was due to the high acidity of the wood and to the large amount of water released in the consumption of calcium hydroxide by the sulfuric acid to form the calcium sulfate. Thus, the strategy had to be changed. Moreover, during hydrolysis, for each monomer of TEOS four molecules of ethanol were released that can dissolve many of organic compounds of the wood, damaging the sample. In order to avoid drawbacks in using TEOS and to significantly slow down the hydrolysis reaction, ethoxy side chains were replaced by propylene glycol, as its size screens the silicon atom, rendering it less accessible to a nucleophilic attack.

In this contribution, the combination of a specially designed ‘hybrid system’ composed of alkoxy silane monomers (Propylene Glycol Modified Silane, PGMS) and calcium hydroxide nanoparticles is investigated and tested. The research presented in this paper includes the synthesis and characterization of PGMS monomers, the formulation of the hybrid systems, and the results obtained following the application of the new hybrid systems on Oseberg samples.

Materials and methods

Chemicals

Four different hybrid systems were synthesized using the following chemicals (shown in Table 3): Nanorestore paper[®] Propanol 5, dispersion of $\text{Ca}(\text{OH})_2$ nanoparticles in 2-propanol supplied by CSGI, Florence (5 g/L); Propylene glycol (PG) ($\geq 99.5\%$ Aldrich); Tetraethyl orthosilicate (TEOS) (98% Sigma-Aldrich); Hydrochloric acid (HCl) (37% Fluka); (3-aminopropyl) triethoxysilane (APTES) ($\geq 98\%$ Sigma-Aldrich); Triethylamine (Et_3N) ($\geq 99\%$ Sigma-Aldrich); Poly(dimethylsiloxane) hydroxy terminated (PDMS-OH) (average $M_n \sim 550$, viscosity ~ 25 cSt, Sigma-Aldrich). All chemicals were used as received, without further purification.

Sample description and application method

The samples used in this study included alum-treated archeological wood from the Oseberg find, and sound oak, used as a reference in thermal analysis. The sample from Oseberg was treated with alum without the addition of linseed oil (cat.no. C55000/229-232). The wood was classified as diffuse porous, since it could not be identified further due to its high degree of deterioration. The sample was cut into $1.5 \times 1.5 \times 1.5 \text{ cm}^3$ cubes. Oseberg wood samples were treated with four different hybrid systems by soaking for 1 month. The treated samples were then left to dry for 2 weeks in a chamber maintained at 50% RH and 21 °C and characterized using the techniques described below.

Analytical techniques

Differential Thermo-Gravimetry (DTG) curves were recorded in dynamic, non-isothermal conditions, using a TA SDT Q600 instrument. Approximately 8–10 mg were exposed to the following experimental conditions: temperature range 30–1150 °C; heating rate 10 °C/min; N_2 flow 100 mL/min. The instrumental error is ± 1.5 °C.

Samples were analyzed by infrared spectroscopy, using the ATR unit of a Nicolet iS50 Thermo Fisher FT-IR spectrometer, containing a Zn/Se diamond crystal, at a resolution of 4 cm^{-1} (32 scans). Three spectra were taken from each sample before and after treatment with hybrid systems and averaged. The spectral range was $4000\text{--}400 \text{ cm}^{-1}$.

XRD analysis was carried out to evaluate the crystallinity of hybrid systems. Data were collected on a PANalytical Empyrean series two diffractometer equipped with a Cu-K α tube ($\lambda = 1.5418 \text{ \AA}$) and a PIXcelRD detector. Data were collected from 8° to 70° degrees, with 2θ step size of 0.0260, a time per step of 1497.6150 s. Dry samples were ground in an agate mortar to obtain a fine and homogeneous powder. PDF-4+ 2015 database was used for compound identification.

Wooden samples morphology was studied by SEM. Variable vacuum mode (70 Pa) was used. For EDS analyses, a voltage of 20.00 kV, and a spot size of six were used. Analyses have been performed on a FEI Quanta 450 instrument coupled with an Oxford X-Max^N 50 mm² detector. Samples for SEM-EDS were prepared from both untreated and treated woods by cutting approximately ca. 1 cm in length (along the fiber direction) and $3 \times 3 \text{ mm}$ in the transverse direction. For wood treated with hybrid systems, SEM-samples were extracted from the centre of the samples. SEM-samples, were mounted onto aluminum stubs using PELCO[®] conductive nickel paint and left to air dry overnight.

Extent of penetration into the wood was examined by comparing EDS elemental maps of samples taken from the centre of the treated sample.

Gas Chromatography Mass Spectroscopy (GC-MS) analysis of the samples were carried out using Shimadzu GCMS-QP2010 Ultra equipped with a low- to mid- polarity RTX – 20 column (30 m, 0.25 mm ID, 0.25 μm d_p). Helium was used as carrier gas and the temperature increased from 65 to 250 °C with a rate of 30 °C/min. The total running time for sample was 7.16 min. A 1 μL sample was injected using split mode. Mass spectra were recorded over 33–500 amu range, with electron impact ionization energy of 70 eV.

The chemical species were identified using NIST 11 mass spectra library. Quantitative determinations were made by correlating respective peak areas to the summed ion areas from the chromatogram.

Results and discussion

Synthesis of PGMS and preparation of the hybrid systems

Alkoxysilanes form, through a sol-gel-process, silanols that undergo condensations to produce highly condensed gels made of silica colloidal particles [5]. Propylene glycol modified silane (PGMS) was obtained through an alkoxy group exchange reaction between tetraethyl orthosilicate (TEOS) and propylene glycol

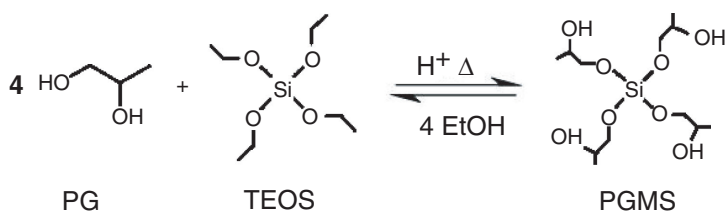


Fig. 1: Reaction between PG and TEOS, in the presence of an acid catalyst to generate PGMS.

(PG) (Fig. 1), following the synthesis method proposed by Yoshizawa [6]. TEOS and PG were mixed together, and the mixture was magnetically stirred at 80 °C for 1 h, resulting in the formation of a transparent solution. Hydrochloric acid was used as catalyst. Ethanol, which is produced during the trans-esterification reaction, was continuously removed by distillation over a Vigreux column. At the end of the reaction, excess of ethanol and tetraethyl orthosilicate were removed using a rotavapor.

In order to optimize the yield of PGMS, different stoichiometric ratios of PG, acid and TEOS were investigated (Table 1). The relative yield of PGMS was determined by GC-MS according to the equation: Yield (C) = $C/(A + B + C) \cdot 100$ in which A, B, C are the relative intensities of PG, TEOS and PGMS, respectively.

Ratio 2 with the highest PGMS yield (57%) was selected for further testing. In order to reduce the amount of hydrochloric acid, a second series was prepared and analyzed in the same way (Fig. 2). Results are shown in Table 2. Ratio 2.3 was chosen to use further given its best PGMS yield related to the quantity of acid.

The idea of using PGMS instead of TEOS relies on the different polymerization rate of these two monomers. The polymerization of TEOS is very fast in an acidic environment. The final result is the formation of very compact silica that fills the pores, strongly modifying the wood porosity. Given the PGMS' longer gelation

Table 1: Ratios of TEOS and PG used in PGMS synthesis.

Ratio	TEOS (Vol %)	PG (Vol %)	HCl (Vol %)	Vol ratio	PGMS yield (%)
1	44.4	55.4	0.2	0.9 : 1.1 : 0.004	51
2	49.9	49.9	0.2	1 : 1 : 0.004	57
3	61.4	38.4	0.2	1.2 : 0.8 : 0.004	56
4	68.4	31.4	0.2	1.4 : 0.6 : 0.004	55

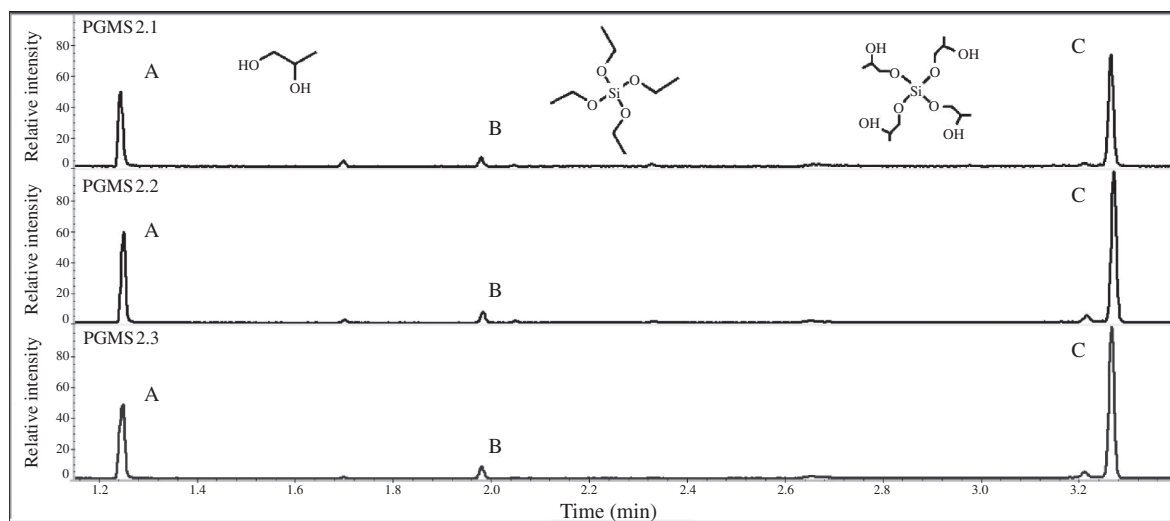


Fig. 2: Total ion chromatogram (TIC) of 2.1, 2.2, 2.3. Retention time: PG = 1.24 min; TEOS = 1.97 min; PGMS = 3.26 min.

Table 2: Different acid volumes applied to Ratio 2 of PGMS required.

Ratio	TEOS (Vol%)	PG (Vol%)	HCl (Vol%)	Vol ratio	PGMS yield (%)
2.1	49.9	49.9	0.2	1 : 1 : 0.004	57
2.2	49.9	49.9	0.1	1 : 1 : 0.002	59
2.3	49.9	49.9	0.01	1 : 1 : 0.0002	65

time at pH 2, which is approximately the same pH of alum treated wood, polymerization was observed after 1 month of soaking, allowing for full penetration of the monomer into the acidic wood samples [6].

Another issue is that when alkaline nanoparticles (NPs) are added to the PGMS mixture (at pH 4), they can be consumed before they are introduced to the wood. To prevent this it was necessary to increase the pH of PGMS solution (from 4 to 8) before adding NPs. In this way, the blend made of NPs and monomers of PGMS could penetrate more deeply and homogeneously before the onset of the polymerization reaction. As the acidity of this wood is slowly reduced by NPs (i.e. pH changing from 2 to 5.5) a simultaneous slow polymerization process of PGMS occurs within the wood, catalyzed by the acid it already contains. It can be considered complete after 2 months.

Three different compounds were tested to adjust the PGMS pH solution:

3-aminopropyl triethoxysilane (APTES), trimethylamine (Et_3N), and polydimethylsiloxane hydroxy terminated (PDMS). PDMS was also considered as it could form a more flexible 3D network [7]. Each pH adjuster was added dropwise to PGMS, under vigorous stirring for 1 h at RT; the final volumes used are shown in Table 3. All pH measurements were carried out by using pH strips.

Application of the hybrid system to the wood

It was hypothesized that interactions between the remaining lignin in the wood samples and the polymerized hybrid system would be possible due to the presence of significant amounts of carboxylic acid groups in the lignin. Interactions are likely both physical (adsorption) and may involve several types of chemical bonds such as hydrogen-, coordination- and covalent bonding, as well as acid-base interactions.

Penetration into the wood samples improved, since PGMS has a longer gelation time at pH 2 [6] and no solidification of the PGMS solution in the presence of the acidic wood samples was observed after 1 month. This was confirmed by both FTIR and SEM. Moreover, FTIR measurements indicated the formation of CaSO_4 through the neutralization reaction of sulfuric acid with alkaline nanoparticles [3]. This is shown in spectra of the Oseberg sample treated with hybrid systems by the presence of two bands at 659 cm^{-1} and 594 cm^{-1} , attributed to antisymmetric bending vibration modes of SO_4^{2-} (Fig. 3) [8]. The strongest peak at 1090 cm^{-1} was however difficult to assign due to overlap with the alum signal and symmetric stretching vibration of Si–O–Si found in the same region [8, 9].

As well, the peak found at 819 cm^{-1} , corresponding to the stretching mode of the O–Si–O bond, could confirm that hydrolysis of PGMS occurred in-situ [10, 11]. This could be also confirmed by the increase in absorbance of the peak at 1090 cm^{-1} , which is assigned to the symmetric stretching vibration of the Si–O–Si bonds [12].

Table 3: Formulations of hybrid systems used to treat the Oseberg samples.

	PGMS (Vol %)	NPs (5 g/L) (Vol %)	pH adjuster (Vol %)	Final pH	Vol ratio
PGMS : NPs	33	67	–	8	1 : 2
PGMS : NPs : APTES	33	66.92	0.08	8	1 : 2 : 0.002
PGMS : NPs : Et_3N	33	66.92	0.08	8	1 : 2 : 0.002
PGMS : NPs : PDMS	31	62.75	6.25	8	1 : 2 : 0.18

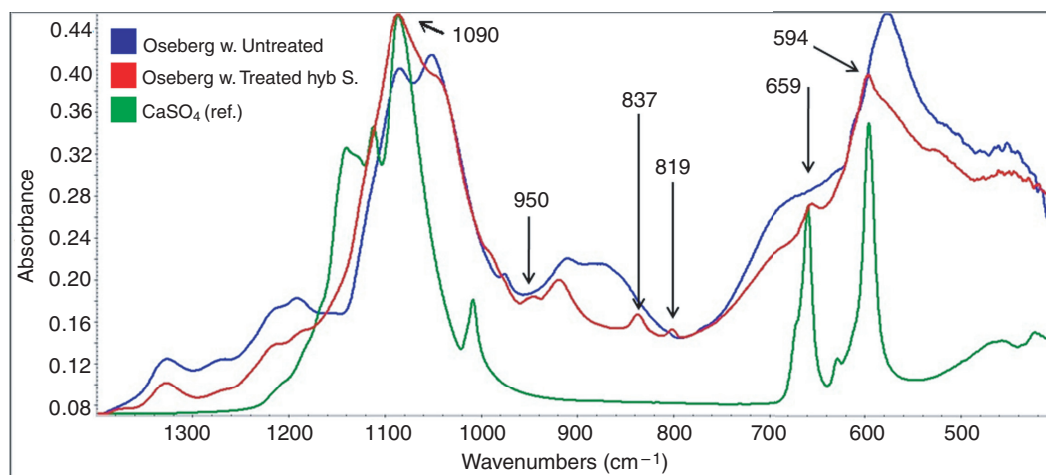


Fig. 3: Infrared spectra of the region 1400–400 cm^{-1} of the Oseberg sample before and after treatment with hybrid system PGMS : NPs comparing to CaSO_4 reference spectrum.

Each treated sample showed the peak at 950 cm^{-1} , attributed to the non-bridging oxygen mode Si–O–Ca [13], confirming the interaction of calcium ions with the Si-based polymer, indicating the formation of a three dimensional network [14]. Moreover, a notable result is the Al–OH absorption peak identified at 837 cm^{-1} from deformation of OH groups linked with Al^{3+} ions [15], which could indicate an interaction of the polymeric network with alum.

Figure 4 shows the presence of a broadened peak at $2\theta = 23^\circ$ which could indicate that the polymer network formed after the treatment contained a significant proportion of an amorphous phase [16]. Moreover, peaks, which can be assigned to calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$), are also present.

The treatments with all hybrid systems offered a stabilization of the wood at the macroscopic level, enabling it to be cut without powdering (as evidenced during the preparation of samples for SEM analysis). In particular, the toughness was improved as well, indicating the possibility of increased flexibility and rubber-like elasticity of the treated samples [7]. However this must be investigated further through quantitative mechanical testing.

Using EDS, it was possible to observe that aluminum, potassium and sulfur elements were distributed quite unevenly, accumulating particularly in the vessels (Figs. 5 and 6).

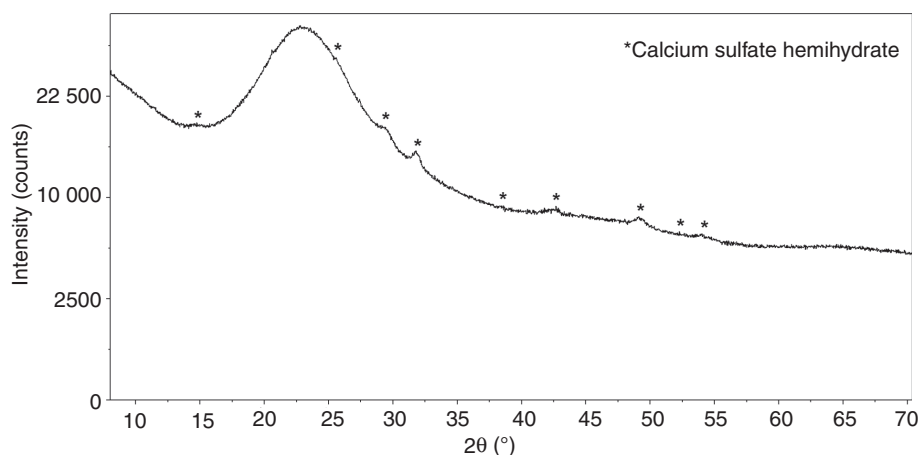


Fig. 4: X-ray powder diffraction pattern of hybrid system PGMS : NPs used to treat Oseberg wood. The asterisks symbolize signals for calcium sulfate hemihydrate.

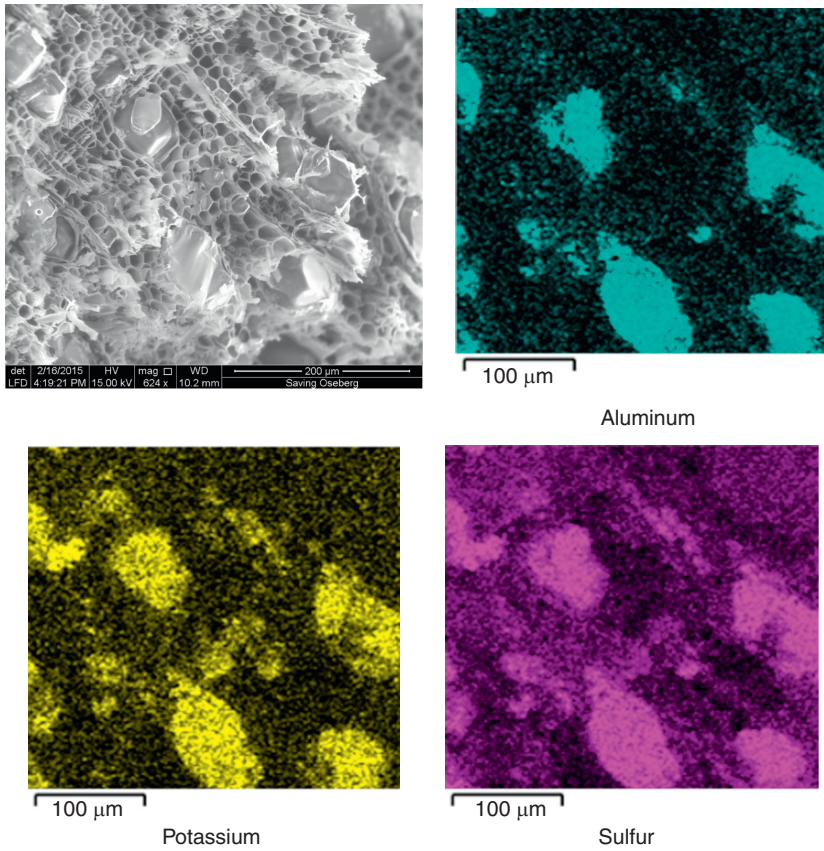


Fig. 5: Elemental maps from Oseberg wood before the treatment with hybrid system, taken from the core of fragment.

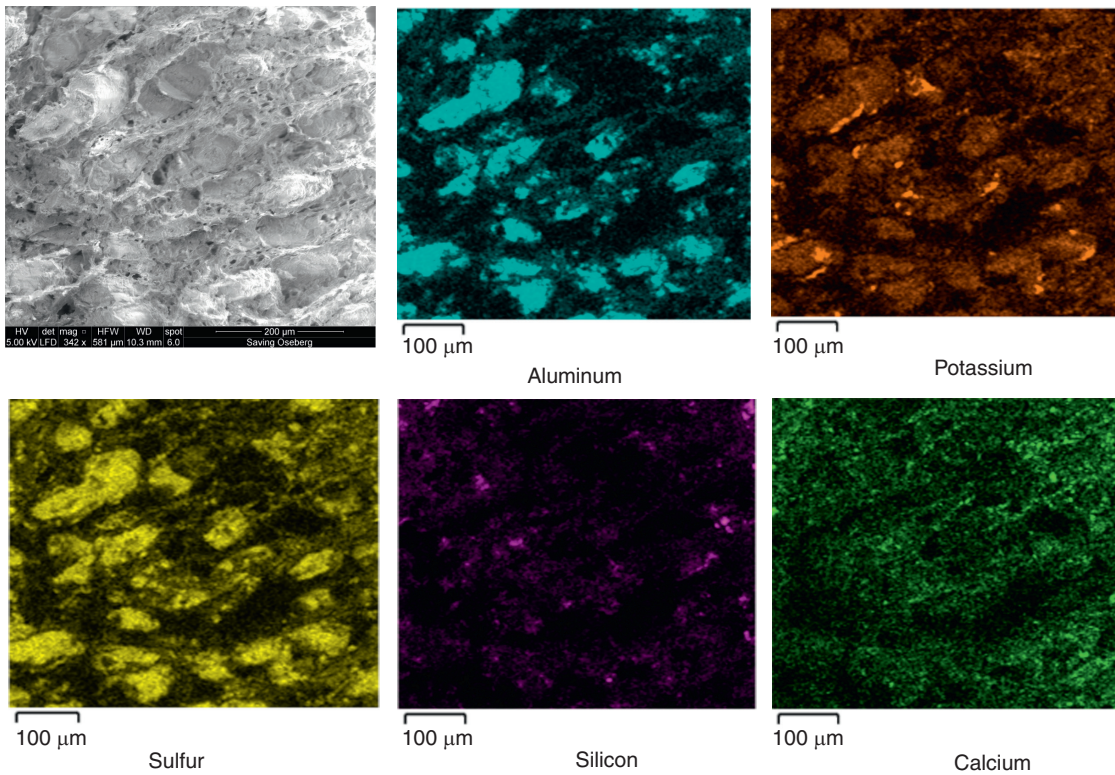


Fig. 6: Elemental maps from Oseberg wood after the treatment with hybrid system (PGMS:NPs).

The maps of calcium and silicon, acquired on cross-sectioned samples at about 0.5 cm from the treated surface, show that these are evenly distributed indicating a good penetration of the wood samples by the hybrid system (Fig. 6).

The effects of treatment on degraded wood were monitored by DTG. As already reported in the literature [17], the pyrolysis temperature of cellulose (T_p) can be used to monitor the efficacy of the deacidification treatment, where samples with a higher pH value show an increase in T_p , indicating higher resistance to thermal degradation [18]. The first region of DTG curves from 60 °C to 100 °C is attributed to the loss of physically adsorbed water from the wood sample. Curve profiles indicate that the range between 120 and 200 °C is directly related to the removal of physically adsorbed water from the silicon network (see for example Figs. 7–10). Physically adsorbed water is completely removed at 300 °C [19]. Figure 11 clearly shows the main pyrolysis process for fresh wood that proceeds in a range from approximately 200 °C to 370 °C. In this region there are two peaks which the literature [20, 21] shows to be related to hemicellulose and cellulose

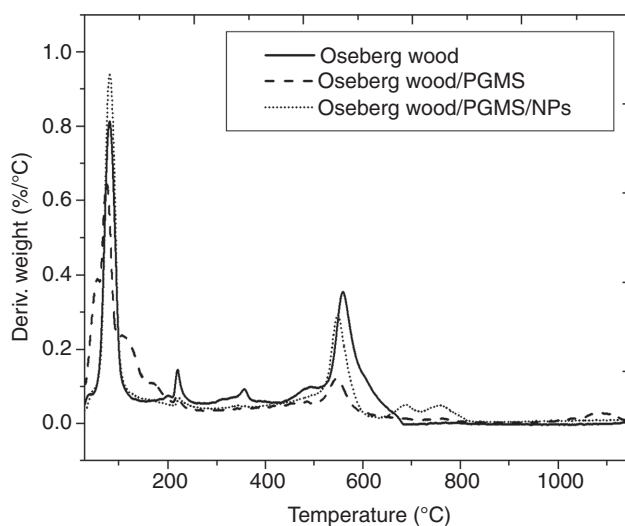


Fig. 7: Comparison between DTG curves of Oseberg wood, Oseberg wood treated with PGMS and Oseberg wood treated with PGMS/NPs.

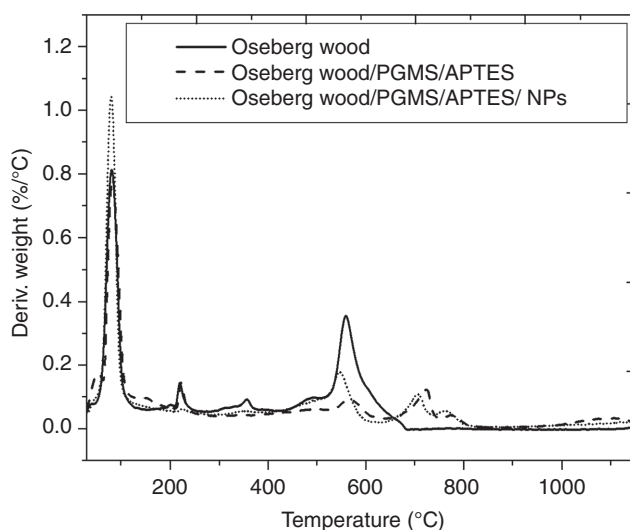


Fig. 8: Comparison between DTG curves of Oseberg wood, Oseberg wood treated with PGMS/APTES and Oseberg wood treated with PGMS/APTES/NPs.

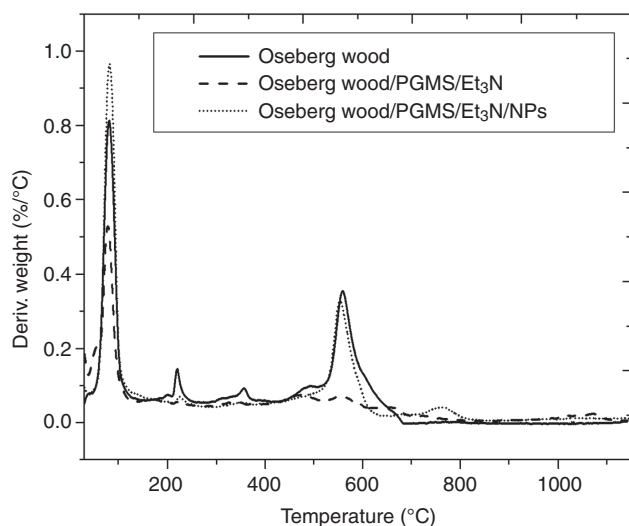


Fig. 9: Comparison between DTG curves of Oseberg wood, Oseberg wood treated with PGMS/Et₃N and Oseberg wood treated with PGMS/Et₃N/NPs.

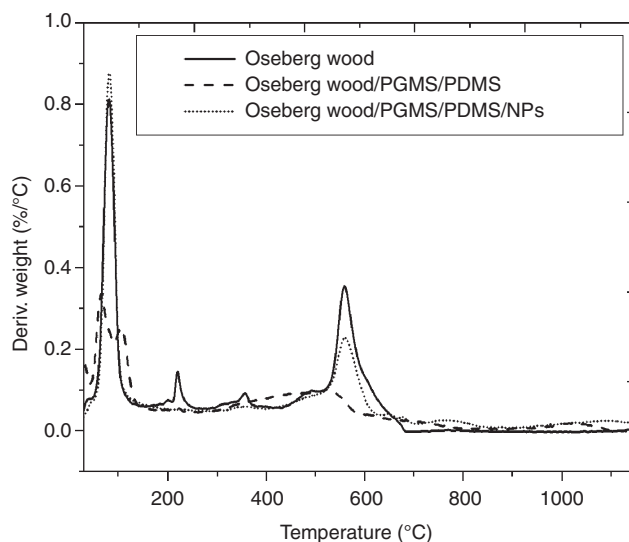


Fig. 10: Comparison between DTG curves of Oseberg wood, Oseberg wood treated with PGMS/PDMS and Oseberg wood treated with PGMS/PDMS/NPs.

decomposition, while lignin is decomposed in over a wider temperature range [22]. The process of devolatilization of lignin is practically completed above 700 °C. As the alum-treated wood samples here investigated are highly degraded, the signals associated with the pyrolysis of hemicellulose and cellulose are almost negligible and becoming narrow compare to that of fresh wood. The only thermal event that can be clearly seen in the curves is associated with the pyrolysis of lignin; thus, the temperature corresponding to the maximum rate of lignin mass loss will be reported as T_1 . Thermal analysis of wood samples treated with the four different hybrid systems containing nanoparticles showed no significant variation in T_1 relative to untreated samples. On the other hand, in systems without nanoparticles T_1 shifted towards lower values. Thus, the addition of NPs was regarded as improving the thermal resistance of lignin and hybrid silicon network itself. It has been hypothesized that the bivalent positive calcium ions could also contribute to increase thermal resistance due to chelating complexes formed with hydroxyl and methoxy groups in the lignin [23]. Moreover calcium ions could take part in the silicon network [14, 15] explaining its greater resistance to thermal degradation. In

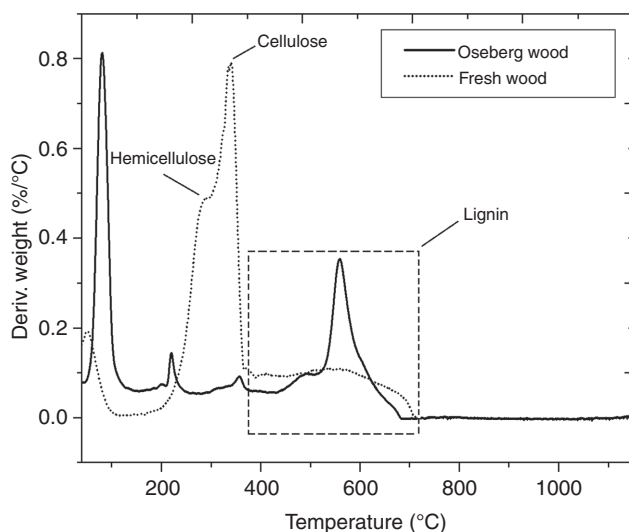


Fig. 11: Comparison between DTG curves of fresh oak and Oseberg wood. The DTG curve of fresh oak shows main thermal degradation signals of wood in good condition.

particular, wood treated with hybrid systems PGMS/NPs/Et₃N and PGMS/NPs/PDMS showed thermograms very similar to untreated Oseberg wood (Figs. 9 and 10). Moreover, the sample treated with PGMS/NPs/PDMS system showed a further increase in mechanical strength based on qualitative observations when handling and cutting it.

Conclusions

The investigations were carried out on alum-treated wood from the Oseberg find which has low abundances of cellulose and hemicellulose, such that samples are mainly composed of lignin and alum. Treatments of archeological wood with alkaline nanoparticles and PGMS monomers increased both robustness and final pH of the wood. Treated wooden samples had a final pH of ca 5, an increase in 2–3 pH units. Moreover, the condensation appeared to occur without causing any distortion of cell walls or appreciable shrinkage [24]. The system made of PGMS/NPs/PDMS seemed to be the best formulation since it was most effective in increasing pH value and significantly reducing wood powdering during handling. Quantitative mechanical tests on treated samples will be undertaken in future studies.

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Graphical abstract

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Conference paper: Hybrid systems made of propylene glycol modified TEOS (tetraethyl orthosilicate) and alkaline nanoparticles ($\text{Ca}(\text{OH})_2$) have been engineered to deacidify and consolidate, in a single step, alum-treated wooden objects from the Oseberg find.

Keywords: alkaline nanoparticles; alum salt; archeological wood; hybrid systems; in situ polymerization; Oseberg finds; pH control; POC-16.

