DOI: 10.1002/masy.200650605

Nanotechnology for Vasa Wood De-Acidification

*David Chelazzi, Rodorico Giorgi, Piero Baglioni**

Summary: The conservation of the seventeenth-century Swedish warship Vasa is a challenge due the unique history of its recovery and the delicate interventions made for its preservation. In the past years the strong acidity of wood came out as a threat for its conservation. The large amount of sulfur, produced by metabolic action of bacteria in the seabed, partly converted to sulfuric acid, catalyzes the chemical degradation of the wood through the acid hydrolysis of cellulose. This contribution reviews recent studies on the degradation of Vasa wood. We show how wood acidity can be neutralized by the application of calcium or magnesium hydroxide nanoparticles, forming an alkaline reservoir inside the wood that protect it from further acid attack. This has been evidenced by the thermal analysis carried out on fresh wood, Vasa wood, artificially degraded wood, and paper samples studied as reference cellulose-made materials. Pyrolysis temperature of cellulose was studied, as an important parameter of degradation, also related to the acidity of wood. Decreases in the pyrolysis temperature of degraded cellulose were correlated to decreases of its polymerization degree. Thermal analysis has been also used to investigate the wood de-acidification efficacy after the treatment with alkaline nanoparticles. Hydrothermally aging, carried out on de-acidified Vasa wood samples demonstrated that de-acidification with nanoparticles facilitates protection of wood toward further acid degradation.

Keywords: aging; de-acidification; nanoparticles; thermogravimetric analysis (TGA); waterlogged wood

Introduction

Wood is a complex material extensively used in the realization of many artworks. The preservation of ancient shipwrecks is a challenge in the field of cultural heritage conservation since natural aging and different environmental conditions can be the cause of many different degradation phenomena involving wood, iron (from bolts) and other materials used in the realization of the ships.

The Swedish warship Vasa represents a challenging case in conservation of waterlogged wood. It sank in its maiden voyage, in 1628, and remained on the seabed for 333 years, until it was recovered in 1961. A spray treatment with polyethylene glycol (PEG) has been carried out for 17 years, preventing wood from shrinkage after drying, and the ship is exhibited since 1990 in the Vasa Museum, in Stockholm.[1] In the last years, Vasa wood experienced, a strong increase in acidity, which threatens the preservation of the wreck.[2,3] Acid, in fact, catalyzes the hydrolysis of cellulose, the main constituent of wood. The overall acidity comes as the result of many interconnected chemical reactions. Sulfuric acid and sulfates originated from elemental sulfur produced by the bacteria in the wasted anoxic water of Stockholm harbor. Accumulation of reduced sulfur is common for wooden shipwreck preserved in seawater, and was recently reported also for the Mary Rose wreck (XVI century).[4] Iron

---

Department of Chemistry and CSGI, University of Florence, via della Lastruccia 3-Sesto Fiorentino, 50019 Florence, Italy
Fax: +39 055-457-3032
E-mail: baglioni@csgi.unifi.it

compounds, produced by the corrosion of bolts and cannon balls, catalyze the oxidation of sulfur and reduced sulfur compounds such as hydrogen sulfide.[5,6] Iron also catalyzes the oxidative hydrolysis of cellulose[7], and probably degrades PEG starting from the end groups of the polymer, producing formic acid.[8] Furthermore, PEG acts as solid-state electrolyte, transporting iron ions towards the PEG-wood interface, increasing iron surface concentration and probably degradation.[9,10]

Conventional de-acidification treatments were carried out on wood, but failed, and very low pH values were detected all over the ship timbers.[2] We received samples of Vasa wood (Figure 1) from the Swedish Maritime Museum authorities, and treated them with an innovative method for de-acidification, already successfully tested on paper. The method is based on treatment with non-aqueous suspensions of alkaline nanoparticles, after the removal of PEG with water. The results were promising: pH of archaeological wood (mainly oak and pine) turned to values close to those of fresh wood.[11] The alkaline nanoparticles created a reservoir inside the wood which acts as a buffer against forthcoming acidity, as we verified by artificially hydrothermal aging of the treated samples.[12]

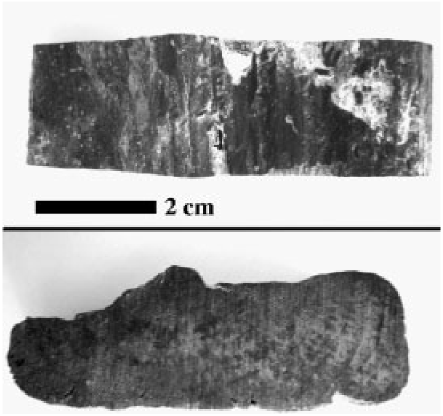

Figure 1.
A block cut from the samples of Vasa wood. White stains are PEG excesses, while the black color of wood is due to inclusion of rust particles by PEG.

Improvements in the conservation *status* of treated wood, after the neutralization treatment, were investigated by thermal analysis. This technique is commonly used for the characterization of polymers, and the small amount of sampling required for the analysis makes this technique suitable for applications in the conservation of cultural heritage field.[13]

This work deals with the correlation of the thermal behavior of archaeological wood with its degradation. The measurement of the degree of polymerization of cellulose (DP), an important molecular parameter, is usually done through viscosity measurements for paper and textiles.[14] The application of this procedure to wood is made difficult by its insolubility in bis(ethylenediamine)copper(II) hydroxide solutions. For this reason we performed thermal analysis on wood and paper samples, measuring also DP for paper through viscosimetry and investigating the correlation between DP and the pyrolysis temperature of cellulose, measured by thermogravimetric analysis (TGA). We could, thus, semi-quantitatively evaluate the degradation *status* of cellulose in wood, using paper as a reference material.

At the present time, our research efforts are concentrated on the realization of suspensions of alkaline nanoparticles in fluorinated solvents, because of their chemical inertness and lower surface tensions, which would grant a deeper penetration in the wood matrix. Another important task is the development of wood consolidating materials to replace PEG that, until now, seems to be one of the main materials used to preserve wood from shrinking, particularly for wrecks.[3]

Methods and Materials

We cut 3 cm square blocks along the wood radial direction, from the samples of Vasa wood we received. The blocks were soaked with distilled water in order to remove

PEG, which would prevent particles from penetration into the wood fibers, and were immersed in 0.07 M nanoparticles dispersion in 2-propanol.

$Ca(OH)_2$ and $Mg(OH)_2$ nanoparticles were prepared following the procedure according to literature.[11,15]

$Mg(OH)_2$ nanoparticles are regularly shaped in the crystalline form of brucite. Their size spans from 50 nm to 200 nm, and is centered at 90 nm, as evidenced by TEM analysis. $Ca(OH)_2$, nanoparicles, in the crystalline form of portlandite presented sizes spanning from 150 to 300 nm, centered at 200 nm. The only impurities from the synthesis procedure is sodium chloride, and it was washed out with centrifugation cycles with lime water (for $Ca(OH)_2$) and with water ($Mg(OH)_2$).

Acidity of wood was measured using a pH glass electrode after suspending 1 g of wood powder in 5 g of water, for 24 h, at room temperature.[16] The pH was also locally determined with an indicator paper (sensitivity of 0.5 units). In order to get reference materials to study the degree of polymerization of cellulose and correlate it to thermal parameters (pyrolysis temperature of cellulose), we used Whatman filter paper n. 1 (99% cellulose, supplied by Sigma-Aldrich). Fresh oak and pine blocks were used for thermal characterization of non-degraded wood samples.

Acid aging of wood and Whatman paper was carried out soaking samples in a sulfuric acid solution (pH 1.2) for 4 hours.

Hydrothermal aging of the samples was carried out under controlled conditions ($T = 80\,^{\circ}C$, R.H. = 78%), obtained using a saturated KCl solution.

DTGA (differential thermogravimetry analysis) curves were recorded in dynamic, non-isothermal conditions, with a TA SDT Q600. The experimental conditions were: temperature range: 30–500 °C; sample weight: 2–5 mg; heating rate: 10 °C/min; N_2 flow: 100 ml/min. The experimental error was $\pm 1\,^{\circ}C$.

XRD on Vasa wood powder was performed 3 days after treatment with nanoparticles, using a Bruker D8 Advance diffractometer, equipped with a Cu $K\alpha$ ($\lambda = 1.54$ Å) source. We deposited randomly 1 mg of the dried wood powder onto a Plexiglass sample container. The XRD patterns were recorded at a scan rate of 2°/min, under nitrogen atmosphere.

Viscosity measurements were performed to evaluate the polymerization degree (DP) of cellulose by dissolving the paper samples in CED at 20% according to the international standard procedure;[14] for DP calculation we used the empirical equation $DP = K[\eta]^{\alpha}$, where η is the intrinsic viscosity, K is 1.5 and α is 1.

Results and Discussion

Vasa wood is a very complex matrix. Many chemical compounds are present, and their distribution inside the pores and the fibers is very inhomogeneous. We focused on cellulose, trying to evaluate the conditions of the polymeric chains inside the wood. A preliminary study was carried out on Whatman filter paper used as model for cellulose degradation. We considered cellulose from paper as the simpler "model" system and studied the effects of acid and de-acidification treatments on it. We investigated paper by measuring pH and polymerization degree (DP) and by thermal analysis.

Acid aging of paper samples, carried out with sulfuric acid, decreased the pH from 5 to about 2. In Figure 2 the DTGA curve of an acidified sample is shown. Pyrolysis temperature drops down to a lower value with a ΔT with respect of the fresh sample of 48 °C (13%). The decrease can be explained considering that hydrolysis of cellulose, catalyzed by acid, produces chains with lower molecular weight that require less thermal energy for their degradation. Oxidation of the glycosidic ring also occurs, weakening the glycosidic bonds. Furthermore, the acidic environment promotes the swelling of the cellulose fibers, so that the individual bonds are less protected from hydrolysis, and also cellulose dehydration, one of the first steps in

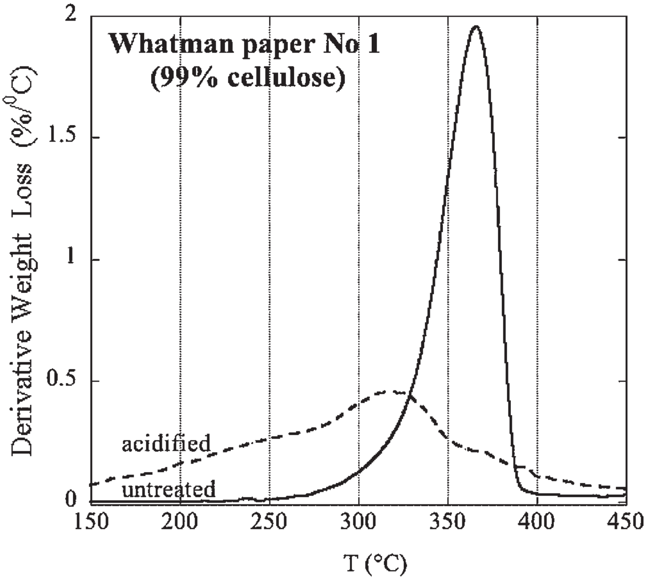

Figure 2.
DTGA curve of Whatman filter paper (99% cellulose), before and after degradation with sulfuric acid.

thermal degradation of wood, is acid-catalyzed. Acid catalyzed dehydration can bring to the formation of anhydrous sugars whose glycosidic linkages can be easily hydrolyzed. Viscosimetry studies performed on the acidified paper samples showed that polymerization degree decreased accordingly to the maximum pyrolysis temperature. DP changed from 940 for the fresh samples to 540 for the acidified ones (loss of 43%), a value usually corresponding to heavily degraded paper. Furthermore, the acidified samples are more brittle than the fresh ones.

We can safely state that maximum pyrolysis temperature of cellulose, measured by differential thermogravimetric analysis (DTGA), is an important parameter related to the chemical environment surrounding cellulose, and to the length of the polymeric chains.

Investigation of wood samples was carried out by thermal analysis. Considering that the Vasa ship was built mainly with oak and pine wood, we investigated fresh wood samples of both species as reference materials. We treated some wood powder, from fresh oak and pine samples, in the same way as for paper (cellulose), i.e. degrading them with sulfuric acid. The acidified wood powder showed a strong decrease in the maximum pyrolysis temperature ($\Delta T = 15$–$20\,^{\circ}C$ for oak, and $30\,^{\circ}C$ for pine).

The Vasa wood exhibited lower surface and bulk pH values (1–3) with respect to the fresh wood samples (4.5 for oak, 5.5 for pine). Figure 3 shows the DTGA curves of Vasa wood. DTGA analysis on the samples pointed out that the thermal behavior of Vasa wood is strongly different from the fresh samples, and similar to the acidified ones. The strong decreases in the pyrolysis temperature of cellulose were found for both oak and pine wood ($\Delta T = 20\,^{\circ}C$ for oak, $30\,^{\circ}C$ for pine) from Vasa. These data suggest that cellulose still present in the Vasa wood is heavily degraded. It is interesting to point out that also PEG pyrolysis temperature undergoes a strong decrease: it is of $380\,^{\circ}C$ in Vasa wood, while fresh PEG 1500 pyrolyzes at $413\,^{\circ}C$. This confirms that also PEG is degraded, producing species with lower molecular

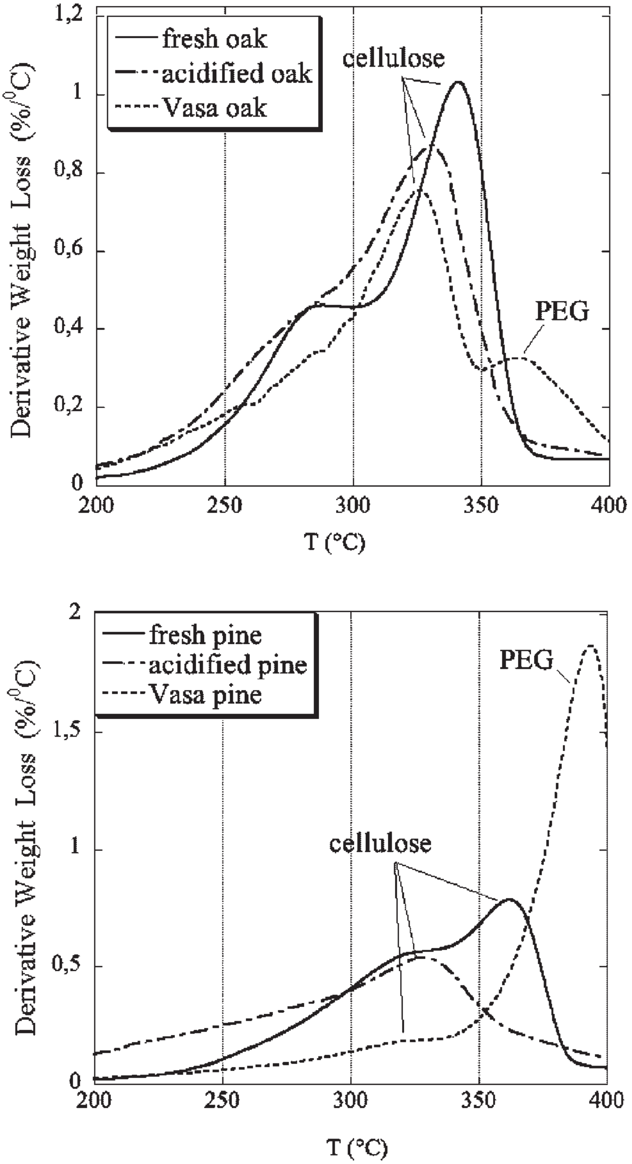

Figure 3.
DTGA curve of Vasa oak and pine wood, confronted with fresh and artificially aged wood.

weight. PEG was already shown to be unstable in the air in previous experiments.[17]

Experimentations to preserve the Vasa wood from further degradation are in course. Efforts are being done in order to stop the oxidation of elemental sulfur inside the wood and prevent iron from continue degrading cellulose.

The conventional neutralization treatment that was initially performed on Vasa by the Swedish curators was based on the application of poultices of a washing soda/ baking soda solution ($NaHCO_3 : Na_2CO_3 \cdot 10H_2O = 7:3$, 5% in water, pH$\sim$10) on the surface of wood. This method increases the surface pH to high values (9–10), but then it reverts back to acid in a relatively short time (weeks). The limit of the method is that it does not create an alkaline reservoir inside the bulk of wood to neutralize the acid that continues to develop into the wood matrix. Furthermore, a treatment with a strong alkaline aqueous solution could be harmful for the residual cellulose in wood.

A possible solution to solve the problem of the de-acidification is the application of alkaline (mainly $Ca(OH)_2$ and $Mg(OH)_2$) nanoparticles suspensions in non-aqueous solvents, previously applied by us on paper and canvas to de-acidification [5,18] Nanoparticles penetrate into the fibers, adhere to them, and, after volatilization of the solvent (propanol in our case), release hydroxyls that neutralize acidity. The slow release of hydroxyls in non-aqueous solvents would prevent the method from being harmful for wood cellulose, and the creation of an alkaline reservoir is expected to grant long-term protection to wood.

Wood samples treated with nanoparticles exhibited the same pH (measured by water extractions) as fresh wood. Local pH measurements just after the treatment, performed with indicator paper, showed higher pH on the surface just after treatment (8–9 for $Ca(OH)_2$ treated wood, 6–7 for $Mg(OH)_2$) and lower pH values in the bulk (from 4 to 6). The higher values are due to deposits of nanoparticles, and the excess turns into carbonate buffer in a few days. XRD spectra on wood powder sampled from the treated Vasa wood showed, 3 days after the application, peaks due to calcite, formed from portlandite.[11]

The time scales of pH restoration are strongly dependent on the penetration and distribution of nanoparticles into the wood fibers. After a year from application, areas soaked with particles still show alkaline pH (from 7 to 9). Below the surface (1.5–2 cm depth) wood shows an average pH around 5. Deeper areas, not reached by the particles, show more acid pH (2–4), especially in oak wood.

The effects of the de-acidification treatment were also monitored by TGA. De-acidification was expected to cause changes in the thermal behavior of wood. Dehydration reactions, infact, are dependent on the acid concentration in the wood matrix and the applied temperature.

Both $Ca(OH)_2$ and $Mg(OH)_2$ nanoparticles increased the resistance of Vasa wood toward thermal degradation, and the maximum pyrolysis temperature was reverted to values close to those of fresh oak and pine wood. Clearly the treatment did not ‘‘re-establish’’ the glycosidic bonds in the polymeric chains, but efficiently neutralized acidity, creating a chemical environment no longer hostile to cellulose.

The application of nanoparticles suspensions implies the removal of PEG that would otherwise prevent them from penetrating into the wood. TGA analysis showed that the removal of PEG from Vasa pine wood already improved the thermal behavior and the pH of the samples[11]. Recent studies by Glastrup *et al.*, showed that that the contribution to the overall acidity coming from the degradation of PEG, giving formic acid, is small. We hypothesized that some iron compounds, included in PEG, were removed with the washing.

The penetration of the nanoparticles inside the wood bulk was also investigated. Cross-sections of treated wood were sampled at different depths, below the surface. The samples were powdered and analyzed by TGA. In the wood treated with $Ca(OH)_2$ particles, high pyrolysis temperatures were found for samples around 1 cm below the surface, while for $Mg(OH)_2$ treated wood, for samples around 2 cm in the wood bulk. We could, thus, state that the higher penetration of $Mg(OH)_2$ particles is due to their smaller dimensions (average dimension = 90 nm) respect to $Ca(OH)_2$ (200 nm).[12] Our research efforts are focused on the realization of suspension of particles with smaller size, so that they can penetrate deeper inside the wood bulk. For the same reason, experimentation with different non-aqueous solvents is also in progress. Fluorinated solvents have lower surface tension and viscosity than propanol, allowing a better penetration inside the wood pores, and, thus, a deeper particles delivering.

Hydrothermal aging of the samples treated with nanoparticles suspensions (in propanol) have been performed in order to evaluate the durability of the treatment. The maximum pyrolysis temperature was checked during the aging, and the de-acidified wood showed good thermal resistance even after 120 hours in the very drastic hydrothermal conditions.[12] Conversion to real aging time is difficult, but it seems possible that nanoparticles would grant long term protection to wood, also considering that larger quantities of particles could be delivered inside the wood fibers with longer applications.

Conclusions

Vasa wood is a very complex material, considering the presence of sulfur and iron compounds, and of PEG. Preliminary studies on cellulose indicate that acid degradation of the polymeric chains can be characterized by TGA measurements. Maximum pyrolysis temperature of cellulose was found to be an important parameter, related to the degree of polymerization of the chains. The TGA analysis highlighted a severe degradation of residual cellulose in the Vasa wood. Application of non-aqueous nanoparticles suspensions of $Ca(OH)_2$ and $Mg(OH)_2$ efficiently de-acidify Vasa wood for a time longer than the conventional aqueous alkaline treatments.

Acknowledgements: We thank Ingrid Hall-Roth and Emma Hocker (from Vasa Museum) for providing wood samples from Vasa and Lars Ivar Elding (University of Lund) for helpful and stimulating discussions. We also thank Professor Mats Almgren (University of Uppsala), Luigi Dei, Alessio Becheri, Marco Lagi, and Ilaria Santoni (University of Florence) for useful discussions. CSGI and the Ministry for Education and Research (MIUR, PRIN-2003) are also gratefully acknowledged for partial financial support.

[1] B. Håfors, Conservation of the Swedish Warship Vasa from 1628, *Vasa Stud.* **2001**, *18*, 1.

[2] M. Sandström, Y. Fors, I. Persson, The Vasa's New Battle. Sulphur, Acid and Iron, *Vasa Stud.* **2003**, *19*, 1.

[3] M. Sandström, F. Jalilehvand, I. Persson, U. Gelius, P. Frank, I. Hall-Roth, *Nature* **2002**, *415*, 893.

[4] M. Sandström, F. Jalilehvand, E. Damian, Y. Fors, U. Gelius, M. Jones, M. Salome, *PNAS* **2005**, *102*(40), 14165.

[5] C. Baird, "*Enviromental Chemistry*", W. H. Freeman Publishers, New York, 1999, p.427.

[6] R. T. Lowson, *Chem. Rev.* **1982**, *82*, 461.

[7] J. A. Emery, H. A. Schroeder, *Wood Sci. Technol.* **1974**, *8*, 123.

[8] K. Kilminster, *Preserving Our Past. An Investigation into Archaeological Wood from the Shipwreck of the Batavia.* B.Sc. Thesis, Western Australia University, Perth, Australia, 2001.

[9] E. Guilminot, F. Dalard, C. Degigny, *Corros. Sci.* **2002**, *44*, 2199.

[10] F. M. Gray, in: "Polymer Electrolytes", J.A., Eds., RSC Materials Monographs; The Royal Society of Chemistry, Cambridge 1997, p1.

[11] R. Giorgi, D. Chelazzi, P. Baglioni, *Langmuir* **2005**, *21*, 10743.

[12] R. Giorgi, D. Chelazzi, P. Baglioni, *Applied Physics A*, in press.

[13] I. Sandu, M. Brebu, C. Luca, I. Sandu, C. Vasile, *Polym. Degrad. Stab.* **2003**, *80*, 83.

[14] ASTM 04 243–99 Standard Test Method for Measurement of Average Viscometric Degree of Polymerization of New and Aged Electrical Papers and Boards.

[15] R. Giorgi, C. Bozzi, L. Dei, C. Gabbiani, B. W. Ninham, P. Baglioni, *Langmuir* **2005**, *21*(18), 8495.

[16] M. Gindl, S. Tschegg, *Langmuir* **2002**, *18*, 3209–3212.

[17] J. Glastrup, *Polymer Degradation and Stability* **1996**, *52*, 217.

[18] R. Giorgi, L. Dei, M. Ceccato, C. Schettino, P. Baglioni, *Langmuir* **2002**, *18*(21), 8198.