

Chapter 3

New Consolidants for the Conservation of Archeological Wood



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Abstract The preservation of cultural heritage is of great importance worldwide and, as such, has been the focus of an increasing number of research projects in recent years. In spite of considerable efforts around the world, significant problems have arisen with the conservation of many shipwrecks. The most common issues facing conservators are structural instability upon drying and biological degradation stemming from the aquatic flora and fauna active around the excavation site. However, many important artefacts – such as the sixteenth century warship *Mary Rose* – also suffer from metal ion saturation from degraded bolts and fittings. In most cases Fe^{3+} is the greatest problem, which catalyses the production of sulfuric and oxalic acid in the waterlogged timbers, adding chemical degradation to the potential conservation issues. Moreover, the Fe^{3+} also feeds biological degradation by providing bacteria with an iron source for sustained growth. As such, multi-functional consolidants are greatly needed to tackle not only the many-pronged conservation issues already visible, but also to prevent others from evolving over time. This paper discusses the recent successes in the development of such materials from

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sustainable, bio-based sources and some potential areas for the future development of these tools.

Keywords Waterlogged archaeological wood · *Mary rose* · Poly(ethylene glycol) · Bio-based polymers · Supramolecular materials · Conservation

3.1 Background

Although the timbers of the sixteenth century warship *Mary Rose* are generally well conserved there are three major problems facing conservators: structural instability upon drying, biological activity in the timbers and high concentrations of iron present from the degradation of bolts and fittings in the ship, which contribute to the chemical degradation of wood [1–7, 10]. Current conservation strategies involve spray treating with increasingly concentrated solutions of poly(ethylene glycol) (PEG) in water that have been doped with a broad spectrum biocide. The spray treatment of the *Mary Rose*, which has recently concluded, is shown in Fig. 3.1.

PEG became popular in the early twentieth century, with the large-scale industrialisation of the chemical industry, and represented a major advance over the alum treatments that had been used previously. The alum conservation method had involved immersing artefacts in concentrated alum (potassium aluminium sulphate) solutions at 90 °C, the alum then recrystallised within the timbers and prevented dimensional changes on drying. Unfortunately, artefacts conserved in this manner suffer over time from the generation of sulfuric acid by the alum. The significantly reduced pH within the wood, often as low as pH 1, has resulted in mechanically weak timbers that require further stabilisation [8]. The introduction of PEG to conservation science, with its low cost and relatively low toxicity, represented a significant advance in conservation technology compared to alum. PEG treatment works by solvent displacement. Spraying solutions of PEG at the wood or soaking the wood in PEG replaces the water in the timbers with PEG molecules. Structural instability during the drying process is, therefore, reduced as the vapour pressure of PEG is significantly higher than water. Thus the wood dries, while the fragile cells are supported by the PEG within.

However, in recent years several disadvantages of PEG have become apparent. In particular, its ability to act as a solid-state ion transporter [9] its degradation to acidic by-products [4, 5, 10, 11] the need for additives to provide anti-bacterial properties or remove iron, [3, 12] and the cost of long-term use. Moreover, the long-term use of PEG in wood conservation was found to increase the likelihood of plasticisation of the timbers, leading to eventual brittleness and further instability [13, 14]. These drawbacks all point to the need for new treatments to be designed. As PEG does not counter-act the presence of iron in the timbers, the chemically induced degradation of the *Mary Rose* is currently left unchecked.

In recent years there has been much interest in the use of non-synthetic materials for conservation and several research groups have investigated the use of bio-based



Fig. 3.1 The sixteenth century warship *Mary Rose* undergoing spray treatment with solutions of PEG200 and PEG2000 at HM Naval Base dry-dock in Portsmouth, UK. (Image reproduced with permission from the Mary Rose Trust)

polymers as alternative consolidants [15–17]. While these materials certainly pave the way for the future improvements in the consolidation of waterlogged wooden artefacts, they still lack the multi-functionality required to be minimally invasive to the artefact while producing the maximum conservative effect. A new conservation treatment is presented here based on a supramolecular polymer network constructed from chitosan and guar [18]. This material is a dynamically cross-linked 3-dimensional bio-based polymer network. Cross-linking of the guar and chitosan network is provided by host-guest ternary complexation using a macromolecular host unit known as cucurbit[8]uril and complementary guest molecules methyl viologen (guar) and naphthyl units (chitosan), providing the basic dynamic structure, Fig. 3.2. Metal-ligand interactions implemented by a strong Fe^{3+} chelator pen-

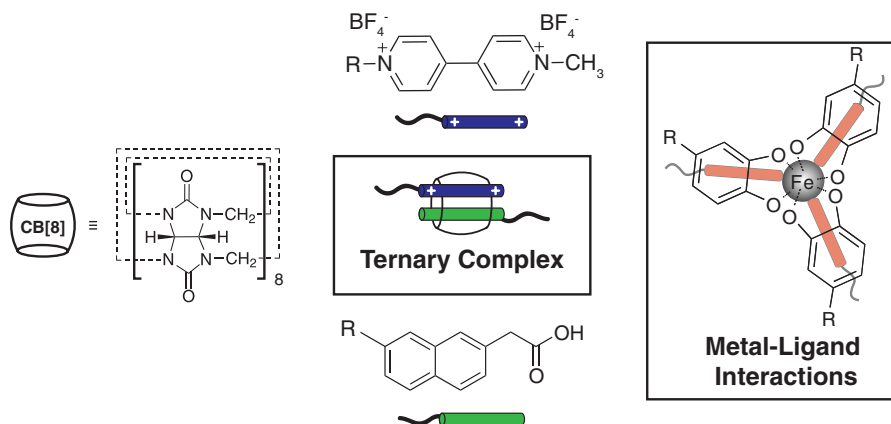


Fig. 3.2 Schematics and structures of the ternary complexation between methyl viologen (blue bar), 2-naphthylacetic acid (green bar) inside the cucurbit[8]uril macromolecular host (barrel) and the metal-ligand interactions promoted by the dihydroxyphenylacetic acid unit (red bar) around Fe³⁺ centres

dant from the chitosan backbone (Fig. 3.2), give the functional material the ability to chelate and trap iron while increasing structural stability. Thus, allowing the material to adapt to the chemical environment of the wood.

The inclusion of methyl viologen as a guest molecule also enhances the antibacterial character of the polymer network and will provide the material with increased biological resistance relative to conventional conservation treatments (Fig. 3.2). The polymer is known as *PolyCatNap* due to the incorporation of catechol (*Cat*), promoting the formation of metal-ligand interactions, and naphthol (*Nap*), allowing for the host-guest complexation, onto the backbones of the bio-based polymers used to construct the network. Exploiting environmentally compatible bio-based materials with reversible cross-links through host-guest chemistry and metal-ligand interactions makes a safer, greener alternative to current strategies and will potentially extend the lifetime of many precious waterlogged wooden artefacts under conservation around the world. [15, 16, 19].

3.2 Experimental Results

A number of analytical and instrumental techniques have been used to verify the ability of *PolyCatNap* to chelate iron and its structural stability. As a first step, accelerated ageing tests were performed on the polymeric components of the supramolecular consolidant and compared with the results obtained from PEG under the same conditions, which were adapted from a paper by [11]. Under these conditions PEG showed an increase in acidity of 2 pH units when tested before and after the experiment. Whereas, with the chitosan and guar, no change in pH was observed

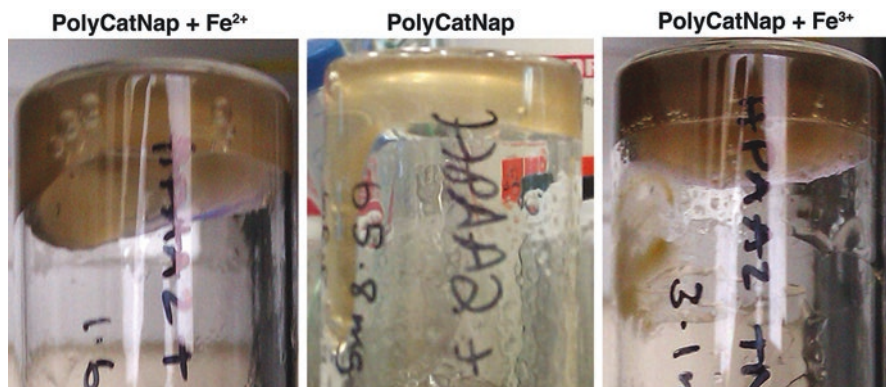


Fig. 3.3 (a) *PolyCatNap* with the addition of 1 mM FeSO_4 (Fe^{2+}), (b) *PolyCatNap* immediately after preparation and (c) *PolyCatNap* with the addition of 1 mM $\text{Fe}_2(\text{SO}_4)_3$ (Fe^{3+})

over the duration of the experiment [17]. Additionally, there was no observed change in the Fourier-transform infrared (FTIR) spectrum for the bio-based polymers while the PEG showed an increase in the carboxylic acid peak, which explains the increase in acidity of the PEG solution. Secondly, chelation of iron (Fe^{3+}) by the consolidant material was confirmed by colour change of the strong iron-chelator functionalised polymer chain; additionally, an increase in viscosity of the polymeric material was observed in the presence of Fe^{3+} . This can be seen in Fig. 3.3.

Figure 3.3b shows the liquid polymer directly after preparation, while Fig. 3.3a shows the solution after the addition of Fe^{2+} and Fig. 3.3c after the addition of Fe^{3+} . The initial consistency of the polymer solution resembles thick honey, upon the addition of Fe^{3+} the solution becomes a gel as the metal-ligand interactions begin to form around the Fe^{3+} centre adding another layer of structure to the material and increasing its strength. Interestingly, upon addition of Fe^{2+} the material becomes significantly weaker than even the original polymer before the addition of any metal ions. Although the catechol units have no affinity for the Fe^{2+} , the amine groups on the chitosan backbone do and can ‘mop up’ the available Fe^{2+} . This alters the orientation of the chitosan chains and prevents the guests of the ternary complex unit from coming into direct contact with one another, thus, weakening the material.

Rheological measurements confirm these observations and show that the complex viscosity of the new consolidant is higher than that of PEG and increases further in the presence of Fe^{3+} , confirming its ability to trap iron and structurally stabilise timbers [18]. While iron sulfate is the most common iron salt in the timbers, the response of the consolidant to other iron salts, specifically nitrate, citrate, chloride, oxide and phosphate, was also tested (Fig. 3.4).

The rheological response of iron (II) sulfate (FeSO_4), iron (III) chloride (FeCl_3) and iron (II) citrate (FeCit) were found to be equal to or weaker than the response of the polymer solution alone, Fig. 3.4a, c. On the other hand, *PolyCatNap* in the presence of iron (III) oxide (Fe_2O_3), iron (III) phosphate (FePO_4), iron (III) nitrate (FeNO_3) and iron (III) sulfate ($\text{Fe}_2(\text{SO}_4)_3$), displayed enhanced mechanical properties

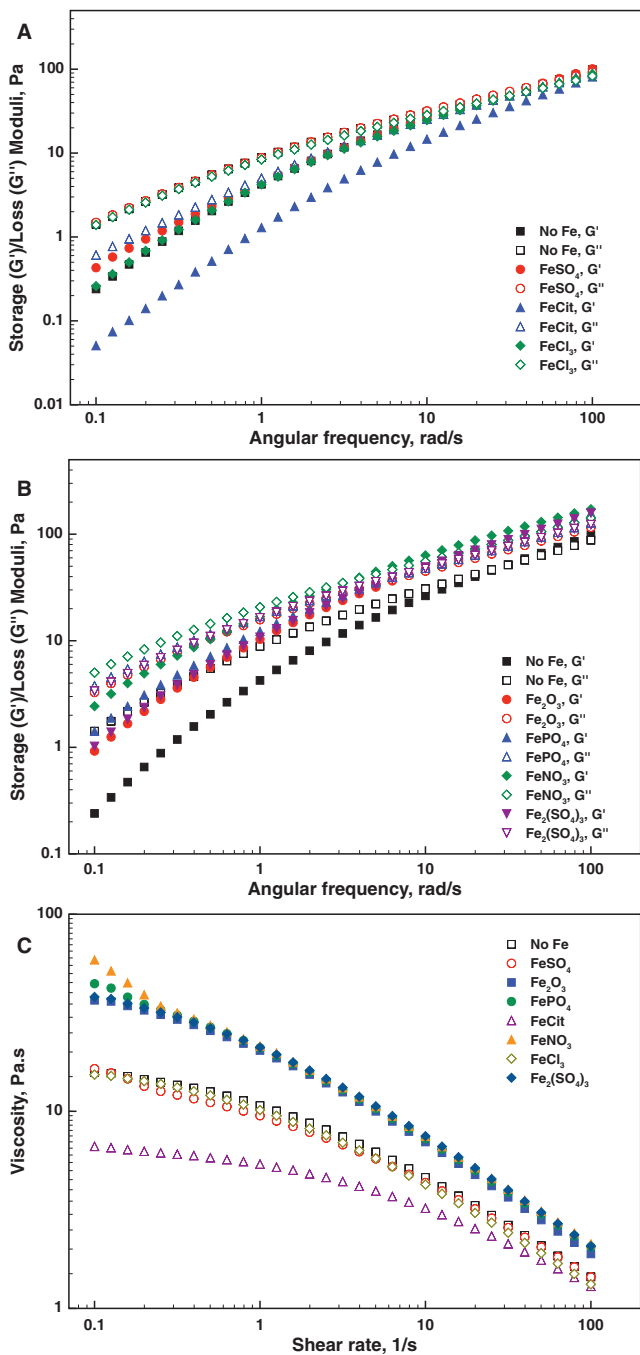


Fig. 3.4 Rheological study of the effect of counter-ions, plots of storage (G') and loss (G'') moduli (Pa) as a function of angular frequency (rad/s) where the addition of Fe produces (a) no significant change and (b) a significant change from the iron-free solution and (c) plot of viscosity (Pa.s) as a function of shear rate (1/s) for all samples

with a viscous liquid to gel transition at lower angular frequencies and a higher viscosity relative to shear rate, than the metal-free solution, Fig. 3.4b, c. This is important as the 3+ oxidation state is that in which the iron can catalyse the production of acid in the timbers. To expand, the material always showed an increase in complex viscosity and the storage and loss moduli of a gel at lower angular frequencies once Fe^{3+} was present. This is extremely promising as there is also the possibility of iron phosphates, oxides and nitrates in the timbers, in addition to sulfates. Disappointingly, the same does not appear true for chlorides, of which there is also a large amount present in the timbers. Further investigation will be required to understand why this appears to be the case. However, in general, the counter-ion does not significantly affect the response of the consolidant, and iron can be chelated as long as it is in the correct oxidation state.

The viscous liquid-to-gel transition evident in the rheological analysis was confirmed by small angle X-ray scattering (SAXS) for the polymer networks containing iron (III) sulfate. The material structure becomes more ordered in the presence of Fe^{3+} , which correlates with the addition of the extra metal-ligand cross-links. [18]. Interestingly, after several days the solutions containing iron in the 2+ oxidation state appeared to resemble the solutions containing Fe^{3+} . Further study of the Fe content of the solutions using X-ray absorption near edge structure (XANES) spectroscopy elucidated that after several days the Fe^{2+} in the solutions had been fully oxidised to Fe^{3+} (Fig. 3.5).

This ability of the polymer to oxidise the iron to the 3+ oxidation state, and subsequently chelate the iron within the polymer network, is particularly useful for the stemming of the iron-catalysed degradation. As such not only the available Fe^{3+} is

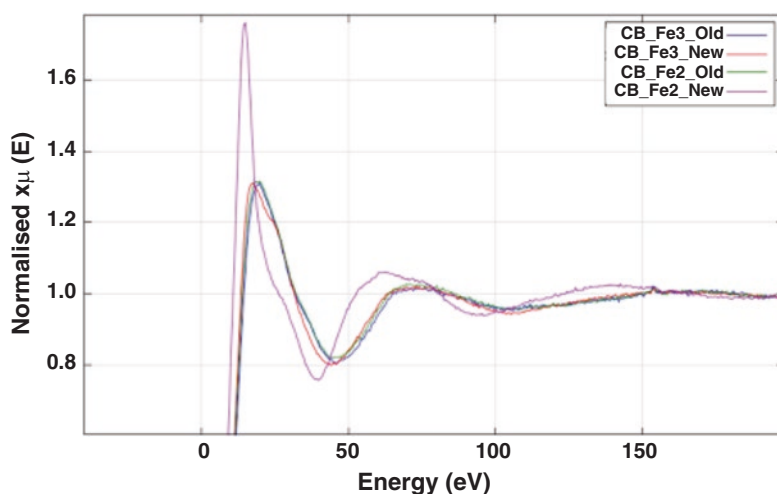


Fig. 3.5 XANES spectra of (pink) freshly prepared *PolyCatNap* containing 1 mM Fe^{2+} , (red) freshly prepared *PolyCatNap* containing 1 mM Fe^{3+} , (green) *PolyCatNap* containing 1 mM Fe^{2+} after several weeks, (blue) *PolyCatNap* containing 1 mM Fe^{3+} after several weeks

taken up into the network but adjacent Fe^{2+} can be converted to Fe^{3+} and chelated before it is naturally oxidised and used to generate acid in the timbers.

These analyses have all shown that the new consolidant can react to the chemical environment of the wood, that is the metal content, and based on this adapt its mechanical properties, which will in turn effect the mechanical stability of the wood. Lastly, bacterial enumeration experiments show that the supramolecular polymer network material can effectively hinder the growth of several strains of bacteria including *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa*, which is extremely promising for the treatment of bacteria in the ship's timbers [18]. Thus, the new *PolyCatNap* consolidant can be used to treat all three major conservation issues in waterlogged wood simultaneously.

3.3 Treatment of Artefacts

As an example of treatment potential, the supramolecular polymer material was applied to the surface of an arrow found with the *Mary Rose*, with high concentrations of iron salts on the surface, Fig. 3.6.

During the optimisation of the *PolyCatNap* networks, two different naphthyl-containing units (2-naphthoic acid (2-NPA) and 2-naphthylacetic acid (2-NPAA)) were tested to determine if the distance between the naphthol and the chitosan backbone altered the material properties of the final network. The solid content of the polymeric network (4 wt. % or 8 wt. %) was also optimised to determine the concentration that best removes surface iron deposits. The naphthol unit is separated from the chitosan backbone by either one (2-NPA) or two (2-NPAA) methyl units. The 2-NPA is denoted as **1** in Fig. 3.6 and was prepared at a concentration of 4 wt. % total polymer solids in a 1 vol. % solution of acetic acid at pH 6.5. The 2-NPAA is both **2** and **3** in Fig. 3.6, where **2** is a 4 wt. % polymer solution and **3** is an 8 wt. % polymer solution, both prepared in the same acetic acid solution. The supramolecular consolidants were applied to the surface, allowed to dry and the films removed from the surface. In doing so the surface iron deposits would also ideally be removed leaving the wood surface undamaged. This was only possible with **3** (Fig. 3.6b–d), as **1** and **2** were difficult to remove from the surface and left a polymer residue on the artefact.

It can be seen in Fig. 3.6b–d that on the edges of the treatment area there is a small white deposit, this is believed to be the formation of a surface salt but further tests are required to determine its exact composition and cause. These negative effects were not observed with polymer **3**, which was easy to remove from the surface and, as can be clearly seen in Fig. 3.6c, d leaves no white deposit formed on the treated area of the artefact. It is possible that the slightly increased spacing between the functional unit and the backbone allows more efficient cross-linking of the network and as such a more stable material.

Under the area where polymer **3** was removed, it is also evident that the colour of the arrow has changed from orange (indicative of the iron salts) to the brown

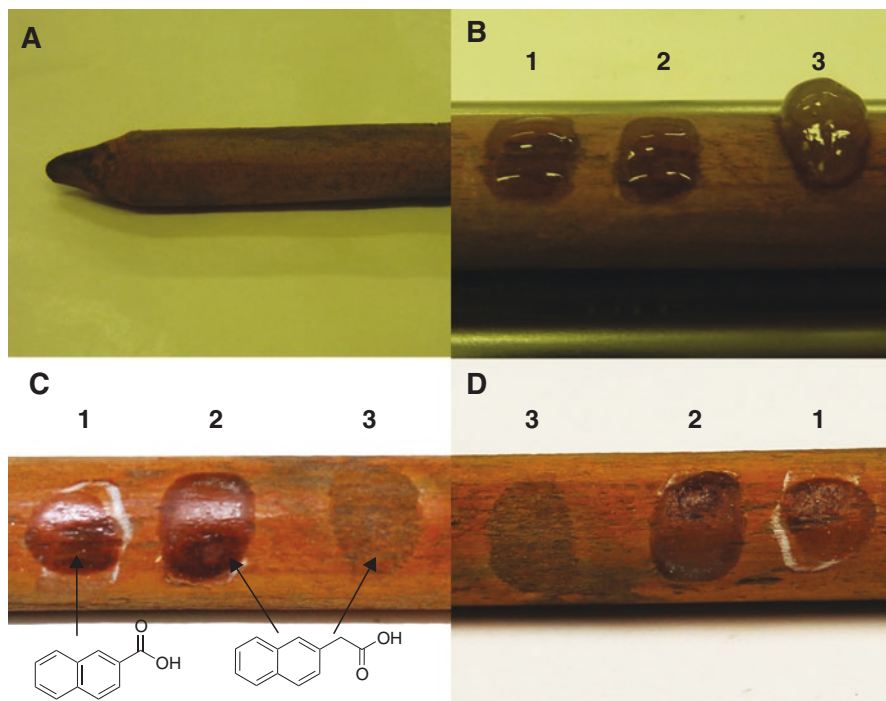


Fig. 3.6 An arrow, found with the *Mary Rose*, with significant surface iron deposits being treated with the supramolecular polymer consolidants; (1) 4 wt. % *PolyCatNap* with 2-NPA (2) 4 wt. % *PolyCatNap* with 2-NPAA, (3) 8 wt. % *PolyCatNap* with 2-NPAA. The images shows the arrow before treatment (a), directly after treatment (b), after 7 days showing also the structures of the 2-NPA (left) and 2-NPAA (right) units used in the optimisation study (c) and after 28 days (d)

colour of the original wood. The polymer likely encapsulated the surface salts in the matrix and allowed facile removal of the salts from the surface without damage to the surface of the artefact. However, such a thick polymer gel could not be used to penetrate the wood and chelate the iron content within the timbers. As such, future experiments will involve studying the diffusion of the material at lower solid content through an archaeological timber sample to determine the feasibility of using *PolyCatNap* as an internal treatment alternative to PEG spraying.

3.4 Impact for the Museum Community

While the synthesis and isolation of the cross-linking unit in this supramolecular system, the molecule cucurbit[8]uril, is patented the molecule is commercially available and the preparation of the consolidant network is detailed in Walsh et al. [18]. Free, open access to research across the museum community is essential for the optimisation of this material. It is quite clear from preliminary studies that this

material works very well for artefacts such as those found with the *Mary Rose*, their degree of degradation and the biological and iron content is suitably counter-acted by this material. However, this is only one artefact and open access to this material across the museum community will help us understand how widely applicable this material can be. This will allow us to determine if these materials really have the potential to outperform PEG treatments as the standard treatment in the first stages of conservation.

3.5 Areas for Further Development

While a large number of artefacts are affected by iron-catalysed degradation processes, without exception all large waterlogged wooden objects are subject to mechanical instability during drying. One of the key issues with preventing mechanical instability in treated objects is the weight of the consolidant used [21]. With this in mind several recent papers have focussed on maximising the mechanical stability by minimising the weight of the consolidant. Again, bio-based polymers show great promise in mitigating the issue of consolidant weight, despite the fact that the individual polymer chains are generally longer than the oligomeric PEG consolidants. The reason for this is their tendency to form networks within the wood, resembling woods' own structure, which lends support to the damaged wood without adding extensive weight [16, 18, 20]. An image of such bio-based polymer networks, specifically chitosan and alginate, within the treated wood is shown in Fig. 3.7.

Our current work is focussed on expanding the range of adaptable consolidants to react to mechanical changes in the wood in addition to the chemical changes induced by the presence of iron. It is well described in the literature that the distribution of load in waterlogged wooden artefacts rarely remains static over time. [21]. Thus, materials must not only react to chemical changes within the wood but also changes in load distribution. Ideally, the mechanical properties of these materials should

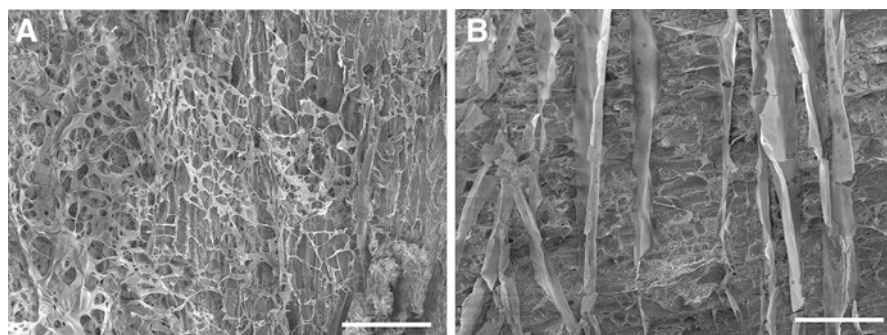


Fig. 3.7 Scanning electron micrographs of archaeological wood treated with (a) a 0.5 wt. % chitosan solution and (b) a 0.5 wt. % solution of sodium alginate

increase as the compressive load on the wood increases. We are particularly interested in the development of new structurally superior consolidant materials based on chitosan and alginate. These mixed, bio-based materials combine the naturally antibacterial properties of chitosan and the excellent mechanical properties of alginates. In preliminary work, networks based on varying concentrations of these two bio-based polymers showed enhanced mechanical stability in their base form, greater than the initial mechanical properties of *PolyCatNap*. Additionally, they show excellent mechanical adaptability to a number of metal ions and combinations of metal ions in solution, an important property as there is unlikely to be just one metal ion within a specific artefact, particularly when Na, Ca and K are so abundant in Nature. Current research is focussing on how to introduce these materials into the wood without effecting the excellent materials properties of the network.

Furthermore, the chemistry of developing such adaptable consolidants is not the only obstacle to their realisation. The analytical instrumentation used to determine the presence of the consolidant in the wood during the treatment process is another significant limitation. Lignin, cellulose and PEG have such distinctly different chemical signals that any number of analytical techniques can differentiate them from one another, allowing the conservator to localise the presence of PEG within the wood. Using bio-based, and specifically polysaccharide-based, consolidants present significant obstacles to the detection of the material within the wood. In particular, the major issue is the difficulty in making a real-time assessment of consolidation progress *in situ* without the need for destructive sampling. Thus, we are not only focussed on understanding the structural behaviour of polymer networks under stress but also on incorporating bio-based optical tags within these materials. Such hybrid, functional materials will function as a green, sustainable sensor that reacts to mechanical changes in the wood with a clear optical signal. As such, the wood under conservation can be monitored *in situ* and catastrophic failure due to excess load can be prevented in good time.

3.6 Conclusion

It is clear that there are many advantages to the replacement of PEG with materials such as *PolyCatNap* and other bio-based (e.g. chitosan/alginate-based) materials. The major advantage of these adaptable networks is their ability to react to and counter-act conservation issues as they present themselves, specifically iron catalysed degradation, biological activity and mechanical instability. Additionally, being primarily sourced from bio-based materials, they are cost-effective, do not form acidic degradation products, can remove surface iron deposits quickly and without damage to the artefact and appear to show diffusion capabilities within the wood. The advent of a new generation of renewable, reversible, greener, more compatible conservation treatments for the preservation of wooden artefacts of historical importance is a significant gain for the museum community and further research on this topic will be of great importance in years to come.

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