Developing new consolidants for archaeological wood

Dissertation for the degree of *Philosophiae Doctor*

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"One should practice what one considers to be one's duty, guided by reasons, instead of blindly following the practices of the world."

- Tuladhara the merchant, the Mahabharata Book of Peace.

Acknowledgements

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Viking Age wood and modern materials science. A position funded by the Museum for Cultural History but officially carried out at the Department of Chemistry. That may seem unusual but I suspect that most Ph.D. studies probably contains of surprises. I, at least, have had quite a few. Some are related directly to my research, some more personal. When I moved to Oslo, I would never have guessed that I would end up learning some Indian cooking, winning a 'most sporting opponent' award at miniature gaming, or singing in front of hundreds of people. Of course, all of these things happened because of the people around me, without whom my time and studies would have been very different (not to mention insanely dreary). The people who helped and encouraged me are far too numerous to list here, I fear, so I have been forced to (perhaps unfairly) cut the list down to the most essential core of all the people who have offered their support.

First of all, I would like to thank my supervisor, Hartmut Kutzke, for encouraging me to move to Oslo and undertake this task. Hartmut, I have enjoyed our discussions, your enthusiastic being and your ability to shrug off adversity and claim it is "also part of becoming a researcher". In particular, I have come to admire your incredible skill at clear and concise writing (a skill I sadly lack). My primary supervisor, Finn Knut Hansen, has certainly been no less fundamental in shaping my work. Finn, I have been grateful for your pragmatic mindset in our discussions, your respect for the restrictions put forth by ethical conservation demands, and – last but not least – your quirky humour which has brightened many a lunch break. It is delightful to discuss problems with you and see how acutely you adapt your knowledge to new situations. Although not formally my supervisor, Susan Braovac has certainly served as one. She has helped with a wide range of problems – from introducing me to the status of the collections to making sure I had a place to live. I have run to Susan whenever I needed conservation facts, a different approach to my experiments, samples, or simply a 'reality check'. To put it briefly: Susan, you are a life-saver (just ask my family).

My colleagues at the Department of Conservation also deserve high praise for welcoming a chemist and treating him as one of their own. I have enjoyed my time with all

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Abstract

The aim of this work was to design and test new kinds of consolidants for archaeological wood as well as figure out what avenues of research seem promising for future investigations. The need for new consolidants is exemplified by the severely degraded state of several parts of the Oseberg find – the most richly ornamented Viking Age find in the world – which is undergoing active degradation due to being extremely acidic as a result of the original treatment with alum salt ($KAl(SO_4)_2 \cdot 12H_2O$).

Previously tested consolidants often fail at penetrating sufficiently deep into the wood, offering the required mechanical support, or leaving treated artefacts re-treatable. As nothing lasts forever, re-treatability is an essential ethical requirement when working with cultural heritage. Since reversibility is difficult to achieve, the way to ensure re-treatability is to leave most of the pores naturally occurring in wood open, thus leaving canals for future treatments. Finding a very stable consolidant (to postpone re-treatment for as long as possible) is also important, so compounds with ether or ester bonds should probably be avoided as oxygen is likely to degrade them.

Initial tests were carried out on acid-catalysed phenol-formaldehyde (PF). The cured polymer is resistant to acid and chemically similar to lignin (the compound in archaeological wood which usually takes the longest to decay). Acid catalysis leaves less oxygen in the structure of the polymer than base catalysis (which was the route chosen in Bakelite production). Tests showed that the polymer changed look depending upon which solvent is used to dissolve pre-polymer molecules (acetone gives a dark red or brown result while propan-2-ol results in a lighter and more yellow product). The polymer can eventually cure under water and did not become powdery after being kept in an oven at 70°C for more than a year. Unfortunately the bright reddish colour means it cannot be used for the surface treatment of archaeological finds and since both phenol and formaldehyde are toxic, it will be difficult to treat items already on display with PF. On the other hand, the phase separation which happens during polymerisation seems to naturally preserve the structure of archaeological wood by leaving the watery phase in the voids. Unfortunately, some heavily degraded material from the Oseberg find lost its shape during treatment as the alum crystals dissolved in water and further tests are required to develop a protocol for such items.

The field of biomimetics (adapting materials and solutions inspired by nature) may be an important source of future wood conservation. Most naturally occurring polymers are non-toxic and many are water-soluble. Tests began on cellulose crystals (or 'whiskers') which are resistant to acid and occur naturally in wood. While cellulose attaches to the surface of wood, the whiskers agglomerate during the impregnation of archaeological wood and the high ion content in archaeological material makes it tricky to keep the whiskers separated long enough to allow a proper impregnation. It may be possible to inject cellulose whiskers into larger cracks and voids in archaeological material to construct a kind of 'scaffolding' for other consolidants to adhere to, however.

Testing moved on to chitosan which has the advantage of being cellulose-like but can be dissolved in monovalent acids. Tests showed that acetic acid was more efficient than hydrochloric acid and a 2%^{w}/$_v$ chitosan solution in 1 M acetic acid had a pH value of about 5 which is ideal for archaeological wood. In two weeks, the solution penetrated into small test pieces (roughly 0.5x0.5x2 cm) of Viking Age wood and reached an even distribution. After freeze-drying, the pieces had a similar hue to the unimpregnated wood but were considerably more coherent and easier to cut with a razor blade. Hopefully, the anti-fungal/bacterial properties of chitosan, along with its ability to chelate metal ions, will make it an even more suitable consolidant.

Opsummering

Målet med dette arbejde har været at forsøge at udvikle nye former for midler til bevaring af arkæologisk træ samt at forsøge at give eksempler på gode metoder man bør forske på i fremtiden. Behovet for disse understreges af dele Osebergfundets nedbrudte tilstand, som er et resultat af syre dannet på grund af den oprindelige behandling med alun ($KAl(SO_4)_2 \cdot 12H_2O$). Tidligere afprøvede midler til at forstærke arkæologisk træ trænger ofte ikke tilstrækkeligt langt ind i træet, forstærker det ikke tilstrækkeligt, eller efterlader træet blokeret så det ikke kan genbehandles i fremtiden. Eftersom intet varer evigt er det essentielt fra et etisk standpunkt at kunne genbevare kulturelle fund. Da reversibilitet normalt er umulig at opnå i praksis, sikres genbehandling bedst ved at efterlade porer og lumen i træet åbne, så der er plads til at tilføje mere materiale i fremtiden. Det er også vigtigt at finde et stabilt stof så genbevaring kan udsættes længst mulig tid og i denne sammenhæng er æter- eller ester-bindinger et problem da ilt fra luften nedbryder dem.

De første undersøgelser blev foretaget på syre-katalyseret fenolformaldehyd (PF). Polymeren er resistent overfor syre og minder rent kemisk om lignin (der er det stof i arkæologisk træ som er mest resistent overfor nedbrydning). Syrekatalyse efterlader mindre ilt i polymerens struktur end basekatalyse (som typisk blev anvendt til produktion af Bakelit). Det viste sig at polymeren ændrer udseende afhængig af hvilket solvent præpolymere molekyler blev opløst i (acetone giver en meget mørk rødbrun hvor propan-2-ol giver et lysere gulligt produkt). Polymeren kan, givet tilstrækkelig tid, hærde under vand og blev ikke sprød eller smuldrede efter at være opbevaret mere end et år i en 70°C varm ovn. Desværre betyder den dybe røde farve at polymeren ikke kan anvendes til at konservere overfladen af museumsgenstande og eftersom både fenol og formaldehyd er giftige er de ikke ideelle til at genkonservere genstande som allerede er udstillet og er vanskelige at flytte. På den anden side gør faseseparationen som sker under polymerisationen at den organiske fase binder sig til træet hvorimod vandet tvinges ud i porer og bibeholder træstrukturen. Beklageligvis mistede yderst nedbrudt materiale fra Osebergfundet sin form under behandling da den vandbaserede blanding opløste alunkrystallerne som holdt på træets facon, så andre solventer må udvikles hvis metoden skal benyttes på sådanne fund.

Biomimetik (at tilpasse materialer eller design som findes i naturen) kan være en lovende for konserveringsvidenskab. De fleste polymerer i naturen er ikke giftige og mange

kan opløses i vand. Krystallinsk cellulose blev afprøvet da det er resistent overfor syre og allerede findes i træ. Selv om cellulosekrystallerne sætter sig fast på overfalden af træet, begynder de at flokkulere på grund af de mange ioner i arkæologisk træ og trænger derfor kun et par mm ind i materialet. Det bliver derfor problematisk, selv med tilsat surfaktant, at holde krystallerne adskilte under imprægneringsprocessen. Cellulosekrystaller kan muligvis injiceres i større sprækker i træet for at danne et materiale som andre stoffer til forstærkning af træet kan sætte sig på.

Forsøgene blev derfor fokuseret på kitosan som på mange måder minder om cellulose men kan opløses i monovalente syrer. Eddikesyre gav mere stabile opløsninger end saltsyre og 2%^{w}/$_v$ kitosan i 1 M eddikesyre har en pH omkring 5, hvilket er ideelt for behandling af arkæologisk træ. Opløsningen trængte ind i små (ca. 0.5x0.5x2 cm) prøver af træ fra vikingetiden og var fordelt jævnt efter to uger. Efter frysetørring så de behandlede prøver ud som de ubehandlede men var langt mere stabile og lettere at skære med det barberblad. Kitosan er desuden en antibakteriel fungicid og kan binde metalioner, hvilket kan gøre stoffet til attraktivt i forbindelse med behandling af arkæologisk træ.

X

List of abbreviations and expressions

This work contains a number of words and expressions which are common in either chemistry, wood engineering, or conservation. Since these expressions may not be well known to those individuals who do not work within all fields, a list of abbreviations and expressions is given below.

ATR   Attenuated Total Reflectance. An attachment to an IR spectrophotometer where the sample can be placed on a small crystal, often made of diamond, and examined as long as good contact between sample and crystal remains (usually by a metal pin pressing the sample onto the crystal). This eliminates the need for sample preparation (like grinding KBr pellets or cutting thin slices of sample material) as long as one dimension of the sample is small enough to fit under the metal pin.

Björkman lignin   Also known as Milled Wood Lignin (MWL) this is the fairly unchanged lignin one gets by grinding wooden tissue finely and extracting lignin with aqueous dioxane (aka 1,4-dioxacyclohexane).

Cellulose whiskers The small mostly crystalline ellipsoids which remain after cellulose fibres have been treated with acid to make the amorphous material dissolveable in water.

Cinnamyl alcohol (*E*)-3-phenyl-2-propen-1-ol. A basic chemical structure similar to the one found in the monolignols and thus the name is sometimes re-used when naming these.

Coagulation   The initial collision of particles in suspension into larger forms. It may lead to flocculation.

Coniferol   See 'coniferyl alcohol'.

Coniferyl alcohol	4-(3-hydroxy-1-propenyl)-2-methoxy-phenol. One of the monolignols, also called 'coniferol'.
Consolidant	Any material added to archaeological artefacts to reinforce and preserve them.
Coumaryl	See '*p*-coumaryl'.
Dispersion	A liquid in which particles are suspended (as opposed to as *solution* where there are no particles because they dissolve).
DHP	DeHydrogenation Polymer. A lignin-like compound made by dehydrogenating one or more monolignol(s), causing them to polymerise.
DLS	Dynamic Light Scattering. A technique which uses intensity fluctuations of a laser over time to measure particle size and mobility in dispersions.
ESEM	Environmental Scanning Electron Microscopy (see 'SEM'). The technique is the same as regular SEM but uses a low vacuum (rather than the usual high vacuum) which means that it is possible to scan samples without coating them.
Flocculation	When particles in dispersion stick together, potentially leading to huge agglomerates. The initial process is called 'coagulation' with 'flocculation' being larger particles. Obviously, this must be avoided in impregnation baths.
FTIR	Fourier Transform Infra Red (spectroscopy). A common technique which determines the relative amount of functional groups in a compound by examining the absorption of infra-red light (typically

with wavelengths in the mid infra red region around 2500-25000 nm) by said compound.

Glyoxal   Ethanedial (IUPAC), O=CHCHO. The smallest dialdehyde. It may be used in place of formaldehyde for polymerisation experiments due to lower vapour pressure and thus toxicity.

Holocellulose   The non-aromatic 'building blocks' of wood. Holocellulose is a way of referring to both cellulose and hemicelluloses (but not lignin).

HPLC   High Performance Liquid Chromatography. A standard chromatographic method which separates different compounds usually based on their interaction with the material in a packed column. A detector then measures the amount of components in the solution over time.

In situ preservation   The practice of leaving found items buried (usually when there is insufficient money for proper conservation) in order to avoid exposing them to air and other factors which might degrade them further.

IR   Infra Red. If a kind of spectroscopy, see 'FTIR'. Note that IR often means Mid Infra Red (MIR) the region from 400 to 4000 cm^{-1} (2500-25000 nm).

Klason lignin   The insoluble remains of wooden tissue after treatment and refluxing with H_2SO_4 (initially 72% then diluted during reflux). This lignin has been heavily modified by the acid.

Kraft pulping   The process which separates cellulose from lignin during paper production. The obtained 'kraft lignin' is sulphonated.

MALDI-TOF   Matrix Assisted Laser Desorption/Ionisation – Time Of Flight mass spectrometry. A technique where a UV laser is used to ablate the upper layer of a sample. The constituents are then ionised and led through a mass spectrometer to identify chemical components.

Monolignols   The three basic cinnamyl alcohol monomer 'building blocks' which make up most of the lignin structure: *p*-coumaryl, coniferyl, and sinapyl alcohol.

MWL   Milled Wood Lignin. Also called Björkman lignin.

NMR   Nuclear Magnetic Resonance (spectroscopy). Also simply 'MR' (especially in the field of medicine). A technique which utilises a magnetic field to detect atoms with an odd number of protons. The spectrum is measured as a 'chemical shift' (typically relative to a reference compound/solvent). Each top gives information about the chemical structure of the compound as well as the relative quantity of each type of atom. 2D-techniques (like HMQC or HMBC) can even determine how atoms are connected and thus the chemical structure of the sample can be extrapolated.

Paraloid   A range of common consolidants which can be dissolved in acetone. The most common is probably Paraloid B-72 which is an etylmethacrylate-metylacrylate co-polymer.

p-coumaryl (alcohol)   4-[(*E*)-3-hydroxy-1-propenyl]phenol. One of the three monolignols.

PEG   Poly(ethylene glycol) or 'poly(oxy ethylene)' according to IUPAC - and sometimes seen as 'poly(ethylene oxide)'. An ether chain, $H[-O-CH_2-CH_2]_n-OH$, commonly used to stabilise waterlogged wood by watery impregnation and subsequent freeze drying.

XIV

PF   Phenol-formaldehyde. A very durable thermoset polymer and the first
                      polymer to be mass produced under the name Bakelite. It is resistant to
                      most acids, bases and solvents.

F:P(-ratio)   The ratio of formaldehyde to phenol in a PF polymer. The higher the
                      number the more cross-linked and durable the resulting polymer
                      becomes. Below a value of 1, the polymer does not harden properly.

Raman spectroscopy   Named after C. V. Raman, this kind of vibrational spectroscopy
                      gives results similar to IR spectroscopy. Spectra are recorded by
                      shining a laser at the sample so it is a non-destructive technique.
                      Fluorescence from organic (often aromatic) compounds may make it
                      difficult to obtain spectra from archaeological samples.

Reaction wood   Wood which forms when the tree is under pressure or has some uneven
                      support (for example when leaning). In softwoods such wood is called
                      'compression wood' and forms below the overhang. In hardwoods it is
                      called 'tension wood' and forms above the overhang. Compression
                      wood has a high lignin content while tension wood is made up almost
                      entirely of cellulose.

RH   Relative humidity (the ratio of the partial pressure of water pressure in
                      a given volume of air compared to the saturated water vapour pressure
                      at a given temperature).

SEM   Scanning Electron Microscopy. A kind of high resolution microscopy
                      where images are obtained by scanning the sample with an electron
                      beam which gives information about the topology and electrical
                      conductivity of the sample. Note that samples normally have to be
                      coated (sputtered) with a thin layer of carbon, gold and/or palladium to

make the samples conductive and prevent electrostatic charges which distort the images.

Sinapyl alcohol   4-methoxy-3,5-dimethoxycinnamyl alcohol aka. 4-(3-hydroxy-1-propenyl)-2,6-dimethoxphenol. One of the monolignols.

Specific gravity   This is the ratio of the weight of a given volume of wood compared to the weight of an equal amount of water. Note that this is similar to density (since water has a density of approximately 1 g/cm^3 at room temperature) but unitless.

TAPPI   Technical Association of Pulp and Paper Industry.

Whiskers, cellulose See 'Cellulose whiskers'.

Table of Contents

XX

1. Introduction

From times immemorial, humankind and wood have been inseparable. Wood is integral to everything from structures to tools, boats, and weapons [1](p. 434). Paper has long been integral to communication and learning. Despite the abundance of steel and concrete, wood is still used when building cottages, housing, and furniture (possibly modified – for example into fibreboard). Wood products seem to have an bright future as bio-degradable and environmentally friendly materials. With the ability of trees to absorb CO_2, environmentalists hope to see forest areas spread. Current engineering makes it possible to design what is referred to as 'liquid wood' – a wood-based material which can then be cast into a desired shape, allowing future television sets or computer cabinets to be made from what is essentially wood [2]. Thus wood is likely to continue to play an important role in the history of humankind.

The link between humanity and wood has been interpreted metaphorically as well. The ancient Chinese philosophical system of Five Elements (五 行 - *wǔ xíng*) even considers wood the most human of the fundamental five 'steps' or 'phases' due to its ability to grow [3], [4].

Jorge Agustín Nicolás Ruiz de Santayana y Borrás (better known as 'George Santayana' in the US where he lived) wrote the famous words, "Those who cannot remember the past are condemned to repeat it."[5]. Taken as a general encouragement to understand the past, one might believe that wooden finds are essential in describing our ancestors. This is not always so. Past cultures have been defined from leftover stone and ceramics since organic materials are not found at archaeological sites as often as inorganic ones. This makes any surviving wood rare and thus precious [1](p. 436).

Sadly, the abilities which sometimes make wood desirable, such as biodegradability, cause problems when one wishes to preserve wood from earlier times. Archaeological wood is often found submerged in bogs or similar wet places which provide a certain measure of protection from biological degradation. Such finds are often extremely fragile and warp and collapse upon drying, making it vital to consolidate these precious bits of history in order to preserve them for future generations.

Even once treated and put on display, wooden artefacts may prove problematic. In the case of the most richly ornamented Viking Age find in the world, the original treatment proved damaging to the wood (this is fully explained in chapter 2 'The Oseberg find' on page 7). This exemplifies the need to understand the possible degradation processes occurring in treated wooden artefacts as well as to develop new materials without such drawbacks.

Chemists, in general, can make valuable contributions to the field of cultural heritage. Firstly, the 'impurity' of many archaeometrical samples makes it that much more important to try to identify as many constituents as possible. Secondly, conservators are very skilled at treating, displaying, and restoring objects. Unfortunately, they are often forced to work with woefully little information. A wrong guess can obviously lead to a wrong treatment, which may be harmful to the treated artefact. Even if everything about a given chemical analysis cannot be elucidated (if, for example, a vibrational spectrum contains unidentifiable bands), it is much better to get a rough idea about the object than to know nothing (chemically speaking).

Developing new consolidants in particular is a task for chemists as it requires some understanding of the chemical composition of both the proposed consolidants and the wood itself. On the other hand, it cannot be done without taking the practical and ethical concerns of a conservator into account. For this reason, it required a close collaboration between both kinds of professionals. The work has also brought together past and present by including 'historical' chemical materials like Bakelite (patented in 1907 in the US by Leo Hendrik Baekeland [6]) while also looking to modern bio-inspired materials.

1.1 Background

The present state of Oseberg find is the primary reason why this Ph.D. project was initiated. Thus the story of Oseberg is told and comments about alum-treated materials are made throughout this thesis. However, it is imperative to note that the aim of this study is not to save the Oseberg find. Another related Ph.D. project – aiming to identify the degraded wood from the Oseberg and test existing conservation treatments – was initiated shortly

after this project began. Thus this work has been focussed on *defining possible new consolidants for archaeological wood from a chemical perspective while testing some of those materials*. The experiments are focussed on *phenol-formaldehyde*, *cellulose whiskers* and *chitosan* but an extensive literature review is given initially since it is the framework on which ideas about new consolidants have been built.

Several ideas arose which could not be implemented due to time constraints. These possible future consolidants are discussed at the end of the thesis (specifically chapter 8.6 'Future avenues of research' on page 185). For this reason, the work will possibly be more valuable for wooden artefacts which will be found and treated in the future than the displayed items in our museums today.

Since this work was funded by the Museum of Cultural Heritage but carried out mainly at the Department of Chemistry, it was a requirement that this thesis contains sufficient background information to make it readable by both conservators and chemists – and that the so-called 'edutainment' carried out was included since public education and lecturing are an integral part of museum workings (see Appendix A). Thus several concepts are explained at a more basic level than required within the respective fields and the linguistic style is deliberately kept fairly fluent. This will allow future students to read this thesis in order to gain an overview of background and ideas of the project, which means future works can be more focussed on actual experiments performed.

In order to follow conventions (particularly in the field of conservation) some words or expressions are used, which do not correspond to IUPAC (the International Union of Pure and Applied Chemistry) recommendations. Thus the text refers to 'PEG' or 'polyethylene glycol' rather than the recommended IUPAC name 'poly(oxy ethylene)'. Similarly, it has been attempted to write the thesis in British English, balancing between traditional spelling and certain IUPAC recommendations for spelling (for example using '*sulphur'* rather than '*sulfur'*). Also, note that the word 'artefact' is used in the archaeological sense (objects recovered from an earlier culture) rather than the chemical sense (faulty data).

References in this work are placed at the end of the content in which they are used. This does not carry over between paragraphs, so in case a given reference has been used for several consecutive paragraphs, it will be noted at the end of each one. The reasoning

behind this is that it is easier to see where summary remarks and speculations have been made by the author as these are put after the reference.

1.2 Initial ideas and work flow

When the project started, it was realised that there were a bewildering number of directions in which to proceed. Based primarily on discussions with F. K. Hansen, H. Kutzke and S. Braovac these included (but were not limited to):

- Carbon-based polymers (see chapter 6.2)
- Artificial lignin (future ideas in chapter 8.6.4)
- Re-use of waste lignin
- Silicon-based polymers (future ideas in chapter 8.6.2)
- Nanoparticles (for acid neutralisation) (see chapter 7.4)
- Nanoparticles (for structural support)
- Carbon nanotubes
- Biomimeralisation (later changed to biomimetics – see chapter 7.1)
- Bacterially produced cellulose (changed to cellulose whiskers – see chapter 7.2)

Obviously, it would be impossible to cover all these aspects within the relatively short time frame of a Ph.D. project. Unfortunately, it was not obvious which of these approaches would be most advantageous. At the same time, discussions at the Department of Conservation led to a list of requirements (as seen in chapter 5.2 on page 75). Although it was realised that it would most likely be impossible to satisfy all the requirements of such a list, it served as a guideline of ideal goals throughout the project. This led to the initial phase of the project being a literature review in order to better determine which approaches seemed possible to implement while fulfilling as many of those requirements as possible.

In the initial stages of the project, it was envisioned that artificial lignin would be an interesting road to pursue, so tests on phenolic polymers were started as they would be chemically similar to lignin. It was believed at the time that relevant information about phenol-formaldehyde (PF) would be readily available and this would allow easy implementation of the compounds. Tests on phenolic compounds were discontinued for two reasons. Firstly, became apparent that actually treating archaeological wood with PF was

much more difficult than originally envisioned. Secondly, the people at the Department of Conservation expressed their increasing concerns about the toxicity of the monomers required during impregnation. In stead, the project was turned towards biomimetics as this field dealt with so-called 'green' chemistry. Although water is a problematic solvent for alum-treated material (see for example Figure 6.16 on page 110), it would be ideal for treating new waterlogged finds. Initial tests started on cellulose as it is already present in the degraded wood. Sadly, it was difficult to keep the cellulose dispersed. Chitosan was thus investigated as an alternative. Despite initially promising results, the project ran out of time and many roads were left as ideas for future avenues of research.

2. The Oseberg find

Since the threat of degradation now facing the Oseberg find was a significant reason this Ph.D. came about, the find will be described in some detail although the work itself has not been solely focussed on the artefacts from Oseberg. Additionally, the Oseberg collection serves as an excellent example of unforeseen consequences arising due to the choice of consolidant and thus demonstrates the need for the development of new treatments.

The Viking ship from Oseberg is probably one of the most famous

Figure 2.1: Photograph of a Norwegian 20 kr coin showing the profile of the Oseberg ship.

historical artefacts in the world and helps explain why the Viking Ship Museum in Oslo is the most visited museum in Norway [7]. Along with the animal head posts and sledges, the profile from the Oseberg ship has been used as a worldwide symbol of the Viking Age. The profile of the ship can be seen on the Norwegian 20 kroner coins – as seen in Figure 2.1 – which is fitting as the Viking Age collections are considered national symbols.

Sadly, most of the Oseberg collection is in a precarious state due the long-term effects of the alum originally used to preserve the waterlogged wood (for more on the treatment itself, see chapter 4.1.3 'Alum treatment' on page 54). The treatment was successful and has kept the items on display for more than a hundred years. It was probably the best alternative given the choices available at the time of consevation. Still, several complications now threaten the stability of the wooden items.

2.1 The contents and history of the find

The discovery of the ship was made on the 8th of August 1903 and the excavations started in June 1904 and finished later that year. From this point it would take another 21 years before all artefacts were treated and reassembled. The discovery at *Lille Oseberg* generated so much interest that people flocked to the excavation site and fences, signs, and a guard even had to be posted. The discovery was a turning point in Norwegian history because laws at the time did not require such historical artefacts to be turned over to the state, allowing the owner of the property. Knut Rom, the farmer who discovered the Oseberg ship on his lands, was allowed to sell it to whomever he pleased. After the excavations were complete, the agreement with the government had still not been settled. An estate owner, Fritz Treschow, bought the ship for 12000 kroner and generously donated it to the Norwegian state. To prevent finds from falling into the hands of private collectors in the future, the government passed a bill to prohibit the export of antiquities or sales to the highest bidder [7].

The mound was originally 6 m high and about 40 m in cross section. It is situated about 4 km from the sea 15 m above sea level (note that both these numbers were smaller in Viking times). Most of the timber was very well preserved, being laid out on blue clay and with clay-containing peat covering the cairn. The weight of this arrangement pressed down on the ship and broke the keel in two. This damaged many of the objects inside. Some time after the burial, grave robbers took away anything made of gold and/or silver – and even parts of the bodies [8].

The mound contained, among other things, the skeletons of two women, fifteen horses, an ox, food, equipment for travelling by both land and sea, an entire ship, and four sledges. Damage from the crushing weight of the mound meant one of the sledges was put together from 1068 pieces [8]. It is unknown who the buried women were but they were clearly worthy of great respect. It is assumed that one of them had inherited land after a late husband or that they served in some important religious position [9].

The highly ornate surfaces of the wooden items makes them special and in this regard the Oseberg find is the most unique of all Viking Age finds. Examples of these items as they appear today can be seen in Figure 2.2.

Carbon dating gave an age of A.D. 720±80, although the style of decorations would indicate a later date [8]. Current research puts the date of the burial at 834 A.D. Note that the ship had been in use for several years at the time, so the wood is old enough to be in the range of the carbon dating. The ship itself is not only the most ornamented Viking Age vessel found but also the earliest Scandinavian vessel found with a sail. The design was different from finds of ships dated just 50-75 years later, with the Oseberg ship having lower sides – presumably because it was meant to sail in fjords and along the coast rather than across the open sea [9].

Figure 2.2: Examples of the highly ornate items from the Oseberg find. To the left, the partially alum-treated wagon. To the right an animal head post which has never been consolidated.

2.2 Conservation history of the find

To understand the consolidant choices available to conservators at the time, one must remember that polymer chemistry was not developed. Although Thomas Graham began distinguishing between *crystalloids* and *colloids* in 1861, these were still thought of as agglomerates of smaller molecules rather than single large molecules until about 1930. H. Staudinger and Pickles, starting in the late 1920's, both attempted to convince others that such structures are in fact large linear molecules [10](p. 1-2). The first commercial plastic, Bakelite, was not patented until 1907 [6]. Thus plastics were unknown at the time the Oseberg find was treated and relatively few viable conservation methods existed.

The ship itself was treated with creosote and linseed oil. Another application of linseed oil and white spirit was performed in 1957 [8]. Since the ship itself was never treated with alum, but simply dried and lacquered, it is currently in significantly better shape than most of the other artefacts from Oseberg [11].

Many of the other pieces were treated with alum (for more on the treatment itself, see chapter 4.1.3 'Alum treatment' on page 54) and a following application of linseed oil and lacquer. It was found that the alum treatment flattened the surfaces and thus blurred the details of the many fine carvings. To prevent this, some of the objects (such as two sledge shafts) were kept under water in a formalin solution for 50 years (until 1954) [8].

The waterlogged wood has lost most of its cellulose and only about half the dry matter expected in fresh wood remains in the Oseberg wood [8]. Both cellulose and lignin was left in the wood after it had been contained in water for 50 years after excavation (although more exact measurements are not given) [12]. After having been stored in water for so long, the wood had become very soft and on several occasions fungi had grown in the containers despite the added 2% formaldehyde. The displays were glass sides on a brass bottom. Some of the finds had been skewered on lead spikes covered with 'Bakelite' (which may or may not have been phenol-formaldehyde, see the second paragraph of chapter 4.1.5 'Phenol-formaldehyde treatment' beginning on page 59). The released ions reacted with the silver alloys in nails ornamenting the carvings. This turned the liquid green and deposited powder and crystals of lead oxalate. In at least one case, crystals of metallic copper were also found on the brass rods [8].

To minimise treatment of objects, some of the water was replaced with trimethyl carbinol and then dried in vacuum. Thus two of the animal head posts on display today consist merely of the degraded wood with nothing to stabilise the core of the objects. The method also left some transverse cracks despite every precaution – and despite the fact that this had not happened in the preliminary experiments [12].

Different bulking materials were tested on the waterlogged Oseberg wood. Urea formaldehyde has been used at various institutions for preserving waterlogged wood. The results seem to depend heavily on the state of the wood and its acidity – and was thus deemed too risky for the Oseberg wood. *Cetalol S. A.* is an alcoholic mix which can be melted and solidifies on cooling. It was found to twist and crack the wood upon treatment.

Jasperol, which is a sulphonated mix of alcohols from spermaceti oil, was too soft and gave the surfaces a 'fatty' appearance. Thus, in many cases, PEG (Poly Ehtylene Glycol, another name for poly[oxy ethylene]) was used. The objects were left in the PEG solution for 'some days'. Despite some cracking and shrinkage, many of the coarser objects were successfully treated this way [12]. The short time of impregnation may have made the shrinkage and cracking much worse than it really had to be (see chapter 4.1.4 'Poly(ethylene glycol) treatment' on page 57).

There was no room to display the Oseberg find at the existing Historical Museum. In fact the Tune ship and the Gokstad ship were already stored in sheds. Thus a new museum was built specifically for the Viking ships. It was not completed until 1957, although the first wing was finished earlier and the Oseberg Ship moved there in 1926 [7].

A fairly constant RH (relative humidity) is maintained in the display cases by storing supersaturated salt solutions in the stands [12]. This practice is still in use [11]. Monitoring is going on at the time of writing to determine how much effect the changing seasons have on the Oseberg ship in order to determine if further precautions are necessary.

2.3 Current challenges

Some years back, the conservators at the Viking Ship Museum noticed that bits had fallen off the sledges. This led to an extensive project where the supports were rebuilt and the items on display better stabilised. During this work it became evident that the objects are now unable to stand without support in the way shown on old pictures taken just after the original conservation [11].

There are several problems facing the alum-treated objects of the Oseberg find – especially the complex mounted objects like the sledges. First of all, the alum-treatment seems to have generated sulphuric acid as the salt decomposed during the initial heating. The pH value of the finds now lies in the range of 0-2 when tested by wet pH strips. Such an acidic environment has degraded both the cellulose and the lignin in the finds. The acid causes the paper wrapping originally used to pack the items on storage to disintegrate. Much worse, the finds themselves are often so deteriorated that they would powder where it not for a thin layer of lacquer holding everything together [11], [13].

The state of a given piece of alum-treated wood can be judged by looking at it since darker parts are typically the most fragile [11]. This can be directly linked to studies of lignin wood pulps which show that those with the highest delignification factor also display the most colour. The most likely explanation being condensation as the degradation of lignin seems to occur through demethylation, ether bond cleavage, and breakage of the Cβ-Cγ bonds [14]. Many of the treated wooden items (especially pieces in storage) are now very dark and powdery.
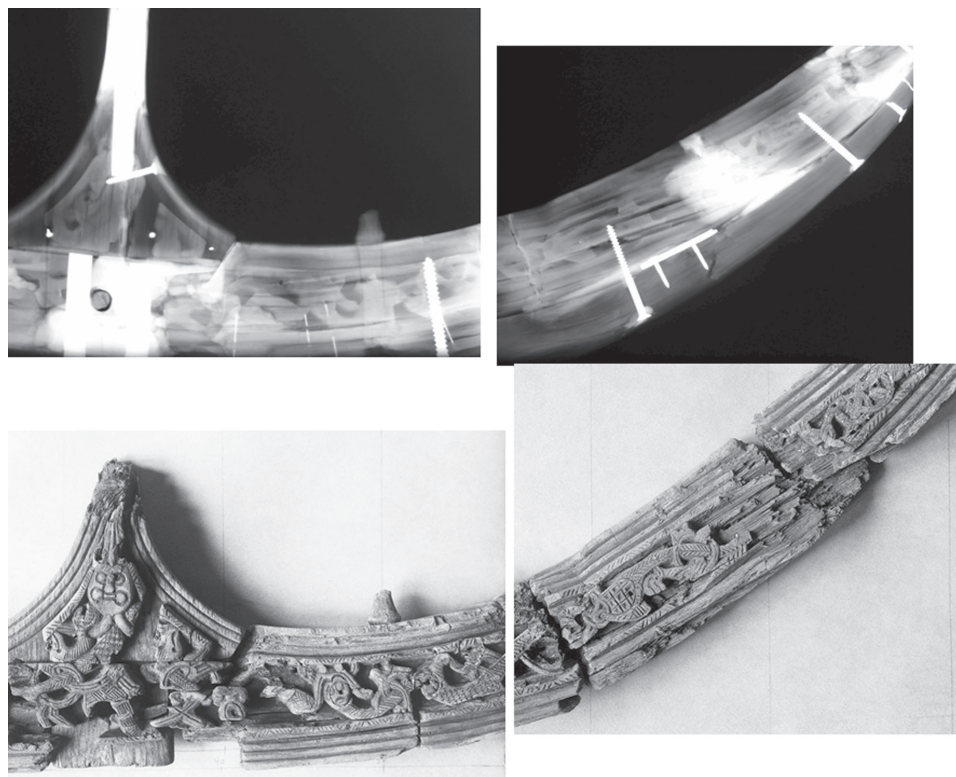
Figure 2.3: X-ray images (top) and photographs (bottom) of a part of one of the sledges from the Oseberg find. Note the vast amount of filler material and screws in the artefact. © Museum for Cultural History, University of Oslo.

In addition to the general degradation, most of the mounted pieces are filled with screws and nails attaching them to their frames. An example of this can be seen in Figure 2.3. The corroding metals release ions which may act as catalysts, speeding degradation along.

Iron in particular seems to catalyse various active degradation processes in the *Vasa* (the most famous shipwreck in Sweden), both of holocelluloses (the non-armoatic organic content of wood) and of PEG. Comparison between computer simulated and actual MALDI-TOF (Matrix Assisted Laser Desorption/Ionisation – Time Of Flight mass spectrometry) data indicate that a random cleavage of PEG chains is going on. The problem seems more pronounced in the middle of the wood. Thus iron is a far more serious problem than sulphur [15]. On the other hand, corroded metal pins seemed to act as a biocide in at least one previous study [1](p. 339). Despite this positive side effect, ensuring that metal ions do not catalyse the degradation of the remaining Oseberg material is of vital importance.

Sulphur is a concern in museums in general. Acidic sulphate salts on the surface of the *Vasa* hull presents a similar case. It is estimated that there are still about two and a half metric tonnes of S in the hull, all of which would generate another six tonnes of acid. Exposure to moisture seems to generate sulphur-containing salts in the outermost layers of the wood. This links water to acid formation [16]. Considering that the degraded finds from Oseberg were treated with a sulphate salt, sulphur contents are obviously very high in these finds as well. Moisture is also readily available through the air.

Since it is tricky to keep the *Vasa* completely dry, various methods for neutralising the salts have been investigated, with a prominent solution being ammonia vapours. A mild exposure does not seem to degrade the PEG or wooden structure. While neutralisation with nanoparticles might be possible, the extremely alkaline environment around the particles would likely damage the lignin as well. It is also unlikely that CO_2 will convert the hydroxides to carbonates as quickly as is often estimated (if it penetrates very far at all). While ammonia might reduce the crystallinity of cellulose, the reduced amount used in vapour penetration is not likely to affect the lignin severely [16]. Still, ammonia is a very strong base and it would be preferable to find a less severe method for de-acidification – both for the *Vasa* and for the items from the Oseberg find.

The advanced state of decay within the Oseberg wood makes it difficult to treat without permanent damage. Many items require urgent attention and re-treatment. Currently, the pieces are falling apart. One must wonder if it is better to abide by all the recommendations of good conservation practice or if it is more important to save the objects. The wrong kind

of irreversible treatment means that the objects may decompose in the future with no hope of saving them. On the other hand, such deterioration will occur anyway, given the current circumstances – and on a much shorter time-scale – leaving us without what might be considered the most unique Viking age discovery on Earth.

3. Structure and composition of wood

In order to invent new consolidants for archaeological wood, it becomes necessary to understand the physical and chemical composition of wood itself. The following section first examines the physical structure of wood and then moves on to discuss the chemistry related to fresh wood. Notes on degradation of wood is given and archaeological wood discussed.

Wood has existed since the Devonian era (from 416 to 359 million years ago). This was the time when fish evolved lungs and legs. Seed-bearing plants spread across the land, forming the symbiotic relationship with insects still known today. True lignin-containing plants and trees evolved at the same time [17]. Currently, lignocelluloses have been proposed as an alternative to fossil fuels [18], making wood a potential source of renewable energy.

3.1 Structure of fresh wood

Even prior to degradation, wood is rather complex and difficult to define. Roger M. Rowell[1] was visiting Oslo and explained that he had not managed to put together a definition of wood any shorter than: "A porous three dimensional, hydroscopic, viscoelastic, anisotropic bio-polymer composite composed of an interconnecting matrix of cellulose, hemicelluloses and lignin with minor amounts of inorganic elements and organic extractives."

Wood is usually cut in one of three planes, the transverse (cross sections), the radial (going through the centre of the stem) and tangential cuts (similar to radial cuts but not going directly through the centre of the stem). These are illustrated in Figure 3.1. While different kinds of wood are obviously different on a macroscopic level (branches are not the same as roots), the same is true at a microscopic level. Softwoods (or gymnosperms) are mainly conifers whereas hardwoods (or angiosperms) are mainly flowering trees [19].

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1 Rowell is a professor emeritus at the University of Wisconsin, Madison, USA. He has contributed to numerous books on the subject of wood and wood chemistry.

Archaeological softwoods typical in Norway include spruce and pine, while typical archaeological hardwoods include oak, birch, and beech [11]. Both types of wood have a thin, living outer layer under the bark, called sapwood, and a darker interior material, called heartwood. The cells have growth rings in climates with distinct seasons as thicker and more open earlywood and narrower layers of more dense latewood. Softwood lacks the ellipsoid vessels which are found in hardwoods (these can be seen in Figure 3.5 on page 41) [19].

In the middle of each wooden cell is a void called the lumen. The cell wall consists of three main regions: the middle lamella, the primary wall, and the secondary wall. The middle lamella holds cells together and has a high lignin content. The primary wall contains largely randomly orientated cellulose fibres. The term 'compound middle lamella' refers to a middle lamella and primary walls of two cells on either side of it. The secondary cell wall is composed of three layers. In the first, S_1, the cellulose is arranged in a helical fashion. The next layer, S_2, is the thickest and thus influences the characteristics of the secondary wall the most. The innermost layer, S_3, contains almost no lignin since cellulose has a higher affinity for water. The structure of a cell can be seen in Figure 3.2. Pits allow cells to communicate. The pit membrane is composed of carbohydrates (not phospholipids) and is a remnant of the primary wall [19].

Interested readers are directed towards Ref.[19] where a more thorough description of wood cell physiology can be found.

Pores in fresh wood have sizes in the range of 10-400 µm [20](p. 12). This allows solvents to penetrate but might cause problems when particles flocculate (see chapters 7.2.3.2 'Zeta potential measurements' and 7.2.4 'Coagulation by iron ions' beginning on page 147).
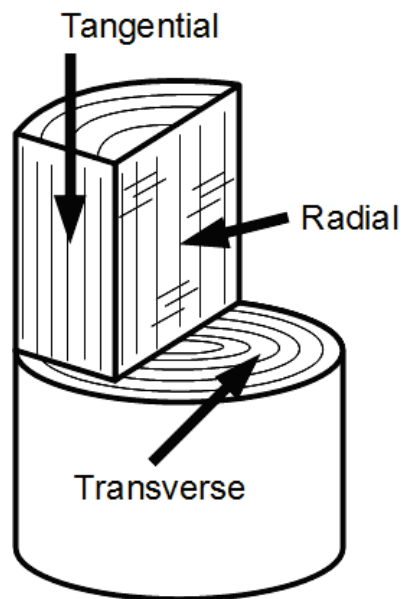
Figure 3.1: Illustration of the three kinds of planes wood is usually cut in. Notice that horizontal ray cells can be seen in the radial plane.

Many solvents cause wood to swell or shrink. Dilute acids have less effect than dilute bases. Concentrated acids, on the other hand, not only cause increased swelling but also destroy the wood through hydrolysis. Most aqueous solutions cause swelling similar to that of water, but some saturated solutions may cause increased swelling. Non-polar solvents usually cause the least swelling, while solvents like dimethylformamide or 1-butylamine cause even worse swelling than water [20](p. 28-29). This means that choice of solvent can be extremely important when treating archaeological wood.
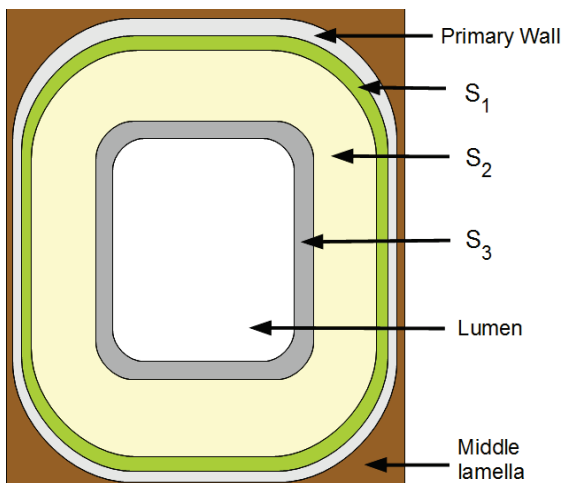
Figure 3.2: Schematic showing the composition of wood cell layers. The middle lamella holds cells together. The outer layer is called the Primary wall while there are three layers in the secondary wall: S_1, S_2, and S_3. Note that the S_2 layer is significantly thicker than the other layers.

3.2 Chemical composition of fresh wood

Plant cell walls have a highly complex 3D structure. The number of polymers and their interactions makes it difficult to isolate and investigate each individual polymer. Cellulose has the most regular crystalline form and is thus the easiest to separate, but it is still energy-demanding to free it from hemicelluloses and lignin. The kraft-pulping process often boils the components at $170°$ in 2 M caustic soda and sodium sulphide – usually degrading the components in the process [21].

Cellulose is the most common bio-polymer and lignin the second most common [22], [23]. Cellulose, hemicellulose and lignin typically make up about 95% of fresh wood. Fats, waxes, resins etc. only make up about 1% while inorganic material (often called 'ash' because it remains when wooden samples are heated to $600°C$) also makes up a few percent of the wood [24](p. 112-113).

Lignin forms a three-dimensional network within the wood, bonding to the polysaccharide fraction. If the polysaccharides are decomposed using acid, the lignin remains as a brown amorphous powder [20](p. 17-18).

Tests for characterising wood can be found on Ref.[24] p. 122+. The typical composition of hardwoods and softwoods can be seen in Table 1 below.

Table 1: Main composition of softwoods and hardwoods [20].

Constituent	Softwood (%)	Hardwood (%)
Cellulose	45-50	40-45
Hemicelluloses	15-20	20-30
Lignin	25-30	20-25

Wood normally has a pH between 3 and 5.5. This means that a weakly acidic environment will not damage the wood. Hardwoods, having a lower lignin content than softwoods, are more susceptible to acidic or alkali degradation. Wood absorbs alkaline solutions more readily than acidic ones, and are more quickly degraded by oxidising compounds (like HNO_3) [25].

3.2.1 Cellulose

Cellulose is a single well-defined polymer of D-glucose (unlike hemicellulose or lignin which are made up of various chemical structures). It is the main structural polysaccharide of plant cells and make up about 40-45% of wood. Each molecule contains about 7000-12000 glucose units, $(C_6H_{10}O_5)_n$, joined by eliminating water from hydroxyl groups. The structure of a cellulose molecule can be seen compared with chitin and chitosan in Figure 7.16 on page 156. Each cellulose molecule is about 3-5 µm long. Hydrogen bonding both keep the individual molecules linear and leads to strong connections to other molecules. Each bundle of molecules is called an 'elementary fibril' and has a diameter of 2-4 nm. The alignment is so regular that about 70% of the structures are crystalline. This results in a high tensile strength and (usually) low solubility [24](p. 112-113). Experiments with crystalline cellulose are described in chapter 7.2 'Cellulose whiskers' beginning on page 129.

3.2.2 Hemicelluloses

Hemicellulose is also called polyose. Unlike cellulose, hemicelluloses consist of a variety of related molecules which usually have branched chains consisting of 100-200 sugar residues. Hemicellulose and pectins make up about 20-30% of wood tissue mass. However, pectins are a minor component in wood, making up 1% mass or less (during early growth pectins constitute the cell wall and are thus later found in the middle lamella). These polymers mainly contain galacturonic acid units and are highly soluble in neutral water. The hemicellulose polysaccharides are different from cellulose in that they may be dissolved in aqueous alkali. They were thus thought to be intermediaries in cellulose construction and called 'hemicellulose' [24](p. 113-115).

Exact components vary among tree species and wood structures. In softwoods, the major hemicellulose is glucomannan which makes up 10-15% of the wood mass. It is composed of mannose, glucose, galactose and acetyl in the ratio 4:1:0.1:1. Other major components are arabinoglucoronoxylan, which makes up 7-10% of the wood (and consists of xylose, 4-O-methylglucuronic acid, and arabinose in the ratio 10:2:1.3), and galactoglucomannan which makes up 5-8% of wood (consisting of mannose, glucose, galactose, and acetyl in the ratio 3:1:1:1). There are usually about 100 residues per molecule in softwood holocelluloses. Hardwood hemicellulose polymers, on the other hand, are usually made up of about 200 residues per molecule. The typical components are glucuronoxylan, which makes up 15-30% of the wood (consisting of xylose, 4-O-methylglucuronic acid, and acetyl in the ratio 10:1:7), and glucomannan which makes up 2-5% of the wood (and consists of mannose and glucose in the ratio 1-2:1) [24](p. 113-115).

3.2.3 Lignin

Since lignin offers strength to the cell structure, and is difficult to degrade, it is particularly interesting when discussing wood conservation. Since the possibility of polymersing lignin-like compounds was discussed from the very beginning of this project (see chapter 1.2 on page 4 and chapter 8.6.4 on page 187 for initial and future thoughts), its chemistry will be described somewhat more thoroughly than was attempted for the holocelluloses.

Lignins are amorphous phenolic polymers, found only in vascular plants, that make up 20-30% of most wood [24](p. 115). Developing lignin to support them was a crucial step which allowed plants to move onto land, and the basic pathway still in use in plants today has been in use for 400 million years [22], [26]. Lignin is thus one of the most abundant biopolymers (second only to cellulose) as roughly 30% of the organic carbon in the biosphere is bound in lignin [23], [27]. Despite this accessibility, it has been hard to re-use lignin from pulp by-products – partially due to the complex structure of lignin [27].

There is some confusion as to where certain kinds of plants and algae actually contain lignin – and even how lignin should be detected, so it is not surprising that the exact mechanism behind lignin formation is not understood [28].

To give an idea of how long lignin has been studied chemically, a few key points in the early history of lignin chemistry are mentioned. The composite nature of wood was discovered in 1838 by A. Payen who recognised that lignin was an "encrusting material". The term 'lignin' was introduced in 1865 by F. Schulze. P. Klason proposed in 1897 that lignin was chemically related to coniferyl alcohol. He even assumed that part of the structure was made up of coniferaldehyde or some hydroxyconiferyl alcohol rather than pure coniferyl alcohol. These views – put forth as early as 1917 – influenced the way lignin was thought of in the future. Klason removed carbohydrates from wood by hydrolysis with sulphuric acid in 1908. Later, similar methods used other (possibly mixed) acids. In 1956-57, Björkman and Persson discovered that almost one third of the lignin is extractable with dioxane-water (9:1) after finely grinding the wood and suspending it in toluene. Lignin extracted by this method is still known as "Björkman lignin" or *milled wood lignin* (MWL). It contains less than half a percent of carbohydrates. Similar experiments with milled wood have since been developed, but one must beware that they are not identical to the lignin *in situ* [29].

The exact chemical composition of lignin varies not only between different plants but even between different kinds of tissue within the same plant [30]. In fresh wood, lignin makes up 15-35% with 60-80% found in the secondary wall (even though the middle lamella has a higher concentration of lignin) [31](p. 9). It lends support to plants while making the cell wall impermeable to water. Thus it is not surprising that it is in trees, which have extreme needs of both structural strength and water, that high levels of lignin are found

[32]. While fungi can degrade lignin (see below) it is otherwise a resistant polymer and it is estimated that lignin will not be completely decomposed in soil until about 25 years have passed [33] - although another study indicated that excess lignin used to anchor mulch was noticeably degraded after a single year [34]. Lignin makes up 15% of all terrestrial biomass [35] and thus lignin removal is a key step in preparing cellulose for paper manufacture. Delignification would allow industrial use of delignified sawdust in stead of more expensive cellulosic and cotton materials [23].

Lignins isolated from wood have polydisperse molecular weights ranging from thousands to hundreds of thousands. They are primarily made up of three cinnamyl alcohols ((*E*)-3-phenyl-2-propen-1-ol) (only varying in the number of methoxyl groups attached to the aromatic ring). During polymerisation they form a complex three-dimensional structure. The molecules are held together by ester and carbon bonds, making lignin resistant to hydrolysis. This means that lignin can be synthesised from the components left when wood is dissolved in 72%$^w/_w$ sulphuric acid. On the other hand, lignins are not resistant to oxidation and can be removed by bleaching [24](p. 115-116).

The exact classification of lignin depends both upon the genus of tree and the kind of tissue within said tree. Softwood lignin is mainly made from coniferyl alcohol. Hardwoods are made up of syringyl-guaiacyl lignin composed of coniferyl and sinapyl alcohols (the molar ratios typically fall within the range from 4:1 to 1:2). The exact composition affects the extent of cross-linking within the polymers. Generally those containing guaiacyl and p-hydroxyl have the most cross-linking as unmethoxylated carbon atoms in the aromatic ring may link to the phenolic oxygen of other monomers. This also means that hardwood lignins are usually easier to degrade than softwood lignins [24](p. 115-116). Hardwoods are rather heterogeneous when it comes to lignin distribution. Guaiacyl type lignin is found in the secondary wall and middle lamella with syringyl lignin in the ray cells [24](p.119).

Since identification of lignin was not a part of these studies, interested readers may consult Ref.[28] for a description of the most common chemical tests for lignin. Unfortunately, these tests often give false positive results for non-lignins, and other complementary methods of testing – such as IR (Infra Red), UV/VIS (Ultra Violet/Visible) or ^{13}C NMR (Nuclear Magnetic Resonance) spectroscopies – are recommended [28].

Lignin is made up of mainly of three interlinking hydroxycimmaryl monomers **H**: *p*-hydroxyphenyl, **G**: guaiacyl, and **S**: syringyl. Small amounts of other units exist as well. The relative amount of each monomer varies between cell types. Hardwood lignins normally consist of **G** and **S** units with traces of **H**, while softwood lignins are mainly composed of **G** units with few **H** units [22]. The lignins and the different types of linking are shown on page 521 of Ref..[22] while various ways of forming lignin are shown on p. 526 of Ref.[22]. Kraft lignin is mainly composed of guaiacyl units, while hardwood lignin extracted with organic solvents contains both guaiacyl and syringyl units [36].

The three alcohols p-coumaryl (4-[(E)-3-hydroxy-1-propenyl]phenol), coniferol (4-(3-hydroxy-1-propenyl)-2-methoxy-phenol), and sinapol (4-(3-hydroxy-1-propenyl)-2,6-dimethoxphenol) are called monolignols. When these are dehydrogenised, several resonance structures result. This means that many different kinds of polymerisation are possible, and a high degree of disorder is present within actual lignin [30], [37]. After basic synthesis, lignin precursors are transported to the cell wall where they are polymerised [22]. The monolignols themselves are fairly unstable and toxic and do not exist in abundance in plants. Glycosidation through reaction with the hydroxyl group renders them non-toxic and enables them to be both stored and transported. The monolignols concentrate in various parts of the plant. If they have physiological properties beyond being the building block of lignin, these have not been discovered yet [32].

The typical bond types can be exemplified by the following model compounds [40]: arylglycerol-β-aryl ether (β-O-4 unit), phenyncoumaran (β-5 unit), pinoresinol (β-β unit), and dibenzodioxocine (5-5'-O-4 unit).

The most common bonds in softwood lignin (although hardwoods have a similar configuration) are: gualicylglycerol-β-aryl ether (40-60%), phenylcoumaran (10%), diarylpropane (5-10%), biphenyl (5-10%), diphenyl ether (5%), and pinoresol (<5%). Structures of these compounds can be found in Ref.[30].

It has also been attempted to identify the components using IR spectroscopy. IR assignments for lignin compounds can be found in Ref.[36](p. 1657-9).

The exact method by which lignin is polymerised has been tested and debated. Both enzymatic and purely chemical mechanisms have been suggested. All that can be said for

sure is that enzymes do not control the shape of the formed polymer rigorously [38], although enzymes can effectively degrade not just the overall lignin structure but even the aromatic rings [39]. The reaction paths for lignin polymerisation in both angiosperms and gymnosperms have been mapped. [14]C marking indicates that the reaction which incorporates acids into lignin goes through cinnamic acid which in turn can be converted into for eample p-coumaric or sinapic acids. Many of the exact enzymes responsible for the reactions have been identified and isolated [30].

UV light (from the sun or lamps in the laboratory) induce a change in hydroxycinnamaic acids so that 20-30% of the solutions are made up of *cis*-isomers. Similar reactions may occur in the bark of trees (note that most investigations are carried out on bark-free wood). It is interesting that beech bark may stem from the dehydrogenative polymerisation of *cis*-alcohols when the core wood is composed of *trans*-isomers [47].

The key to understanding how white rot is still able to decompose lignin (see chapter 3.3.1.1 'Fungal degradation' on page 29) has come mainly from chemical analysis of the leftover wood. Thus it has been found that the content of both methoxyl groups and *β-O-4* structure decrease when lignin is attacked by white-rot. It seems that there are three major ways in which the lignin is degraded: cleavage of the propyl side chains (between the α and β C's, forming benzoic acids), cleavage of the β-aryl ether bonds, and degradation of aromatic compounds through oxidative ring opening. Other results indicate that the process includes both oxidative and reductive reactions. Various enzymes have been employed to study the exact degradation mechanisms [30].

Lignin is particularly interesting because it is biorenewable [36]. Phenolic medical drugs are also gaining in popularity as many antioxidants found in fruits and vegetables are phenolic compounds. Thus it seems that a varied intake of these compounds help prevent a number of diseases (while dietary supplements consisting of a single kind of these antioxidants curiously enough have no proven beneficial effect) [26]. The potential to use lignin as a base for these drugs as well as for building materials makes the material attractive to many fields – including that of conservation science. More on these thoughts can be found in chapter 8.6.4 'Artificial lignin' on page 187.

3.2.4 Chemical modification and synthesis of lignin

The aromatic contents of lignin seems to make it more resistant to typical archaeological degradation then the rest of the wooden cell structure (see chapter 3.5.2 'Properties of waterlogged wood' on page 38 for further elaboration). This means that a lignin-like structure would not only be compatible with wood but also durable. The following section summarises some of the attempts to polymerise lignin in order to determine if the methods can be applied to conservation science (this discussion can be found in chapter 8.6.4 'Artificial lignin' on page 187).

The idea of making synthetic lignin is not new, and papers on this subject can be found as least as far back as 1932. These early attempts at making lignin mainly involved heat-treatment of wood components in an attempt to form the polymer [41]. Most artificial lignins are sulfonated to allow better solubility in water. The sulfonic salt changes into sulphonic acid below pH 3, causing lignin to precipitate (as the acid is not very water soluble) [42].

Lignin has been extracted directly from wood in order to form lignophenols. The process was very quantity-efficient [18].

Freudenberg and others showed that dehydrogenation of coniferyl alcohol with air could produce a "dehydrogenation polymer" (DHP) which shared similarities with spruce Björkman lignin [22]. DHP is similar to actual lignin in many aspects, including the complex (and somewhat unpredictable) structure, although lignin contains fewer side chains than DHP [22], [27]. It is made by dehydrogenation of phenolic monomers to form an amorphous polymer structure [27]. Much information about the structure of lignin has been gained through studying DHPs. These are made by mixing the precursor compounds with either peroxidase/H_2O_2 or laccase/O_2 as oxidisers. If the precursors are added slowly the result is an end-wise polymerisation which more closely resembles actual lignin than DHP made from applying everything in one go. When the process was interrupted before the polymer could form, more than 30 different compounds were isolated and identified [22]. Artificial lignins also form many more unsaturated sidechain endgroups than natural lignins since it is easier for many monomers to bond than the few which are accessible at a given

time inside a plant. Thus monolignol radical primarily couple at the β-sidechain position rather than only the 4-O- and 5-positions [43].

Polysaccharides improve the solubility of DHP (through formation of either covalent bonds, colloidal aggregates, or both). Possibly due to this, very little DHP precipitates when polymerised in solutions with high concentrations of polysaccharides. On the other hand, the presence of the polysaccharides seems to promote cross linkages of the β-O-4 type, making the structure of the DHP more closely resemble that of actual lignin [44].

The synthesis of monolignols is a bottleneck in the preparation of lignin model compounds such as DHP. Multiple reaction steps were often required. Borohydride reagents have been used to simplify the number of steps during synthesis. Borohydride Exchange Resin (BER) in methanol can be used to safely and effectively produce clean 4-hydroxycinnamyl alcohols. This method, despite relatively small yields, is still up to three times cheaper than buying the alcohols directly (but note that this is still close to 1000 NOK/g). The exact procedure is given in Ref.[45].

Coniferyl alcohol DHP has been polymerised enzymatically (using horseradish peroxidase) in a phosphate buffer at pH 7.6. The resulting sphere-like structures are believed to be hollow, containing an onion-like structure of several layers separated by solvent or air. On average, each contained 10^8 monomer units [50].

DHP from coniferin seem to form a more end-wise polymerisation than those prepared from coniferyl alcohol. Thus it is closer to MWL in structure. Both the relative amounts of available monomer units and pH seem to be important for the exact structure of the polymer [46].

Although coniferyl and sinapyl alcohols are commercially available, they can be 10 times more expensive then 4-hydroxycinnamalaldehydes – and sometimes even of questionable purity [45]. Monolignols have also been extracted directly from wood in a quantity-efficient way [18]. No matter what approach is used, these monolignol alcohols should not be stored for very long (days at most) before use in order to prevent oxidation [45].

Cis-coniferyl alcohol which is completely identical to the natural molecule may be synthesised – although the yield is only 27% from vanillin [47]. Another approach is to use 2,6-dimethylphenol, which can be polymerised at room temperature to form poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Under oxygen and with organic solvents, the polymer grows to larger units than in water and under normal atmospheric air. The polymer can depolymerise by adding more monomer or repolymerise via oxidative polymerisation [48]. Of course, the cheapest solution may be to use actual wooden lignin. Lignin was produced by treatment with 72% H_2SO_4 for three hours, then ground in a mill [49].

The exact structure of the polymerised lignin depends upon interaction with nearby surfaces. Graphite, for example, seems to interact in a way which causes increased ordering. Lignin in itself is self-ordering, possibly because it is quite hydrophobic. It seems likely that clusters of about 20 monomer units form at first and that these form modules of about 500 monomer units. Finally these modules aggregate to form globules of even larger size [50].

Lignophenols are modified lignin with a high phenolic content. Example molecular weight of such highly cross-linked polymers is about 3500-4000 Da. The product may be prepared from lignocatechol rather than monolignols, but can be polymerised using peroxidase/H_2O_2 in a 0.1 M methanol/phosphate buffer solution. Enzymatic reaction is also a good way of turning lignin into phenolic resin [51]. Lignophenols can also be made using more traditional chemical synthesis although this may require very high temperatures [52]. Lignophenols have been previously used in the consolidation of waterlogged wood where they were shown to have better strength than PEG impregnation. The lignophenol in question is a ligno-p-cresol made by phase separation using sulphuric acid. A 5% solution at 55°C was used for impregnation and the samples were subsequently freeze-dried [53].

Lignocelluloses might be interesting as an alternative to fossil fuels [18]. Ligno-*p*-cresol mixed with cellulose formed network structures which kept cellulose mixed into them from swelling. After drying, the cellulose-lignophenol structures did not change much by swelling with water and re-drying [52].

Plastics reinforced with natural fibre is an environmentally friendly alternative to existing composites. Thus lignin has been used as a natural adhesion polymer in plastics

26

made from cotton and poly(lactic acid). Bast or hemp fibres, which contain some lignin, also adhere better to a poly(lactic acid) matrix than cotton fibres made of pure holocellulose. Lignin enforces adhesion and bound layers more efficiently together (breaks showed fewer delaminations). On the other hand, lignin causes the mix to become more brittle and have a lower impact strength. [54].

3.3 Degradation of wood

Wood found in museum collections rarely resembles fresh wood. This chapter describes the various ways wood may degrade with a focus on waterlogged wood. This information is intended to allow readers without conservation experience to understand how the properties of wood change when it undergoes the transformation from fresh plants into what eventually becomes museum objects.

More than 99% of the organic matter in wood is recycled into CO_2 and H_2O [24](p. 119). Without this biological degradation the surface of the Earth would be covered with undegraded wood [56](p. 422). Less than a percent is waterlogged and becomes part of bottom deposits in lakes and coastal regions. Most archaeological wood is found in waterlogged form [24](p. 119-120).

Wood is a mixture of so many chemical and structural parts that the degradation of each components must be investigated [57](p. 400). When wood used for buildings initially starts to degrade, for example, the cellulose actually becomes more crystalline, strengthening the wood. These changes stop after about 350 years, meaning that after this point archaeological wood simply becomes more fragile [20](p. 19). It is also important to remember that age alone does not affect the hygroscopicity of wood (at least as far back as the Recent Stone Age) while the method of deterioration does affect it drastically [58](p. 94). Although the knowledge that wood decays in soil and/or moist environments is ancient, the mechanisms for such degradation are not fully understood yet [1](p. 438).

In a study with buried alder and oak, 90% and 98% of the polysaccharides and 15% and 25% of the lignin, respectively, was degraded. About 75% of the degraded polymers had

been lost form the samples [31](p. 7). One should also be aware that while certain chemical groups might remain in archaeological remains of wood polymers, it does not necessarily mean that the polymer still possesses sufficient structural integrity to endure even in a museum.

Inland finds are degraded based primarily on local environment and burial conditions rather than age [55](p. 31). Sediments affect oxygen penetration and thus lead to better degrees of preservation at lower depths – with as little as 40 cm having a noticeable effect [55](p. 39-40).

According to Ref.[59](p. 313), there are four deleterious agent groups concerning wood:

Biological: microorganisms, insects, bacteria, and animals (one may wonder why insects are not included in the 'animal' category).

Chemical: photochemical and hydrolytic agents.

Mechanical: physical load, abrasion, and internal stresses.

Physical: hygroscopic (thermal-moisture) changes.

3.3.1 Biological degradation

Wood only escapes biological degradation if frozen or waterlogged under completely anaerobic conditions [60](p. 68) although most so-called anaerobic environments are probably not completely devoid of oxygen [55](p. 29-30).

If the wood is found in the ocean, like most shipwrecks, marine borers pose a serious threat. Shipworm are thin borrowers feeding off the wood. In rare cases specimens of more than two metres in length have been recorded. Gribble are another threat. This is a crustacean species which feeds off the surface of the wood [20](p. 135-136). Note that shipworm are not true worms but rather a type of clam with extremely small shells. Copper containing preservatives have been used to protect wooden boats from these threats (the fleet of Christopher Columbus was one of the earliest examples of such protection) [61]. Many archaeological finds, however, are from bogs or otherwise buried inland, making fungal and bacterial degradation a much larger concern than shipworm.

The various insects which attack wood are described in Ref.[20] chapter 5.1 (beginning on page 51). As insects do not usually attack waterlogged wood, this subject will not be explored further here (even though it is a notable concern when choosing storage conditions for museum collections).

3.3.1.1 Fungal degradation

Fossil evidence shows that white-rot fungi (described below) have existed since the Devonian period [63](p. 145). This suggests that fungi evolved at the same time as trees.

Classifying fungi is a difficult task, and apparently a generally accepted classification does not exist. When discussing wood degradation, fungi may be easily distinguished by the type of damage they cause. Only this classification will be described below. Interested readers are referred to Ref.[20] chapter 5.2 for further information or Ref.[62](p. 19) for a list of several species of fungi known to degrade wood.

This wide range of fungi means that any wood with a moisture content of 20% or more can be attacked. Most fungi require moisture levels between 35 and 60%. Dryer wood, or wood completely saturated with water, is not degraded by fungi. Fungi generally grow best between 15 and 40°C, and become dormant above 44°C or under 0°C (although many can survive -40°C without damage) [20](p. 95-98). Some, however, can operate under the freezing point or above 60°C [63](p. 153 & p. 159). Depending upon exact type, fungi can develop across most of the pH range, with low values around pH 2.5 and an upper ceiling of pH 11 [20](p. 95-98). The optimal pH for brown- and white-rots is around 3.5 to 5.5 with brown-rots favouring the most acidic conditions [63](p. 153 & p. 159).

Fungi attack by inserting enzyme-excreting hyphae into the wood. Holocellulose is decomposed through various hydrolases. Lignin is always degraded by oxidising or ring-splitting enzymes which require high moisture content [20](p. 99-102). Some termites even utilise the abilities of fungus to degrade lignin, forming a symbiotic relationship which allows both species to utilise the energy in lignocellulose for maximum effect. The mechanism has been studied chemically [64].

Wood attacked by fungi becomes either dark brown or whitish, resulting in the terms 'brown-rot' and 'white-rot' fungi. These names were introduced in 1874 and are still in use today. A new type of infection similar to brown-rot was described in the 1950s and called 'soft-rot' [20](p. 99). Some fungi merely 'eat' the nutrients from wood, leaving the structure more or less intact but discoloured. Others bore through cells and destroy the integrity of the wood. Since there are thousands of types of fungi, the distinction into white- brown- or soft-rot is not very precise. Nonetheless, it is often quite helpful as it distinguishes between different types of decay – as long as it is remembered that each type is actually a very broad category [63](p. 142-143). Note that many brown-rot and white-rot fungi are actually closely related, despite causing different types of damage to the wood, and many genera contain both types [65].

By observing the number of normal and free phenolic groups it is possible to estimate what type of fungus has degraded the wood [40].

Brown-rotters mainly decompose the polysaccharides in wood. As lignin is exposed to oxidation through the air, affected areas turn brown. Hyphae are thinner than the cell walls but in contact with them, growing in the lumen. Cracks both parallel and perpendicular to the grain are formed, dividing the wood into cubic pieces. Later on, the cubes can decompose into a powder. Brown-rotters thrive at lower pH values than white-rotters because brown-rot fungi accumulate oxalic acid [20](p. 102). Brown-rotters are capable of degrading lignin but usually only in very small amounts [63](p. 151). They significantly degrade methoxyl groups in the lignin but leave other side groups alone [66]. The overall strength of attacked wood is severely diminished as a result [63](p. 151).

Compared to fresh lignins, lignins exposed to brown rot have a higher relative content of phenolic hydroxyls and carbonyls (both conjugated and unconjugated) but a lower content of aromatic methoxyl. This often leads to the conclusion that lignin is not notably altered by the degradation process. Still, brown-rot produces hydroxyl radicals which attack lignin by electrophilic addition to aromatic components. Additionally, some enzymatic degradation seems to take place, indicating that the lignin structure must be degraded to allow space for the enzymes to act. A comparison with Klason lignin showed that lignin attacked by brown-rot had a very different structure from the model compound. NMR spectroscopy confirmed

that relative polysaccharide content decreases and relative aromatic content increases in wood affected by brown-rot. The leftover lignin loses side-chains but is still polymeric [35].

White-rot fungi are able to decompose lignin as well as polysaccharides. In a sample attacked by so-called 'white pocket rot' less than 1% of the original lignin remained whereas the polysaccharide content was about 80% of the expected value although the ratio varies [24](p. 136), [63](p. 144). Some species, 'simultaneous white rotters', compose both types of compounds equally quickly. Others, 'successive white rotters' or 'corrosion rotters', initially decompose lignin faster than cellulose. The whitening effect on an attack can be ascribed to the increase in relative cellulose content. Attacks leave cell structures intact for a long time as they affect the lumen surface uniformly. Attacked wood becomes softer and is susceptible to swelling as the lignin is removed. Hardwoods are generally preferred over softwoods by many white-rots. Initial attack can dye the lignin in reddish-brown tones, leading to names like 'red-rot' even though the attack is caused by a white-rot fungus [20](p. 102-104). White-rot seems to primarily degrade syringyl units [66]. This means hardwood guaiacyl-syringyl lignin is more rapidly bio-degraded than softwood guaiacyl lignin [28]. Carbonyl structure is common in naturally degraded lignins. Fungal degradation produces benzaldehyde by cleavage of the side chains [39]. Given the right circumstances, at least one species can even degrade extremely durable polymers such as phenol-formaldehyde and a number of other other materials such as DDT (dichlorodiphynyltrichloroethane), TNT (trinitrotoluene), pyrenes, PCBs (polychlorinated biphenyls), and dioxins [67].

At least some white-rot fungi produce a lignin-like material themselves. This substance is most likely made from oxidative polymerisation of hispidin (see ref.[28](p. 481) for the chemical structure). Indeed, some of the compounds which were thought to break down lignin have later been tested and, surprisingly enough, it seems that some of these enzymes can actually polymerise lignin-like materials. The exact process of fungal degradation is still not well understood and several of the reported tests are circumstantial or done without proper control experiments, making it hard to say anything conclusive [28].

Soft-rot seems to be composed of a large number of species taking part in the decomposition simultaneously [20](p. 104-105). Soft-rot is usually considered a surface problem (although more extensive attacks occur) and may leave the wood seemingly intact

at the macroscopic level. Soft-rots are so called because affected wood is very soft while wet and cracks upon drying [63](p. 156). Susceptibility to soft-rot seems to be inversely tied to lignin content, and hardwoods are more often affected than softwoods. Nonetheless, soft-rot can degrade lignin to some extent and does not seem to cause the same rapid depolymerisation of cellulose as brown-rot [63](p. 158), degrading it at a slower rate than brown-rots. They darken the wood, turning it almost black in advanced stages of decay. The infection destroy all cell wall layers, creating cavities within the wood [20](p. 104-105). Soft-rots can often operate in more extreme conditions than other fungi – and even tolerate great variations in moisture content – but generally develop slower than most infections [63] (p. 153 & p. 159). These fungi are found in continually wet or damp wood and are active nearly up to the point where the wood becomes completely saturated with water. Soft-rots are very tolerant and even show resistance to chromium-fluorine salts, although they are still sensitive to copper compounds [20](p. 104-105).

Although fungal degradation is less of a threat to smaller displayed artefacts than timber, the threat of fungal decay is still important when impregnating wood using watery solutions/dispersions [11]. Fungal growth is best prohibited by completely anaerobic conditions [24](p. 136) but this is rarely feasible in a museum. Additonally, mycotoxins can be highly toxic and one should keep this in mind when working with fungi [20](p. 131).

Generally speaking, synthetic polymers are more resistant to fungal attack than natural derivatives such as gelatine, starch, and cellulose. *In situ* polymerisation of methyl methacrylate (MMA) makes wood very resistant to brown-rot fungi. Unfortunately poly(methyl methacrylate) is deposited in cell lumens, meaning that the cell walls may still be destroyed. On the other hand, wood treated with poly(vinyl acetate) or a mix of PVA with styrene is very susceptible to brown-rot attack. Acrylic resins are resistant to mould while shellac and bees wax are not. Epoxy resins are generally considered very mould resistant, but in a test an epoxy resin only performed as well as shellac or wax. Thus the specific choice of epoxy and hardener may be extremely important [20](p. 130).

3.3.1.2 *Bacterial degradation*

Chemical hydrolysis was long thought to be the main cause of decay in archaeological wood until bacteria in the material were identified [55](p. 28-29). Bacteria are generally less damaging to the wood strength than fungi. When working with archaeological objects, however, bacteria can be a significant threat. Bacteria can also spread through the wood very quickly, causing significant damage to wooden objects – especially when coupled with fungal attack. Different kinds of bacteria will attack different parts of the wood in various ways. An overview is found in Ref.[20](p. 132+) and several species of bacteria found in archaeological wood are listed in Ref.[62](p. 19). Note that existence of bacteria does not necessarily prove that they are the primary degraders of wood and further investigation into this is needed [55](p. 30). Although most of the bacteria found in a sample in Nydam Mose in southern Denmark were unidentified [62](p.116), it was possible to identify several species from a 1700 year old spear shaft from this site [68]. Learning more about bacteria might help determine whether a site is suitable for *in situ* preservation or not [62](p.1-2).

Bacteria seem to damage waterlogged wood (especially marine artefacts) to a much higher extent than fungi [69](p. 169) although not much has been published about how bacteria degrade waterlogged wood [24](p. 122).

There are three main types of wood-destroying bacteria, classified by the type of attack: erosion, tunnelling, and cavitation. There may be other types, but their existence has not been scientifically demonstrated [69](p. 162).

Erosion bacteria seem common and can progress inwards in affected wood pieces for at least 1300 years [55](p. 30-31). They cause cell wall erosion somewhat similar to white-rot fungi. The bacteria grow in the lumen and attack the S_3 layer. They may cause cavities similar to soft-rot. The compound middle lamella is not degraded [55](p. 33-34) but heavy damage to the S_2 layer causes the wood to collapse [69](p. 162).

Tunnelling bacteria penetrate into the S_2 layer and cause branching tunnels in the wood. They leave behind a concentric wall-like structure – presumably made from polysaccharides. Several different species of bacteria are probably involved. The end result is similar to that caused by erosion bacteria but although the middle lamella and S_3 layer are severely degraded, large parts of these layers usually remain in degraded wood [69](p. 162-165).

Cavitation bacteria also attack the wood cell wall, forming widening cavities. Unlike soft-rot cavities, bacteria cause damage more or less perpendicular to the long axis of the fibres. Field material on these bacteria is very limited and they have not been reproduced in a laboratory in a satisfactory manner [69](p. 165).

Even under anerobic conditions, bacterial degradation of lignin is limited compared to the degradation caused by white-rot fungi. In experiments with ^{14}C-labelling, the bacteria degraded a maximum of 20% of the lignin over a period of 14 days (while some results were as low as 3%). Soft-rot fungi converted 20-30% of the lignin in 50 days [66].

3.3.2 Physical/chemical degradation

Wood is an excellent light absorber since both cellulose and lignin absorb UV light. Because of this, UV radiation can only penetrate about 75 µm into the wood. This means that insects and fungi pose a vastly larger risk to the integrity of wood [60](p. 85). Visible light can penetrate further (at least 200 µm although other sources specify 2540 µm) but has insufficient energy to break chemical bonds in the wood structure. Brown colouration from weathering is caused by free radicals [70](p. 271-272).

Chemically speaking, oxidising acids damage wood more than non-oxidising acids, and bases damage wood more than acids. Softwoods are generally more resistant to both types of solutions than hardwoods. Exposure at first causes colour changes, but eventually result in hydrolysis of the polysaccharides. This may even happen in anaerobic conditions where slight traces of acid cause degradation over long periods of time. Bases at first cause swelling and then decomposition of hemicellulose and lignin [20](p. 43).

The amorphous regions of cellulose are responsible for the swelling of wood, as the loose structure allows water to react with free hydroxyl groups. Degradation of cellulose can occur in a number of ways such as cleavage of hydrogen and glycoside bonds, breakage of acetal linkages, or end-group reactions. While fairly resistant to alkaline conditions (which mainly cause swelling), cellulose breaks down under acidic conditions as glycosidic bonds are cleaved. The presence of metal ions will catalyse cellulose oxidation by forming free peroxide radicals [57](p. 401-402).

Hemicelluloses are more susceptible than pure cellulose to chemical degradation because the chains contain side groups which obstruct tight alignment of the molecules. In addition, hemicelluloses have a lower crystallinity than cellulose and are hydrolysed to acetic acid under both acidic and alkaline conditions. Acid resistance varies from component to component. In order of lessening acid resistance the monomers are: xylose, arabinose, mannose, and glucose-galactose. In a study, it was found that pinewood pentosan chains were cleaved after only five months in a weakly acidic environment [57](p. 403).

Lignin is more stable than the other wood components but the ester bonds may still be cleaved, affecting the structure of the polymer. UV light may also degrade lignin [57](p. 403).

3.4 Archaeological wood

Wood ages unpredictably. Wood which had been part of a Buddhist monastery for 1800 years was found to be have higher strength than recent wood. This demonstrates the dangers of comparing new and old wood in general [58](p. 98-100). While much research has been performed on fresh wood, it is important to note that this is not always readily applicable to archaeological wood. It appears to me that there are several significant differences:

1) Archaeological wood must be treated by conservators in a museum environment. This means that non-toxic consolidants become important both during treatment and subsequent display and that most kinds of pressure or heating are effectively impossible – at least on larger displayed finds.

2) Archaeological wood is heavily degraded and a method which reinforces the cell wall might not work as most or all of the S2 layer has degraded in many archaeological finds. This means that some consolidants may penetrate better but it also means that the remaining wood is very fragile.

3) The chemistry of the degraded wood is different from that of fresh wood and known consolidants or glues might not adhere properly to a surface with different chemical properties.

4) Biocides and fire retardants are a major concern in the wood industry since wooden buildings are exposed to the elements. On the other hand, biological attacks are

fairly rare in a controlled museum climate (although certain artefacts might be infected when they arrive for conservation treatment).

5) Many industrial applications require fast treatment times whereas waterlogged wooden finds might be impregnated for years before freeze-drying.

For the reasons above, it is not always easy or even possible to predict how a consolidant will affect archaeological based on how it affects fresh wood.

3.5 Waterlogged wood

As most important archaeological wooden finds in Scandinavia have been waterlogged, this state deserves special mention. Readers interested in a description more focussed on conservation are kindly directed to Ref.[62](p.2-8).

Waterlogged wood and fossil or subfossil wood are closely related, and may be referred to collectively as 'buried wood'. The main difference is that waterlogged wood usually has been treated – and become an archaeological object – while fossil woods are usually older than waterlogged wood [58](p. 87).

Waterlogged wood is defined as 'wood in which the pores have been filled to capacity with water'. It rarely happens to living trees but is fairly common with archaeological wood found in bogs or maritime environments [20](p. 24). Usually, such wood has been kept beneath water (often by being buried beneath the water table) for a considerable time. While finds are often well preserved beneath the water table, removal causes large-scale shrinkage and warping [71](p. 35).

3.5.1 Swelling

Swelling, a process which happens to all elastic materials, is defined by three criteria: Dimensional increase and thermal change as a result of taking up another phase, microscopic homogeneity is retained, and cohesion is retained but diminished. Particularly when working with wood, swelling is an important phenomenon [72] since secondary walls of archaeological wood often swell, possibly bulging into and filling the lumen. Such swelling can easily be observed using fluorescence microscopy [71](p. 41).

Cellulose is reported to swell about 31-33% in water. When lignin is concerned, the swelling seems to be closely related to the solubility parameter of a given liquid. It seems that the increased softening of lignin pulps around 60-75°C dramatically increase swelling [72].

Swelling is dependant upon the density of the cell wall, so latewood cells can swell about twice as much as earlywood cells. Aged wood, on the other hand, can swell more than fresh wood – despite having a low density. This is because cellulose does not swell as long as it maintains crystallinity but is exposed to water in degraded wood. In this way it would strengthen the wood a good deal if cellulose could be 'put back together' by some chemical method. Cross-linking with epoxides and isocyanates may be possible. Another idea is to attach an -OH group to the cell wall and then copolymerise this into a larger network [56](p. 426-428).

Woods with a high content of water-soluble extractives seem to reduce activation energies related to swelling and thus cause more swelling than expected. It is, unfortunately, difficult to correlate dielectric constant, dipole moment, or surface tension to the swelling effect of various solvents. The presence of water usually increases the swelling effect of other liquids. Temperature also has a drastic effect on how much wood swells – and even what compounds will swell it (with water, for example, it increases both rate of swelling and ultimate swelling). Sometimes, the compounds which swell the wood most rapidly are not the ones which result in the largest ultimate swelling [72].

The initial response seems to be linear for several types of wood, with the volume increase slowing down over time and the volume becoming practically constant after somewhere between half an hour and four hours. Tangential swelling of fresh wood seems to be linearly related to the density of the sample [72].

3.5.2 Properties of waterlogged wood

Waterlogged wood, due to being partially destroyed, is very light. The specific gravity of fresh wood varies from 0.11 (for balsa) to 1.05 or more (for lignum vitæ). Significant variation can occur even within a single plant, however [59](p. 310). Waterlogged wooden samples are a different matter. Densities in the range of 0.1-0.15 g/cm^3 are not unusual [73]. This means that freeze-dried archaeological wood feels much like balsa.
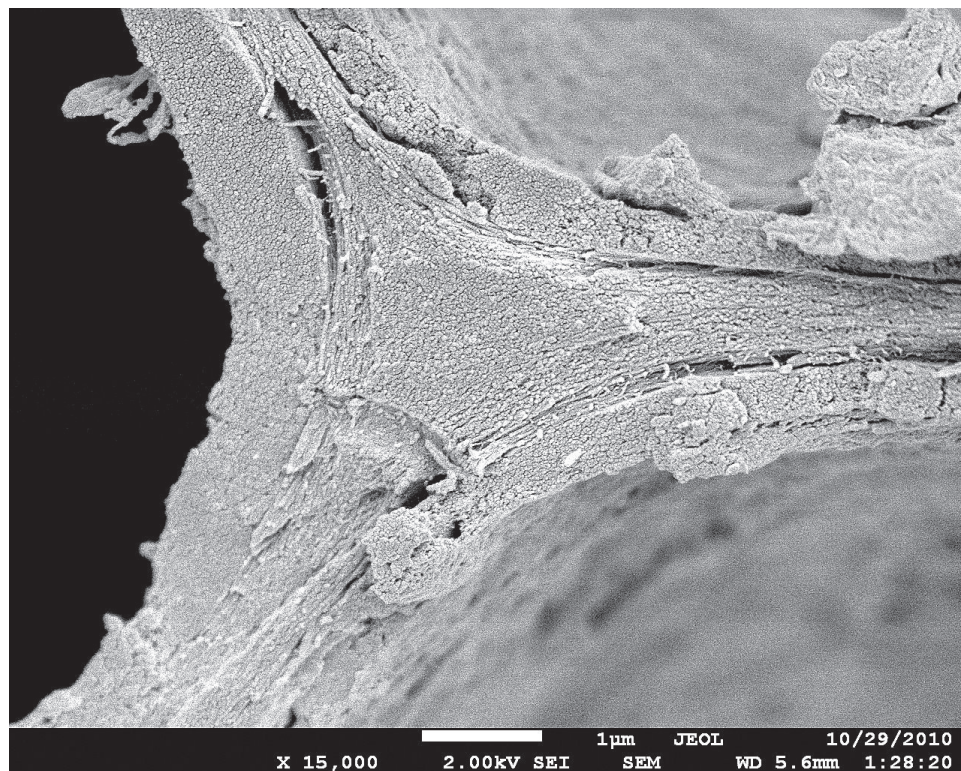
Figure 3.3: Cryo-SEM image of a piece of freeze-dried Viking Age wood from the 'Box 7' sample. Note that the structure of the remaining matrix is composed of layers and that both the middle lamella and remaining cell wall material can be seen although the bulk of the cell wall is gone.

The strength of degrading wood can be directly related to the changes in the structure of holocellulose and lignin within the cell wall. Usually, wood which has been partially degraded does not, chemically speaking, resemble fresh wood [56](p. 421-422). For example, one comparison of fresh and archaeological wood revealed that the archaeological

material contained 50-80% of the expected lignin in fresh wood but only 2-30% of the expected cellulose. Maximum water content ranged from 224 to 775% and densities varied between 0.35 and 0.12 g/cm^3. The complex structure of the residual lignin, as well as superimposed signals from degraded compounds, made it hard to identify archaeological wood using FT-IR spectroscopy [74]. The reduced crystallinity of the remaining cellulose allows shrinkage to occur. If cell walls become thin enough, they cannot withstand drying stresses and collapse. This effect is more pronounced in the tangential direction [58](p. 95). Note that the remaining cellulose might be partially enveloped by lignin and this may make it inaccessible for degradation [62](p. 111).

Waterlogged wood has a significant gradient of deterioration, meaning that the surface is attacked first, turning spongy, while the interior can still be solid [20](p.10-11). When waterlogged wood is degraded by fungi, the cell walls or pit membranes are attacked first and the cells are severely deteriorated. It is often postulated that only the middle lamella remains in very degraded archaeological wood [20](p. 15). Note that the true thickness of the middle lamella is only a few nm and thus much smaller than the structures typically observed in degraded wood [75]. An example can be seen in Figure 3.3 above. Most waterlogged samples have a thicker mix of middle lamella and degraded celluloses, typically 1-2 μm across, as shown in Figure 3.4. A few archaeological wood samples are in quite good condition and resemble fresh wood. One such atypical example can be seen in Figure 3.5 and Figure 3.6 below.
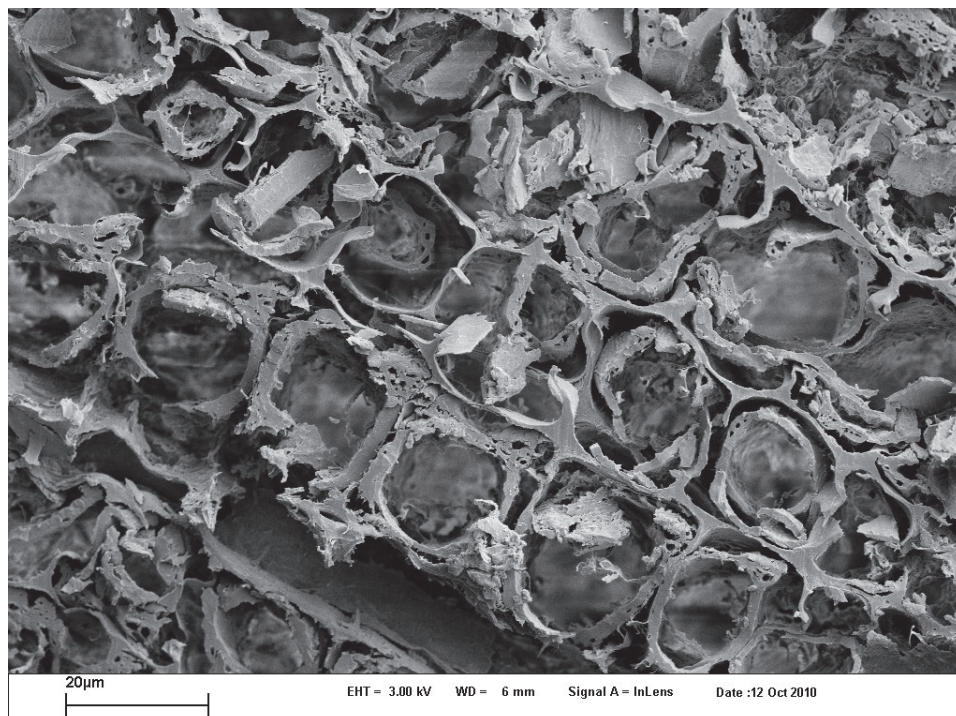
Figure 3.4: SEM image of a piece of freeze-dried Viking Age wood. Note that the cell structure is heavily degraded and some cell wall layers are pealing off the middle lamellae.

The fact that mainly aromatic components can be detected using IR and Raman spectroscopies have led to the assumption that the middle lamella remained [73]. Pyrolysis combined mass spectrometry (PY/MS) has been previously used to obtain information about fresh, decayed, and fossilised wood. Functional groups near aromatic rings in lignin generally remain unaltered – as was the case with a hardwood sample from Italy and a softwood sample from Israel [40]. Unfortunately, neither PY/MS nor vibrational spectroscopy can confirm that the lignin is still fully intact, merely that some aromatic residue can be found in the wood. Thus it is likely that the wood is structurally more degraded than the chemical analyses might indicate.
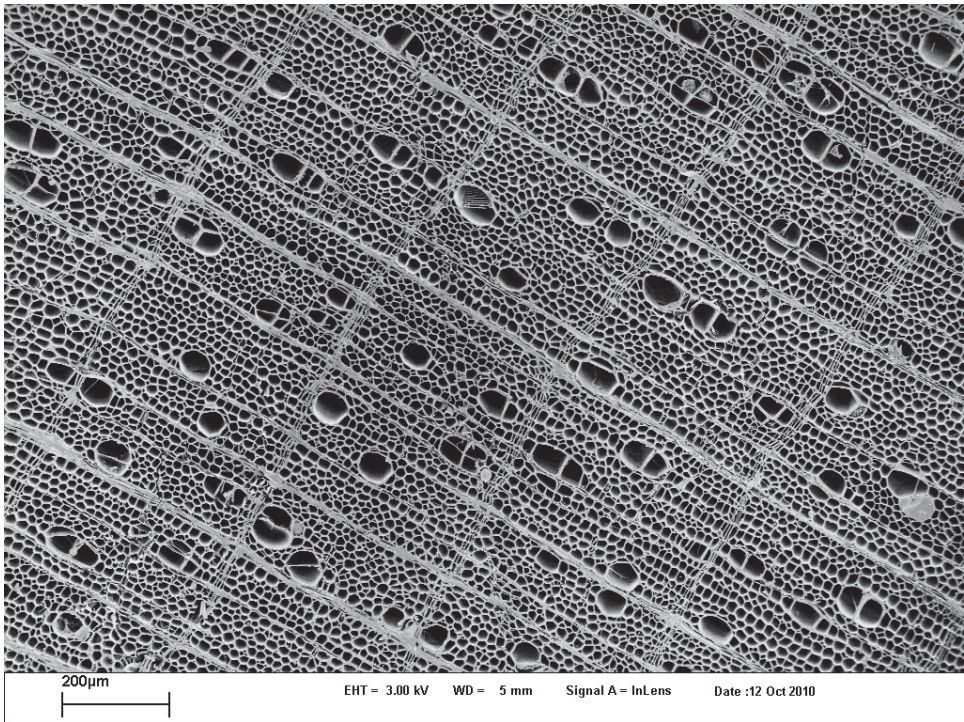
*Figure 3.5: SEM image of a piece of freeze-dried archaeological birch wood (*Betula*). The wood is in excellent shape and thus resembles fresh wood. Note the many larger ellipsoid vessels which identifies the sample as hardwood.*

'Shrinkage' occurs in the cell wall while 'collapse' means that the cell walls fold over against each other. Shrinkage occurs below the fibre saturation point due to desorption of water while collapse occurs as a result of capillary forces above the fibre saturation point. Both cause longitudinal, radial, and tangential cracks. Shrinkage results in cuboidal cracks and exfoliation while collapse is seen as depressions and distortions. The most troublesome part is that the forces vary within a single piece of wood since the surface is more degraded than the core [31](p. 11-12). The collapse caused during drying of waterlogged wood is usually irreversible. Sometimes swelling agents can be added to non-collapsed areas of the wood to compensate for the collapsed parts, but results are uncertain [20](p.31).
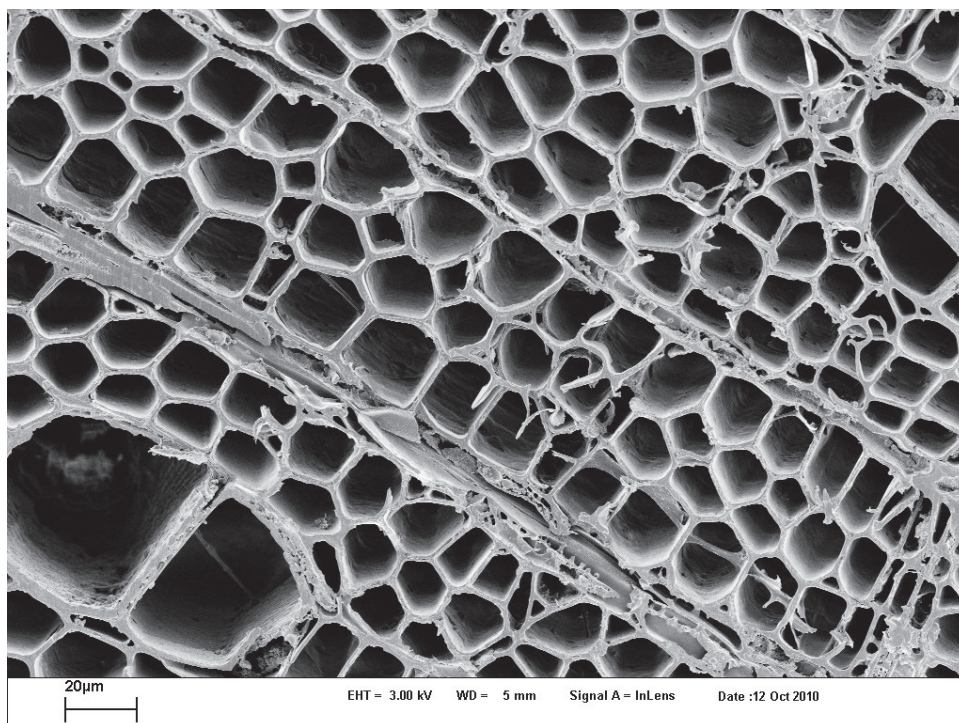
Figure 3.6: SEM image of freeze-dried archaeological wood in good shape. Compare with Figure 3.4.

There is little information on the chemical degradation process of wet archaeological wood. Since cellulose content is usually very low when compared to lignin content, the characterisation of lignin is very important [40]. Although one could speculate that the remaining lignin in waterlogged wood was somewhat water-resistant, the opposite is true. This may be due to increased accessibility of the hydroxyl groups. The age of the wood in itself does not appear to affect the results [20](p. 30-31).

Waterlogged wood looses significant amounts of holocellulose and takes up water, meaning that the lignin content stays relatively unaltered when measured in percent volume. Since oxygen is required for lignin decomposition, archaeological wood (and test samples buried in mud) has more intact lignin than cellulose [20](p. 19), [66].

NMR has been previously used to investigate archaeological wood, showing that the dominant *β-O-4* bond in lignin mostly remains intact. Unfortunately, normal solid-state [13]C

NMR investigations are not sensitive enough to reveal significant information about other chemical bonds. In order to gain better information, 2D-HSQC (heteronuclear single quantum coherence/correlation), quantitative ^{13}C NMR, and ^{31}P NMR spectra may help. These methods require lignin extraction and even acetylation. The HSQC spectra of two different samples (one from Italy and one from Israel) of acetylated lignin showed differences in bond quantity between the samples. Still, the results confirm that even in old waterlogged wood the structure of lignin is not heavily modified. By comparing the results with spruce milled wood lignin, it was possible to determine whether the samples were from angiosperm or gymnosperm wood species [40].

3.5.3   Identification of waterlogged wood

Since the properties of wood change during degradation, one piece of waterlogged wood may not resemble another. When you pick up a piece of waterlogged wood, you will immediately feel whether it is rough, smooth, or slimy. It also becomes readily apparent if the wood yields under light pressure – for example if your fingertips go through the outer millimetres of the degraded material. Since it is difficult to quantify such sensations in a reproducible manner, it is necessary to define a set of parameters which more easily allow conservation professionals to compare different pieces of degraded wood.

An often used quality is the maximum moisture content, MC_{max} (or Umax) which is defined as follows [76]:

$$MC_{max} = \frac{M_{swet} - M_{ms}}{M_{ms}}$$

Where M_{swet} is the mass of the wet (waterlogged) sample and M_{ms} is the dry weight. The waterlogged weight can be measured by carefully touching the selected sample to a piece of paper towel to remove extra moisture before weighing it. The sample is then placed in the oven at 105°C until the water has evaporated (in this case, the samples were left for a week) and weighed again to obtain the dry weight.

The density of the cell wall material, ρ_{ms}, can be found using the following equation [76]:

$$\rho_{ms} = \frac{\rho_{lpor}}{1 + \frac{M_{up} - M_{ss}}{M_{ms}} + R_{sorp}}$$

Where ρ_{lpor} is the density of water in the pores, M_{up} is the mass of the displaced volume of the waterlogged sample, M_{ss} is the mass of the waterlogged sample, and R_{sorp} is the correction factor due to sorbed water.

To measure M_{up}, remove excess water from the waterlogged sample and attach it to a needle. Place a beaker with water on a balance and press tare. Lower the sample into water so that it is just submerged (it is important not to measure the mass of the needle point). To measure M_{ss}, simply let the sample fall to the bottom of the beaker and record the weight. It is important not to remove any water during this operation, so it is advisable to use another needle to detach the sample [76].

R_{sorp} is used to correct for the fact that some of the volume is taken up by cell wall material – rather than simply either sorbed or free water. At 20ºC, R_{sorp} has a value of approximately 0.028. A thorough rationale behind the necessity for R_{sorp} and how it is calculated can be found in Ref.[76].

The mass of cell wall material per volume of waterlogged sample, ρ_{so}, can be calculated using the following equation [76]:

$$\rho_{so} = \frac{\frac{M_{ss}}{M_{up}} - 1}{\frac{1}{\rho_{lpor}} - \frac{1}{\rho_{ms}} + \frac{R_{sorp}}{\rho_{lpor}}}$$

Combined, the three calculated terms define the degraded wood fairly well, estimating both maximum moisture content, cell wall density and cell wall mass per waterlogged volume.

3.5.3.1 Samples used in these investigations

In order not to use up precious sample material, the initial tests were carried out with whatever wood was available. As time wore on, sample material was selected more carefully, trying to match the degraded Oseberg material more closely.

All samples were from the Museum for Cultural History at the University of Oslo[2]. All but one of them were discarded wood from Viking Age excavations but unsuitable for eventual display (some of these pieces might have come from Viking tools and buildings but many of them probably stem from branches or similar). After excavation, they were kept in a cooled room in water.

Note that bits of actual alum-treated Oseberg material were also impregnated with polymer and investigated. These pieces are described in chapter 6.4.1 'Imaging of PF-treated samples' on page 100. Since it was not possible to identify these samples using the methods described in chapter 3.5.3, they will not be described here.

Bits of the samples about 10x15x20 mm big were used for identification (the exact measurements varied from sample to sample). The samples were mounted on a small pin in a water bath at room temperature The properties of each of the test pieces (as defined in chapter 3.5.3) can be found in Table 2 below.

The individual pieces can be described in the following manner:

"*Drammen*": This piece of wood was a large fragment of pine wood (*Pinus*) from Drammen, Norway. This sample was not waterlogged and in good shape. The wood was about 100 years old. It was used for initial experiments with various polymers to get an idea of their distribution inside actual wood. When evaluating the results of these experiments, it is important to remember that the wood was quite different from the other samples used in these experiments.

"*Box 7*": This was a piece of pine wood (*Pinus*) from the excavation of *Slagen prestegård* (Slagen rectory) near Tønsberg, Norway. This wood is from roughly the same location as the Oseberg find and from a find situated very near to it. The site is from the Viking Age. It was used primarily for cellulose whiskers impregnation tests.

"*Stokk 9 sjakt 7*": Spruce wood (*Picea*) from *Slagen prestegård* (see the description of *Box 7* for details). The sample was used primarily for tests with cellulose whiskers.

"*Stokk 3 sjakt 3*": Birch wood (*Betula*) from *Slagen prestegård* (see the description of *Box 7* for details). The sample was used for chitosan experiments – specifically the ones described in *Paper 3*.

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2   Susan Braovac kindly helped find suitable samples from the storage at the Department of Conservation. Bjarte Aarseth, also from the Department of Conservation, found the sample from Drammen.

"*Kaupang 2*": Non-ring porous hardwood – most likely hazel (*Corylus*) although birch (*Betula*) could not be ruled out. The sample is from the Kaupang excavation (Viking Age). The first piece of wood chosen from Kaupang had collapsed which is why this one is referred to as "Kaupang 2". It was used for cellulose and chitosan impregnation tests.

"*Lost sample*": This sample was a piece of Viking Age birch wood (*Betula*). Judging from how deformable it was, it was fairly degraded (comparable to the two 'Stokk' samples). Unfortunately, the sample was stored in a leaky container and dried out before proper identification and measurements were performed. It was used for impregnation and curing tests for PF.

Oseberg material: Alum-treated material from the Oseberg find was investigated. The sample material was from either birch (*Betula*) or alder (*Alnus*) but a more exact identification could not be performed due to the degraded state of the wood. Since the wood had already been treated, and was very fragile, it was not possible to determine MC_{max} or other physical qualities. More information can be found in the PF imaging section (chapter 6.4.1 on page 100).

Table 2: Samples used in this investigation, their maximum moisture content, the density of their cell wall materials, and the mass of cell wall compared to total waterlogged volume.

Sample	MC_{max} [%]	ρ_{ms} [g/cm^3]	ρ_{so} [g/cm^3]
Drammen	159.4	1.304	0.4289
Box 7	480.6	1.274	0.1810
Stokk 9 sjakt 7	927.3	1.278	0.0985
Stokk 3 sjakt 3	657.8	1.285	0.1366
Kaupang 2	651.1	1.410	0.1398

4. Treating and displaying wooden finds

This chapter focusses on the problems surrounding the treatment of waterlogged wood as this kind of archaeological wood has been most relevant in this work. More information about various treatment methods can be found in Ref.[20](p. 252+) with information on biocides, from historical to modern, starting on p. 168. Readers interested in a different description may find good information about conservation and preservation in Ref.[62] (p.8+).

"The process of cheating Mother Nature, of arresting deterioration and preserving what remains of the wood, is not without its price. In order to preserve what remains of archaeological wood, a value hierarchy of attributes must be constructed. The attributes remaining in the excavated deteriorated wood must be ranked within the hierarchy. Conservation methods can be planned to preserve these attributes in descending order of value." [1](p. 437).

Not all finds can be treated the the same way – or have the same requirements for conservation. A list of "concerns" for all phases is given in Ref.[59](p. 331). When doubts arise, the conservators must prioritise. The most important aspects are: form, size, dimension, surface detail, and proportion. Colour and texture are assigned moderate value, while function, composition, and mass are the least valuable characteristics [1](p. 437).

Ethical dilemmas abound in consolidation. Impregnating material may be needed to preserve objects, but also often link irreversibly to the artefacts, possibly altering their fabric. The process may also affect what kind of later analyses are possible as the process usually destroys minor fragments, such as pollen or spores, embedded in the object. Thus it is important to try to maintain the physical properties of the original artefact as best as possible, making it next to impossible to treat it with a single chemical substance [59](p. 304). Sometimes, the reversibility of a treatment might have to be sacrificed – such as if a strong glue is needed to mend a piece which must bear a heavy load [77](p. 387). This, combined with the knowledge that preserved objects will not last forever, has led to the train of thought that it might be better to leave objects *in situ* since the degradation over time is minimal while the finds are kept under anaerobic conditions [73]. The trouble with keeping

large amounts of wood in storage at museums is another reason to look into the possibility of reburial as a long-term storage possibility [31](p. 29). Finally, the funds for excavation often outweigh those available for conservation treatments (at least in Scandinavia), which also points to *in situ* preservation as a possible solution – especially since deciding when to excavate and how to treat objects can be quite difficult [62](p.1).

It should be stressed that archaeological finds do not have to endure in the same way as wood used for the construction of cottages or other outdoor buildings. The museum climate is much more benign. There are usually no fungi and temperature and humidity are controlled. Thus materials which cannot stabilise the wood in nature might serve adequately in a museum where [11].

Unfortunately, large-scale impregnation or treatment means that many theoretically sound solutions cannot actually be implemented. Changing pressure or atmosphere in the museum, for example, is practically impossible. The expense of any chemical used must be carefully considered and the health and safety of the conservators who treat the finds should also be given extremely high priority [11], [73]. Note that these requirements are usually not present in more traditional chemical research and require chemists to change the way they approach problems concerning conservation.

Certain objects, such as many waterlogged wooden finds, are so deteriorated that their physical properties cannot be said to resemble the original material very well. In this case, the impregnating compound has to bear any stresses and – hopefully – distribute these uniformly throughout the object [59](p. 305-306). Especially with waterlogged wood, density may cause problems because the surface can be very porous while the core is dense enough that it is very difficult for impregnating materials to penetrate/diffuse into it [20](p. 36). Once they do diffuse, wood swelling might be a problem. Thus nonpolar solvents are preferable when dealing with dry wooden objects, but waterlogged wood can obviously be treated with polar solvents. The rate of evaporation is similarly important [20](p. 369). When applying liquid preservatives, one must be aware that solutions brushed or sprayed onto wood rarely penetrate it, requiring pressure or vacuum to function properly [20](p. 167). When carried by a solvent, molecules with a diameter of up to 0.55 nm can penetrate into areas of the cell wall which are normally occupied by adsorbed water. Since wood has a

high affinity for water, impregnation materials can be left in solution while the water is adsorbed into the wood [20](p. 21).

Placing wooden objects into cold baths of preservatives, heating them and subsequently allowing them to cool is an efficient yet simple way of drawing preservatives into the wood, potentially reducing impregnation times from days to hours [20](p. 255). Heating might otherwise be problematic when wanting to test treated wood and consolidants since thermal degradation and/or degradation by decay seem to be caused by different mechanisms than the degradation happening in buried wood [20](p. 41).

Another significant problem during conservation of waterlogged wood is to prevent distortion during drying. The variations between different finds of waterlogged wood makes it impossible to come up with a single treatment which works for all finds [31](p. 20).
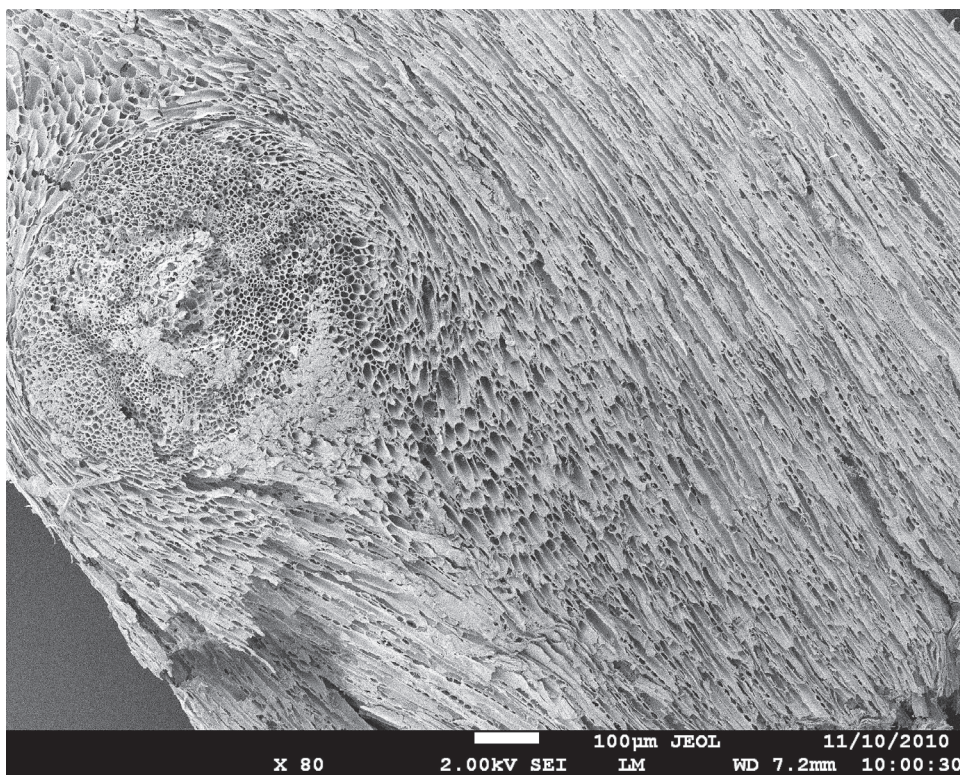
Figure 4.1: Cryo-SEM image of a piece of freeze-dried Viking Age wood from Slagen prestegård. Note that the rays swirl and are not regularly aligned.

The degraded wooden material itself may also react chemically with whatever consolidants are put into it. Wood modified by methacrylic anhydride can form covalent bonds with styrene and methyl methacrylate (through free radical polymerisation). There was no evidence of such bonding between monomers and wood modified with crotonic anhydride [78].

If environmental moisture changes, the wood will change with it. This may cause a cycle of swelling and shrinking detrimental to wooden artefacts on display. RH plays an important role in this, and is a reason why displayed wooden finds should ideally be kept at a constant temperature. The shifting of the wood may not only cause surface layers to peel off (ruining paints) but eventually cause the wood itself to collapse. At RH levels of 65% or more, moulds may also attack the wood [57](p. 404-405). For this reason, it is common to keep the RH close to 50% in Scandinavian museums [11].

Even if the wood is hardly deteriorated, its structure might be somewhat irregular and complex. An example of a natural 'whirl' found in a piece of Viking Age wood can be seen in the SEM (Scanning Electron Microscopy) image in Figure 4.1 above. Although such structures are unusual, their presence clearly demonstrate that no wood – whether fresh or degraded – is a uniform material.

4.1 Conservation treatments

In the following, a list of various treatments will be discussed. This will serve as a point of reference for the design of possible future consolidants as advantages and possible complications will be compared to those of methods already in use. Furthermore, the list should give readers an overview of the breadth of consolidants previously tested on archaeological wood.

Consolidants tested on wood range from animal glues and oils to modern resins. Most of the substances traditionally used are no longer recommended due to poor penetration and/or support of the items – or an irreversible setting process [59](p. 329). Despite numerous compounds which have been demonstrated to enhance wood properties, the exact

mechanisms which cause such improvements are still being investigated. Usually the goal is to incorporate agents into the cell wall to reinforce it [79]. Drying experiments have shown that a thin layer of impregnating material in the outer layer may sufficiently stabilise the find to prevent stress during drying – the obvious example is the *Vasa* [63](p. 188).

Gap fillers are described in Ref.[20] starting on page 553, but since this work deals with the stabilisation of the wooden matrix itself, rather than filling larger gaps in the structure, this subject will not be described in greater detail here. Adhesives will also be left largely untouched. Suffice it to say that applying traditional adhesives to archaeological wood is tricky. Often the impregnation material will interact with the wood and affect adhesion, or the wood itself has to be stabilised before adhesion is possible. Low density woods may so absorb too much adhesive, and uneven edges or fragments also affect the strength of glues [20](p. 542-543).

Sodium chloride was previously added as a preservative and fire retardant but since it damages the wood this practice has stopped. Similarly, SO_2, which was previously used to fumigate libraries, causes formation of acids which damage the wood. Ammonia gas swells wood through formation of ammonium hydroxide but is sometimes used to darken certain woods [20](p. 45).

Some of the more important methods for treating archaeological wood are described below. These are mainly still in use but information about important historical treatments (especially those relevant for the Oseberg find) are also included. For those interested in the most common consolidants, an overview and comparison between PEG, sucrose, lactitol, and Kauramin can be found in Ref.[80].

4.1.1 Freeze drying

Freeze drying is described in Ref.[20] starting on page 499. It avoids collapse by sublimating the water at low pressure in stead of letting it dry normally. The advantage of this method is primarily that the treated wood neither shrink nor warp significantly during treatment. This makes the method ideal when treating very degraded wood (or flimsy structures such as baskets) [20](p. 499).

As wood is cooled, adsorbed water will become supercooled, not freezing until a temperature of -38ºC or less is reached at normal air pressure. Both the viscosity and surface tension of such water increases (the former dramatically and the latter slightly). The wood also shrinks as temperature is lowered, somewhat offsetting the tendency of water to expand. Once water freezes, it may expand by as much as 13% and can cause damage due to increased pressure [70](p. 238). Still, the problems with supercooled water means that freeze-drying of archaeological wood should ideally be performed at very low temperatures to ensure that the water sublimates rather than boils [11], [73].

When water-containing wood cools below the freezing point, the vapour pressure of ice is lower than that of the supercooled water. This difference will drive water vapour away from the supercooled surfaces to condense on ice in cell lumens and voids. How this affects highly degraded wood (with a more amorphous structure than fresh wood) has not been fully examined yet [70](p. 240).

Freeze-drying has been applied to large structures – such as a large Roman boat with a wet weight of about 20 tons uncovered near Marseille which required about 5000 litres of liquid nitrogen to treat [70](p. 251). In such cases it can be fairly expensive. On the other hand, freeze-drying can sometimes be performed in winter in areas where the temperature is suitably low and air currents are strong [20](p. 499-500). Atmospheric freeze-drying of large timbres is thus discussed, partially because of the reduced price of maintaining low temperature in an Arctic climate, partially due to the lighter colour of objects treatable with lower consolidant (PEG) concentrations [70](p. 257).

Before freeze-drying became commonplace, waterlogged wood was dehydrated by a solvent during treatment. In a second phase this solvent was replaced with a monomer or resin. Water-soluble monomers make this easier as they can be added directly to the water the wood is kept in, eliminating the need for an additional solvent [81](p. 221). This achieves the same effect as freeze-drying, namely avoiding warping or collapse. Due to the relative toxicity of many commonly used compounds, freeze-drying is currently preferred – especially when treating larger finds [11], [73].
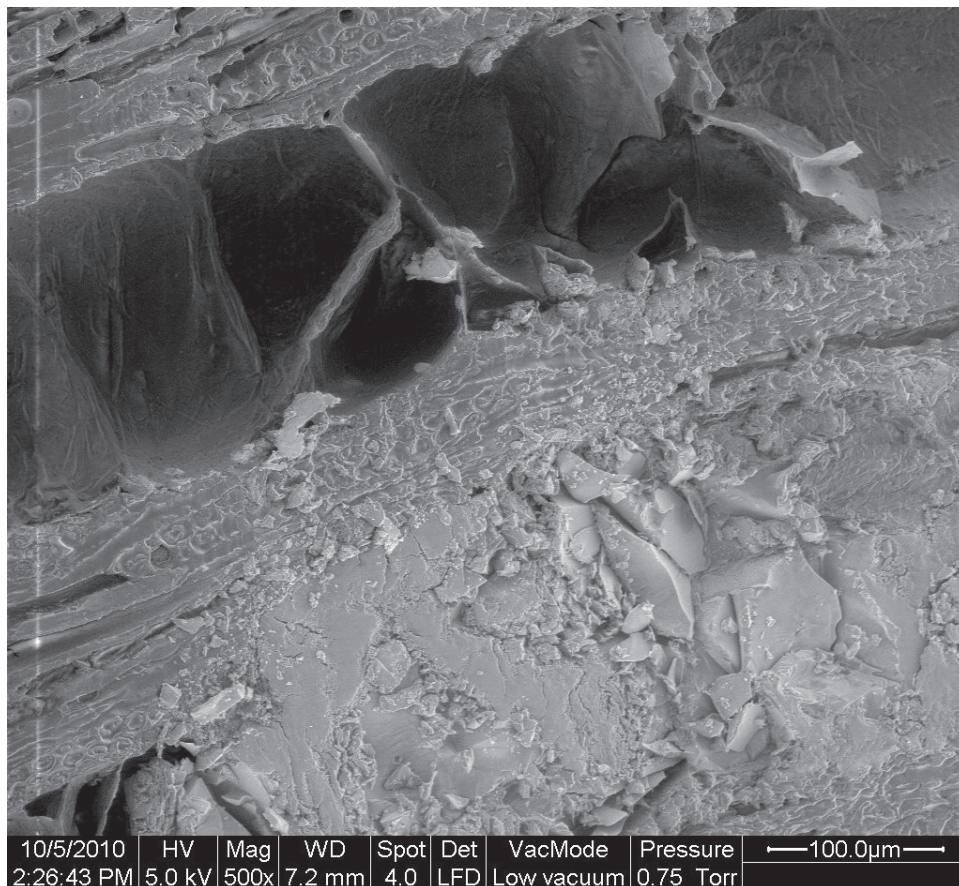
Figure 4.2: ESEM image of a fragment of Oseberg wood treated with alum and linseed oil. Notice how the oil fills the wooden structure while some alum crystals are visible below the middle in the right side of the image.

4.1.2 Natural oil treatment

The first conservation treatment used was probably oils. Tung nut oil was famous in China while linseed oil was common in Europe. The Tung oil has recently been used as a renewable source of material for polyurethanes and might thus be interesting for environmentally friendly materials [82]. Both oils were used in the treatment of archaeological artefacts – for example, several finds from the Oseberg find were coated with linseed oil [11]. Unfortunately, even long-lasting oils like whale oil or tung oil (which are

excellent for treating wooden furniture) seem to degrade over time and are not really suitable for long-term conservation [20](p. 383-4). Linseed oil hardens and expands upon contact with oxygen. This process can take years and if the surface splits the oil may leak out of the objects. Additionally, the oil can be attacked by bacteria, resulting in the smell of rancid butter [20](p. 503).

Unfortunately, oil blocks the pores of wood, making it impossible to re-treat it in the future. An example of Oseberg wood filled with linseed oil can be seen in Figure 4.2 above. Due to this, as well as problems with stability, these oils should not be included in ulaltered form in future consolidants.

4.1.3   Alum treatment

The alum treatment is especially relevant for this study since many items from the Oseberg find were treated with alum (leading to some of the problems described chapter 2.3 'Current challenges' on page 11).

The Dane C. F. Herbst changed treatment of waterlogged wood with the introduction of the alum method in 1858. This method was used extensively in Scandinavia over the next 100 years, until PEG-impregnation followed by freeze-drying became common practice. It replaced preservation with glue during the 18th and 19th centuries and, just prior to the 20th century, with waxes and natural resins as well [20](p. 6).

Alum is the salt $AlK(SO_4)_2 \cdot 12H_2O$ (potassium aluminium sulphate dodecahydrate). During impregnation objects are boiled for about two hours in a supersaturated alum solution at close to $100°C$. Preserved objects are not fire resistant and the alum crystals rupture some of the wooden cells. Such crystals, often attributed to recrystallisation due to moisture fluctuations, form on the surface of the objects [20](p. 372-5). Alum in treated objects (without glycerol) is not particularly hygroscopic. RH values significantly above 90% are required before it begins to take up water [73]. Since the alum crystals are white, the look of the treated objects is more lifelike than that of objects treated with lacquer or bulked with PEG (see Figure 2.2 on page 9 for an example). The crystals inside the wood form in various shapes and sizes. An example of a SEM (Scanning Electron Microscope) image of alum-treated wood can be seen in Figure 4.3 below.
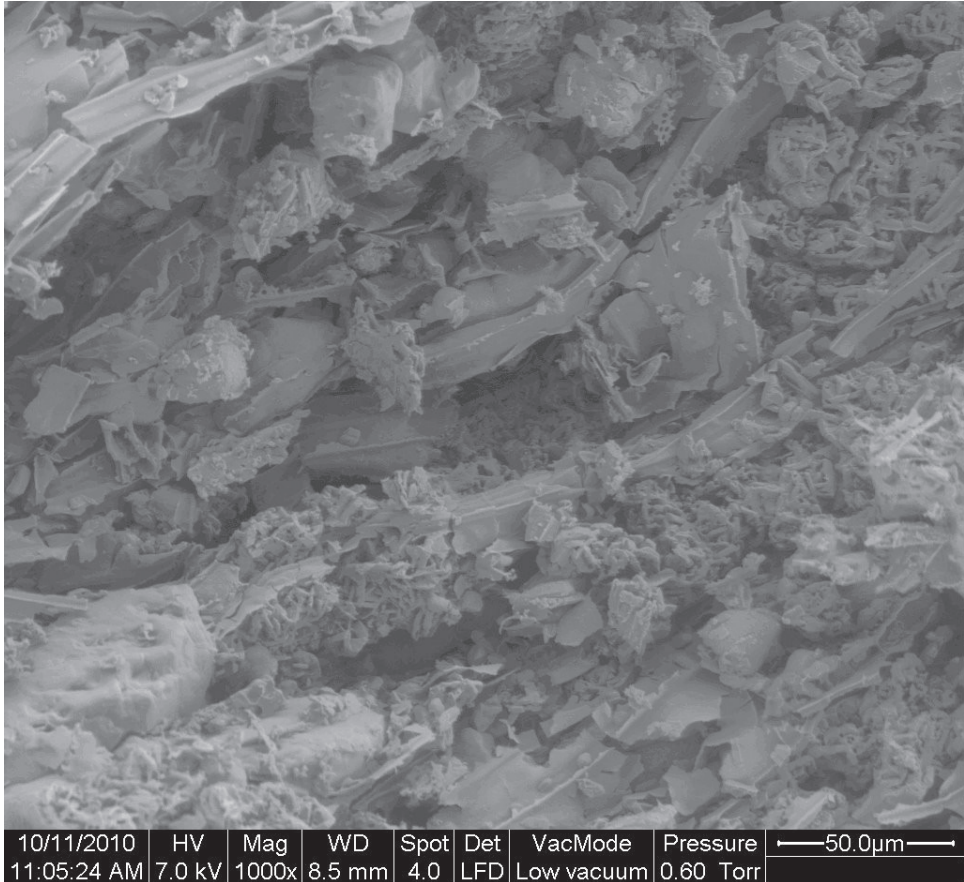
Figure 4.3: ESEM image of alum-treated wood from the Oseberg find. Note that the crystals form various structures but do not completely fill and stabilise the wood.

The distribution of alum has been investigated in newly treated objects with the surprising result that aluminium was not locatable with EDX (Energy Dispersive X-ray spectroscopy) [83]. Since Al can be detected in ashed samples, this may be due to the ions binding intimately to the degraded lignin [11].

Although the alum treatment was used extensively in Scandinavia, not much published research in its effects was easily available ten years ago. A single bachelor thesis from 1992 in Norwegian is one of the few Scandinavian examples of someone trying to conduct studies on alum-treated heritage. This work included IR spectra and x-ray diffraction investigations

of alum and also noted that the glycerol makes alum very hygroscopic. One of the most interesting observations is that the wood seemed to deform to accommodate the shape of the alum crystals (rather than the other way around) [84].

The current state of the alum-treated objects is dire, with high acidity causing the wood to powder. An example of the highly fragmented structure of some alum-treated items can be seen in Figure 4.4 below. Even though some of the damage might have been caused while attempting to cut the wood with a razor blade, this only demonstrates how fragile the remaining material is.
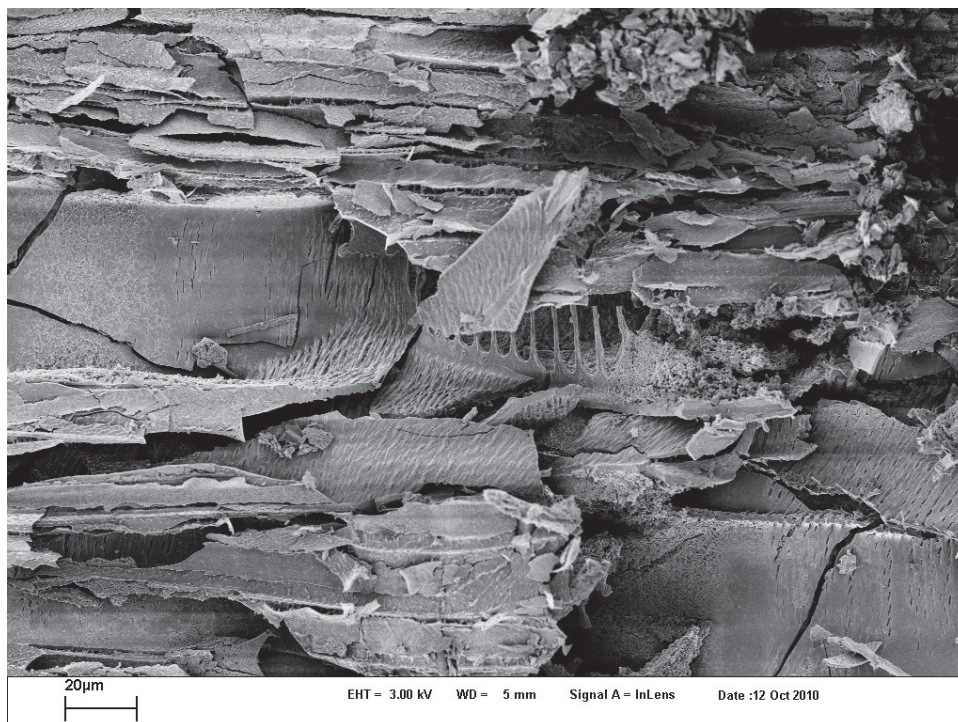
Figure 4.4: SEM image of a piece of alum-treated wood from the Oseberg find cut in the longitudinal direction. Note that the structure of the wood is gone and only a large number of fragments of various sizes can be seen.

4.1.4 Poly(ethylene glycol) treatment

Poly(ethylene glycol) (PEG) or poly(oxy ethylene) (POE) is currently used when treating waterlogged wood and is probably one of the most widespread consolidants. As such, it will be one of the standards potential new consolidants have to be measured against and is thus reviewed here.

PEG was first synthesised in 1859 (ironically in the same year as the alum treatment gained widespread use), it was not produced in large quantities until the beginning of the 1950's. At the end of the 1950's the first tests using PEG to stabilise waterlogged wood were carried out in Sweden and Denmark (tests were probably carried out slightly earlier in connection with the paper industry in the United States) [85](p. 196). When using PEG or sugars for conservation, biocides must be added to the baths [20](p. 501).

PEG was used to preserve some of the artefacts from the Oseberg find [85](p. 198) but the most famous object treated with PEG was the Swedish warship *Vasa*. After 333 years under water, the ship was raised in 1961 and the PEG treatment started the year after. The treatment went on for 17 years before the spraying was complete [86]. Due to doubts about the stability of the method and find, the remaining *Vasa* material with PEG, along with other PEG-treated artefacts, have been analysed to study possible degradation. The results indicate that slight chemical degradation might have taken place [87].

Long chains of PEG do not penetrate far into the wood, while short chains do not stabilise the surface in a satisfactory way. Thus it has become common to add first a low-weight PEG followed by a high-weight one. PEG still require a long time to diffuse into the wood, however, and can become unstable in temperatures and humidities found in the summertime – even in temperate zones [1](p. 442-443). On the other hand, higher concentrations can damage the stability of objects. A 100% PEG solution was found to cause about four times the shrinkage of a 70% PEG solution. Low-molecular weight PEGs may prevent shrinkage if the RH is kept very high (85% for PEG 600, 90% or more for PEG 1500). Long chain lengths, such as those in PEG 4000, seem to change the dimensions of preserved wood in all tests [85](p. 203-204). As a possible compromise, a two-step process for PEG impregnation has been recommended. At first a low-weight chain (such as PEG 200) is introduced in 10-15% concentration, and the PEG content is slowly increased (as far

as 50%). This relatively small molecule penetrates far into the wood and hopefully stabilises the core. A long-chain PEG (such as PEG 3000 or 4000) bath is then used, starting at concentrations of about 40-50% and at elevated temperature (about 60°C). The concentration is gradually increased to 70%. This long-chain PEG stabilises the fractured outer layers of the wood, but does not penetrate into the core of larger objects [20](p. 501). Unfortunately, this dual impregnation is not an ideal solution. Problems with optimal freeze drying temperature when using mixtures of PEG200 and PEG2000 have led to the conclusion that it is practically impossible to freeze-dry at a low enough temperature when low-length PEG is involved. As a consequence it is probably better (or at least sufficient) to use relatively long-chained PEG only in conservation [88].

Metal ions – especially iron – interfere with treatments with PEG. When composite materials are preserved, PEG corrodes the metal parts, making the method unsuitable without additional treatment with corrosion inhibitors to protect the metal. Solutions of HCl at 3.5% can be used to wash out Fe ions from the wood. The acidic wood is best neutralised using dilute solutions of NH_3 [20](p. 502). Not all metals are equally problematic as Ni salts destabilise wet PEG while Fe and Cu salts might prevent degradation. Stainless steel nozzles, on the other hand, seem to enhance degradation [89].

At 80°C, PEG 4000 was found to significantly degrade after about 100 hours with significant drops in melting temperature and heat of fusion after 1000 hours [90]. The slight reduction in molecular weight might indicate that the chain cleavage is end-wise rather than random [89]. Although this could indicate that PEG in archaeological artefacts will also degrade, investigation of PEG in wooden artefacts finds it in relatively good condition after 30 years [91]. Since PEG 4000 degrades noticeably in just four hours at 75°C in dry air but not after 20 hours at 75% RH [89], the moisture content of treated wood might help preserve PEG.

Although PEG is water-soluble, even short molecules, such as PEG 200, cannot be fully removed from the wood after a year. A few percent polymer remained even after repeated washes. When treating actual pieces of wood, it should be remembered that the PEG molecules will diffuse so slowly that it often takes years to remove most of the polymer [80]. This takes away an important reason for using PEG, namely reversibility.

Because the results of PEG treatment have been also erratic, current trends are to look for alternative treatment methods [31](p. 25).

4.1.5 Phenol-formaldehyde treatment

Phenol-formaldehyde (PF) resins have previously been used to preserve waterlogged wooden items. The trade names vary with type and place. Some of the more common are: Bakelite, Durex, Resinol or Kauresin. PFs are difficult to dissolve (most organic solvents do not work, although boiling water or strong acids and bases might). The two main types are acid-catalysed novolacs and base-catalysed resols. Novolacs are often uncured and require hardeners (like hexamethylenetetramine or paraformaldehyde) to finalise cross-linking. Resols usually contain an excess of formaldehyde and the polymer can be cured simply by applying heat [20](p. 435-439). Note that the terms 'novolac' and 'resol' are not always well-defined. This is described further in chapter 6.2 'Chemistry of PF' on page 82. More information on PF is given in chapter 6 'Phenol-formaldehyde' starting on page 79.

Although PF compounds mainly serve as adhesives, waterlogged archaeological wood has been stabilised through the use of these compounds. Composite wooden objects in particular are joined securely through application of a resin. Such resins have some significant disadvantages. Formaldehyde causes allergic reactions (especially to exposed skin) and can even de-gas from conserved objects. In addition, the resins cross-link irreversibly and may alter the appearance of the artefacts. The short hardening times also mean that it is difficult to impregnate large objects with these polymers, and it is impossible to remove the resins with solvents after impregnation [20](p. 435-439).

Some objects thought to be treated with PF are in fact not. Pieces from a degraded wooden bucket, likely from the 1290's, were treated with urea formaldehyde in Wales. Although the wood was in relatively good condition, it could not be dried without warping. Alternatives to the alum method (which was becoming outdated at the time) and both poly(vilyl acetate) and butyl methacrylate were considered but could not prevent warping. Butyl methacrylate had no effect except keeping the water inside the treated objects. Beeswax gave better results than either of these polymers but still left the surface with an undesirable finish. Phenol-formaldehyde (PF) "Bakelite R.568" cured at 150°C was tested

and gave satisfactory penetration and rigidity. The dark colour and the texture of treated specimens meant that PF was abandoned in favour of urea-formaldehyde ("Bakelite Cement G.10897/1" with a subsequent treatment in 5% watery "Bakelite Accelerator Q.11191") [92]. This means that other finds may also be treated with "Bakelite" without actually being treated with PF.

4.1.6 Kauramin and melamine-formaldehyde treatments

With investigations being carried out on phenol-formaldehyde, it is reasonable to investigate the properties of similar polymers – especially since a very similar polymer has already been developed for conservation use.

Melamine resins are not usually very reactive and need high curing temperatures. They are often combined with other monomers with a high concentration of hydroxyl groups. Some types of melamine resins are sensitive enough to acid that large amounts of it will allow curing below 100°C. This process seems to require secondary amine groups (-NH-CH$_2$OR) [93]. Melamine reacts particularly well with formaldehyde and oxirane. It is used to enhance thermal stability in resins due to the ring structure of the molecule. The resins also work as electrical insulators. The main disadvantage is a low solubility in water (3.2 g/l at 20°C and 5 g/l at 100°C), usually meaning that formalin at 80°C has to be used. Melamine dissolution seems to be accompanied by formation of hydroxymethyl derivatives. Melamine can also be dissolved fairly well in polyhydroxy compounds. However, the resin produced from such dissolution (and automatic reaction once acid or base has been added) is reported not to harden below 80°C. Since melamine-formaldehyde prepolymers are usually quite unstable, the water removal needed to cure the resin can be problematic [94].

One reported study on increasing solubility focussed on formaldehyde in watery solution and acetone as a solvent for melamine. The pH was kept at 11. By using catalyst, melamine contents in the 40-50%$^w/_w$ were reached at temperatures in the 40-50°C range [94]. Note that while the above gives some idea of the chemical adjustments possible regarding solubility, the high pH makes the study inapplicable to waterlogged wood. Non-watery solvents are needed in order to reach high melamine concentrations but doing so is not always necessary.

It has been common practice at German museums to preserve archaeological wood with "Kauramin" which is a melamine formaldehyde. The most important reasons for using it are that it is soluble in water and has a low molecular size, allowing for good penetration of wood. The slow hardening process when alcohols are turned into ether means that the polymer will not simply cover the surface of impregnated objects. The wood is made more elastic by adding ethylene glycol, ensuring that fewer cracks form in the preserved wood [95]. As only a little polymer is deposited, Kauramin-treated wood is very light and has only one to two thirds of the weight of the wood in the waterlogged state [80].

The following conservation procedure is based upon Ref.[95]: A 25% solution of the melamine in water is prepared. 0.5% triethanolamin is added since it neutralises acid and helps preserve the wood. 5% urea is added in order to lower the viscosity of the solution. Urea also bonds with excess free formaldehyde. The product, called CE 5549, contains about 1.5% free formaldehyde when bought. The baths are covered in order to avoid evaporation and prevent oxygen from reacting with the formaldehyde (this produces formic acid which catalyses the polymer reaction and shortens the lifespan of the impregnating solution). Once impregnation is complete, the pH is lowered if necessary in order to initiate polymerisation.

The time of conservation is fairly short due to the small size of the melamine compound (5-30 Å). Small objects can be treated in a week and large objects in about a year. Depth of impregnation may be tested through elemental analysis, measuring the oxygen and nitrogen content of the treated object.

After conservation, the wood is rinsed with running water and carefully wrapped in wet wood pulp and finally foil. The wrappings are stored at 50°C in order to cause excess polymer to diffuse into the wood pulp rather than be left on the surface of the artefacts. Pulp is removed before it dries and becomes almost impossible to remove.

A sample of the impregnating solution is left along with the wrapped artefacts to easily test if it has hardened (which usually happens after one to two weeks). Lower temperatures prolong the time of hardening although the polymerisation happens even at room temperature.

After hardening, the artefacts are still wet and must be dried carefully in order to avoid fractures or warping of the wood. The wood is wrapped in polyethylene foil, which allows small amounts of water to evaporate. From time to time, the wood is unwrapped in order to

remove any water from condensation. Smaller objects take weeks or months to dry, while large objects can take years. The method can be combined with microwave drying to speed up the process. In this case objects must be stored in a way which enables air to reach all sides of the object in order to prevent warping. Drying is usually continued until the water content in the preserved object is about 15%.

Earlier comparison with freeze drying (both at -5°C and -40°C) and drying with micro waves showed that the PE wrapping was the most favourable if fractures and shrinkage was taken into account.

The surface of preserved wood is very light and contains chalk. It is treated with water soluble waxes, artificial resins or drying oils to improve the colour of the object and strengthen the surface.

The method leaves the wood in good enough shape for dendrochronological dating and the formaldehyde preserves the object against biological attacks. Wooden objects with organic or inorganic composites (such as stone, leather or textile) may be treated as well. Small adjustments to the shape of the objects may be made even after drying (for example by applying steam).

Further notes on the method may be found online [96].

A couple of tested resin solutions could not solidify until their solutions evaporated, meaning that the wood cell structure was also warped. Electrolytic silsification in sodium silicate worked but gave varied and generally unsatisfactory results. A melamine-formaldehyde called "Arigal C" (originally developed to prevent rotting in cotton textiles) was the best of the tested products. The monomers are applied in watery solution (about 25% polymer in 80°C hot water). Prolonged impregnation times are not harmful but the polymerisation process starts if the pH falls below 7.3. At the end of impregnation 10% catalyst (compared to the volume of the thinned Arigal C solution) is added. Vacuum is used to remove air in the object. The object must be taken out of the impregnating solution in less than 40 hours or the polymer will be difficult or impossible to remove from the surface of the object. Deposits are avoided by rinsing the surface with hot water and wrapping the objects in cotton clots soaked in distilled water. Everything is put in a PE bag to prevent evaporation of water and heated to 65°C for 48 hours. After this drying at no more than 40°C for about 20 hours and then continued at room temperature. The process can be repeated for

delicate objects although the catalyst in the object limits the time an object may spend in the impregnation bath the second time around, so only 5% catalyst is added to the second solution. The re-treatment can also be used to fill cracks formed during initial treatment. The advantages of the method include slight shrinkage, applicability to all types of wood, a minimum of labour required, and high durability [97].

It was found that the Kauramin treatment overall resulted in the least swelling or shrinkage when compared with a number of other often-used conservation materials such as PEG and sucrose. In addition, it was the method least sensitive to wood species as the other methods were better at stabilising pine than they were at stabilising beech and oak. The method also has significant drawbacks. Curiously, the treatment did not work well on fresh oak samples, where collapse occurred in the heartwood (so differences in degree of degradation can be a problem). The pre-polymer cannot penetrate the cured outer resin layer to correct for such faults. This makes premature polymerisation a serious risk – even at controlled pH. The whitish colour of the polymer also mars the appearance of Kauramin-treated artefacts. Another drawback in that curing takes place at 50ºC rather than at room temperature. Finally, drying time must be taken into account as the wrapping in paper makes the objects unsuitable for display while drying (unlike the PEG or sucrose method where the objects may dry in a museum environment). A further problem with Kauramin is that it cannot be washed out of treated objects (unlike PEG or sucrose) [80]. In high concentrations, the polymer might arrange itself randomly, resulting in blocked pores which prevent future treatment of the wood. For this reason, the Kauramin method only applies a little polymer to the treated items, thus preserving the open structure of the wood [98]. Thus the last paragraph on the Kauramin method in *Paper 1* should be worded differently – although the discussion on plastification is still relevant (see chapter 5 'Future consolidants' on page 71 for more information).

Note that the treatments described require temperature control and sometimes even vacuum. The latter in particular severely limits the practical applications of the method. For example, it will be impossible to treat the artefacts from the Oseberg find using a method which cannot be applied directly in the museum.

4.1.7 Treatment by various polymers

In order to develop new materials for waterlogged artefacts, it is vital to avoid problems caused by already tested consolidants. One might think that there is a wealth of polymers which would make wood conservation easy. Sadly, the truth is quite the opposite.

One possibility is to use sugars. Waterlogged wood treated with sucrose keeps the appearance and weight of fresh wood [31](p. 25). Sucrose can effectively stabilise wood but the procedure can be tricky as a near-saturated solution gives the best results. Evaporation of water or a drop in temperature can cause the sucrose to crystallise and become very difficult to remove [80].

Introduction of monomers into wood for *in situ* polymerisation has been discussed at least since 1978. Polymers such as PMMA (poly methyl methacrylate) and PS (poly styrene) (including various co-polymers) were introduced. It was found that wood-PMMA has stress properties similar to solid PMMA but superior to wood. It is also more resistant to static bending. Warping, checking and decay resistance are all improved – possibly due to the changes in hygroscopicity [99]. In a previous experiment, water-soluble monomers gave poor results. N-vinylpyrrolidone (NVP) formed a dark brown gel on the surface of the treated objects and ruined their impression. It also caused splitting or cracking of the impregnated samples – even after radiation curing. Similar cracking was caused in samples treated with a 15% methacrylamide (MAID) solution. Oxygen prevented polymerisation in samples treated with butyl methacrylate. This also caused cracks to form and resulted in a very low overall impregnation. Treatment with acetone and Norsodyne and Ludopal resins gave better results, with a maximum of 3.5% shrinkage of the highly deteriorated wood after treatment. Unaltered Ludopal resulted in some cracks but adding butyl acrylate gave a more flexible resin than the Norsodyne (propylene glycol polymaleate) with similar results (maximum 1.2% shrinkage) [81](p. 226-227).

Certain *in situ* polymerisation methods, such as impregnation with poly(methyl methacrylate), cannot be used with wet materials and polymerisation is so rapid that corrections cannot be made once initiated [20](p. 439-479). Generally speaking, tests with monomers (water-soluble or not) did not give optimal results – possibly due to low viscosity and the inhibiting effect of oxygen on polymerisation [81](p. 232).

Resins, such as urea-formaldehyde or melamine-formaldehyde resins, have drawbacks (toxic reactants, swelling of the wood, poor penetration, wood is still susceptible to bio-degradation) [20](p. 439-479). Thermoplastic resins are more attractive as wood consolidants than thermosetting resins (due to reversibility). It is possible to introduce such resins into the wood in solution (aqueous or non-aqueous) and start the polymerisation through heat, a catalyst, or γ radiation. The most commonly used polymers in resins are acrylics, poly(vinyl acetates), poly(vinyl butyrals), and soluble nylon. Unfortunately, nylon eventually cross-links and becomes brittle, making it unsuitable for impregnation of wooden artefacts [100](p. 362-363). Soluble nylon has poor ageing characteristics and may even flake off, taking wood and paint with it [20](p. 504). Unsaturated resins have higher viscosities and create a more hard finish. Shrinkage is less than with many other monomers, but can unfortunately reach as much as 9%. These resins were tested with acetone as solvent and isophthalic polyester resin as the impregnating polymer [81](p. 232).

Several acrylics have been thoroughly tested using various species of wood and different fungi for degradation. The resistance of many polymers to insect attack is also discussed thoroughly, but such discussions are beyond the scope of this thesis. A list of biodegradability states that polymers like PMMA, epoxy resins, PP, PS, PET, "glasfaserverstärkt" polyester, hard (but not soft) PVC, and PE (in that order) are extremely resistant to biological degradation. Many acrylics used in conservation are rated similarly to PMMA. Interestingly, PF is only rated slightly above average and MF is rated as average even though these polymers are traditionally described as very resistant chemically [101]. The stability and resistance to mould growth of various polymers has been tested. It was found that polymer materials in themselves usually cannot withstand fungal attack without treatment with some form of biocide [102]. Gamma radiation may also be used both for killing unwanted organisms within the wood and/or activate polymerisation of certain acrylics or polyester resins [20](p. 498).

Other compounds, like poly(vinyl acetate), poly(vinyl chloride) or poly(vinyl alcohol), are not hard enough to stabilise the wood and/or do not penetrate very far into the wood. Compounds like poly(vinyl butyral) and unsaturated polyester resins may prove more

useful, but are still time-consuming and difficult or dangerous to handle during polymerisation [20](p. 439-479).

Isocyanate foams are considered when voids have to be filled with a semi-rigid material. Ethanofoams might be used as an interface between rigid nonhygroscopic materials and cosolidated fabric. Latex or vinyl with a microsphere suspension are considered for filling voids – and epoxides and polyesters might be used for the same purpose when an interlocking matrix is needed. Finally, PVC is considered along with stainless steel or aluminium tubing when supporting the direct load through a skeletal structure [100](p. 336). A styrene polyester has been employed in an attempt to limit acidic sulphur efflorescence on French shipwrecks treated with PEG. After a year of impregnation, tests showed that the sulphur was well stabilised. It is also worth noting that already PEG-impregnated artefacts can be re-conserved with a polyester resin (up to 40% concentration). The double treatment does darken the surface of the wood slightly, however [103].

Using azelaic and sebaic acids (dicarboxylic acids with 9 and 10 C atoms respectively) to impregnate the wood may offer an alternative without the need for freeze-drying [104]. Unfortunately it is difficult to ensure proper penetration and the acids also lower the pH of treated wood significantly without offering superior support [73].

4.1.8 Silicon oil treatment

While most polymers used on archaeological wood may be carbon-based, it might be worth it to expand into other kinds of polymers as well. Silicon-based chemistry might offer new possibilities when designing polymers.

An overview of the chemistry and typical interaction between sillicon compounds and wood can be found in Ref.[79]. According to this, sillicon is the second most abundant element after oxygen. Silicates and silicic acid esters are found both in plants, lower animals, and vertebrates (for example in palm leaves, sponges, and nails, respectively). Silicic acid, H_4SiO_4, causes the formation of silicified wood by eventual polycondensation to quartz and opal. Silicofluorides are used as biocides and makes wood less susceptible to weathering and degradation due to light. Water glasses are solutions of potassium or sodium silicates (typically 2-4 mol silicate to 1 mol alkali oxide). Water glasses are used as flame

retardants, binding agents, and coating materials. While colourless in their pure form, they are easily coloured due to impurities. Watery solutions are very alkaline, having pH values of 12 or more, and precipitated in acidic environments. When impregnating (fresh) woods with water glasses, the NA ions must be replaced in order to cause the material to precipitate. This is done by introducing a salt, possibly as a two-step process. Hardwoods gain significantly more weight than softwoods when impregnated. Considerable amounts of chemicals are washed out during impregnation, and the wood is often soaked in acid to prevent this by forcing the silicates to precipitate. Water glass is also highly hygroscopic. The anti-shrink efficiency varied in tested samples (3-69%) but was generally low. On the bright side, water glass makes the wood resistant to fire and fungal attack. Strength is only improved slightly with curing at room temperature and actually reduced when cured at higher temperatures (103°C). When combined with acetylation, the hydrophilic nature of water glass causes a slight reduction in the ability to resist swelling. While some silicic acid monomer solutions enhances wood strength properties, water glass actually reduces them [79].

The COH group in the cell walls can be reacted with silanes (and since cross-linked with carbonols or silanols). Catalysts are usually required. The polymers can either be added to coat the cell walls or a mix with cross-linker can be introduced which penetrates the cell walls. Water in the cells is replaced by acetone or an alcohol. Catalyst is usually added at this point. $MeSi(OMe)_3$ and $Si(OEt)_4$ can both be used as cross-linkers although the former is tri-functional (as opposed to tetra-functional) and results in a more pliable specimen [105] (foreword).

Treating PEG-conserved objects with Si-polymers may cross-link free PEG and restore the original dimensions of the object, counteracting the swelling often associated with PEG treatments [105](p. 31-32).

Organosilicon compounds have been tested on wood. Some of these are poisonous and the impregnation process is irreversible. White deposits may form on the surface of the objects and cracks often develop in the brittle preserved wood – especially with waterlogged wood [20](p. 492-6). Objects are exposed to fumes of catalyst in order to ensure that said catalyst reaches the inner parts of the artefact and causes polymers to cure all the way

through [105](p. 68). Previously tested silicon oils are not miscible with water, meaning that dehydration of the objects to be treated is required. This, unfortunately, easily damages waterlogged artefacts [105](p. 13). Water glass and similar compounds can be gradually decomposed by CO_2 in the air [79]. The high pH value of dissolved water glass and similar compounds also means the wood can be damaged – especially considering the significant impregnation times required.

4.1.9 Supercritical carbon dioxide treatment

Supercritical CO_2 can act as a solvent and remove biocides from wood. Agents such as DDT can be mostly removed, provided that the objects are treated from one side only, and resins may be dissolved and mobilised. The CO_2 may even be circulated for later use [20](p. 264).
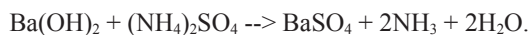
Additionally, supercritical CO_2 is used when drying waterlogged wood – or when impregnating it with PEG – but water in the wood must be exchanged prior to treatment (for example with methanol) [20](p. 289).

4.1.10 Nanoparticle treatments

Nanoparticles offer new ways to preserve cultural heritage by mixing soft-matter and hard-matter systems, and have already been applied to wall paintings, paper, and wood – an overview of which can be found in Ref.[106]. The approach is mainly used in the restoration of frescos since these wall paintings, while long-lived, tend to degrade as the binder ($CaCO_3$) oxidises (or turns into $CaSO_4 \cdot 2H_2O$) – or as environmental pollution interacts with the surface. Such degradation may be chemically counteracted by the following reactions:

$(NH_4)_2SO_4 + CaSO_4 \cdot 2H_2O \; \text{-->} \; (NH_4)_2SO_4 + CaCO_3 + H_2O$

followed by this neutralisation:

$Ba(OH)_2 + (NH_4)_2SO_4 \; \text{-->} \; BaSO_4 + 2NH_3 + 2H_2O.$

Excess $Ba(OH)_2$ reacts with $CaCO_3$ to create new slaked lime which then sets – just as when the fresco was originally painted). This process can usually be replaced with consolidation using nanoparticles. In fact, $Ca(OH)_2$ particles have already been used to preserve Mayan paints *in situ*, where high relative humidity and tropical or sub-tropical climate normally deteriorate both paintings and polymers used to preserve them [106].

Nanoparticles can do more then simply reinforce frescos, however. Cellulose-based materials can be effectively treated with alkaline particles which counteract the acidification process degrading the cellulose polymer. Several aqueous and gas phase methods exist for the neutralisation of acid in paper, but the distribution of the alkaline material is often hard to control, possibly leading to increased vulnerability to moisture or loss of paper strength. Nanoparticles of $Mg(OH)_2$ or $Ca(OH)_2$ can likewise be used to de-acidify paper. Indeed these compounds have also been used to neutralise acidic archaeological wood – such as that from the *Vasa* [106]. In one study of *Vasa* material, the nanoparticles contained crystallites with an average size of 15 nm. The particles themselves were about 90-130 nm, which allowed them to penetrate into the wood. Because CO_2 converts hydroxides to carbonates, long-term degradation of lignin due to the alkaline hydroxides should not occur. The outer 1-2 cm of the wood (where degraded PEG is also found) were successfully neutralised. $Mg(OH)_2$ particles are typically smaller – and thus penetrate further – than $Ca(OH)_2$ particles. Solvents other than propanol might also enhance penetration. Suspension was achieved by using fluorinated solvents which are supposed to be chemically inert. Dispersion was carried out by sonification and penetration was attempted under continuous stirring. Both 0.2 and 0.4 M aqueous solutions were prepared. The procedure does require multiple dryings under nitrogen atmosphere as well as the special solvents. The wood was also washed to remove most of the PEG. No shrinkage was observed while drying the wood (although the wood has already been dried once, which may make the result unreliable). The wooden test pieces were fairly small, about 0.4x4 cm and had a pH of about 5.5 after treatment [107].

Given these successful initial trials, it is reasonable to assume that future conservation materials will include some sort of acid-neutralising particles. It would, however, be ideal to work with less expensive solvents than the tested fluorinated ones.

5. Future consolidants

The current state of the Oseberg collections also demonstrates how the ingenious inventions of today become the headaches of tomorrow. Sadly, most existing treatments have some form of drawback (see chapter 4.1 'Conservation treatments' beginning on page 50). This demonstrates the need for strategic planning towards new and better consolidants for archaeological wood – as opposed to simply testing materials at random. Based on the literature review in the previous chapters, some ideas and requirements for new consolidants can be listed. This chapter deals with those ideas, presenting both the ideal list of requirements for new consolidants and several of the practical considerations which must be taken into account. This is also discussed in *Paper 1* in the appendices.

Stephen Mann writes that "Viewed from afar, the landscape of science appears steadfast and immutable. But in reality, this permanence is underpinned with a loose patchwork of disciplines whose frontiers are constantly being redefined." [108](introduction). "Clearly, an interdisciplinary approach of this magnitude relies on the unlocking of human imagination from the confines of conventional disciplines. A new paradigm is imminent – are we ready for it?" [108](p.37). Although the quote in question is about biomimetics (see chapter 7.1 'The concept of biomimetics' on page 125), it might as well have been written about new consolidants. When approaching wood conservation from a chemical viewpoint, it is important to remember that conservation science very much deals with ethics. What may or may not be permitted is not dictated by an individual or organisation since the treated artefacts have historical value which must be preserved for future generations.

A list of requirements for conservation in general can be found in the *AIC Code of Ethics and Guidelines for Practice,* stating that: "The conservation professional must strive to select methods and materials that, to the best of current knowledge, do not adversely affect cultural property or its future examination, scientific investigation, treatment, or function." [109] While excellent in theory, this becomes difficult in practice. For example, many products originally thought to be reversible have shown various problems (yellowing, brittleness, detachments etc.) making re-treatability more important than reversibility [110]. In the 1960's, resins were applied to archaeological finds. It was thought that these resins

could be removed at any time. Unfortunately this was not so. Many artefacts have ended up permanently damaged due to the process. Generally, the removal of polymer materials is difficult or even impossible, and many organic chemical compounds are harmful given enough time. Thus inorganic compounds are much more effective when treating inorganic artefacts like stones and wall paintings [106]. In a test (involving stonework and artificial UV ageing) with Paraloid B 72, Paraloid B 67, and Dri-Film 104 (a Si-based product), all three polymers underwent irreversible modifications, changing colours and making their complete removal impossible. After 2000 hours of ageing, about 60% of the B72 and and 70% of the B67 was no longer soluble. This applied to polymers in actual stonework. When applied to Petri dishes, only a few percent of polymer material was insoluble [110].

The *AIC Code of Ethics and Guidelines for Practice* also states that: "The conservation professional shall promote an awareness and understanding of conservation through open communication with allied professionals and the public." [109]. The diverse nature of wood means that there is no single optimal treatment to a given class of wooden objects. Thus a dialogue between groups – focussing on each individual specimen to be treated – is the only way to improve communication and treat each artefact appropriately [1](p. 447-448).

While important, useful communication is often hard to implement due to a 'language barrier' between different fields – such as chemistry and conservation. Often it is hard for conservators to ask questions the chemists understand – or for the chemists to deliver a usable reply. It takes time and a willingness to explain all about one's own field.

There are also certain conditions which make communication more difficult. Many studies on wood simply state that the wood was found in, for example, 'good condition' but they rarely specify any details beyond possibly shrinkage [60](p. 68).

5.1 Practical considerations

The shortcomings of existing consolidants need to be considered before designing a new one. First of all, the consolidant must remain stable and endure in normal air (see chapters 4.1.2 and 4.1.4) and possibly endure the presence of metal ions without degrading (see chapters 2.3 and 4.1.4). Another important requirement is that the consolidant is fairly evenly distributed throughout the wood in order to avoid forming an outer 'shell' with a

fragile core (see chapters 2.3, 4.1.3, and 4.1.7) or prevent future treatment by other polymers (see chapters 4.1.5 and 4.1.6). It is a significant advantage if the consolidant is resistant to acid (see chapters 2.3, 4.1.3, and 4.1.4) although this might be accomplished by adding a neutralising agent (see for example chapter 4.1.10). Speaking of pH, the treated wood should be kept slightly acidic as alkaline conditions damage the wood (see chapters 3.2 and 4.1.8). The consolidant should be compatible with the existing wood (for example not damage it due to being alkaline as in chapter 4.1.8). Last, but certainly not least, the ethics and practical considerations of conservation must be taken into account, meaning that consolidants should be non-toxic and avoid plastification (see chapters 4 and 4.1.5).

In order to achieve a method that lasts forever (or, since nothing lasts 'forever' than at least several centuries) and leaves the finds re-treatable at such a time, several approaches must be investigated. Will it be better to use inorganic particles which are very difficult to degrade, or should it be attempted to mimic the structure of the existing wood? Existing studies – while valuable – often focus on a single compound or set of curing conditions, making it hard to generalise the results. Alternatively, usable methods may provide great initial stability of the treated items but bond permanently with the wood, making it impossible to re-treat the objects later on (and, sadly, meaning that such finds will probably be irrecoverable once the treatment starts to fail). Thus the main aim of this study was to discover in what general directions the most promising ways of conserving wood lie (or, failing that, at least what should *not* be attempted in the future).

Preservation with reactive chemicals is called a number of things such as 'plastination', 'reactive filling', or '(chemical) bulking' [105](Foreword). It is important to note, however, that this might not mean that the wood is being completely filled with polymer. This scenario is called 'plastification' and essentially turns the porous wood into a solid lump of matter. Such plastification is a danger to the above requirement of leaving an open structure. In order to ensure retreatability it is essential to be able to predict the shape of the added consolidant in the wood. The ideal consolidant simply adheres to the existing degraded wooden matrix, adding an extra layer of a stable material while leaving the lumen open for future consolidants.

The choice of solvent may be as vital as the choice of consolidant. Polar solvents, for example, tend to get adsorbed in the wood, lowering mobility of impregnating materials [100](p. 363). Reaction with existing materials must also be considered. The highly degraded alum-treated objects, for example, cannot be re-treated using watery solutions (see chapter 6.4.1 'Imaging of PF-treated samples' beginning on 100 for some of the actual trials) or related solvents such as ethanol – while toluene seems to react less with the alum crystals [11]. From a chemical perspective, using toxic solvents is not a problem as long as they do not damage the wood. Such wood will not usually be treated by chemists in well-equipped laboratories, however. This means that there is a constant balance between the practical problems of working with toxic or expensive chemicals (possibly directly in the museums themselves) and the least damaging way to treat wooden artefacts.

While it is easy enough *in theory* to encase objects in a museum in airtight display cases filled with nitrogen, it is often difficult in practice. Either the cost of the display cases or the required durability means that most museum objects are typically stored in normal atmospheric air – often with some system in place to regulate humidity [11]. This means that most consolidants will be exposed to oxygen, which accelerates degradation. Although the problem can be postponed by adding an anti-oxidant to the polymer mix, this can only prolong the inevitable. Ether and ester groups of polymers are easily cleaved through radical depolymerisation in an oxygen atmosphere [111]. It is probably best to choose a polymer lacking such groups. If this is not possible, ring structures should be chosen over linear molecules with similar chemical compositions and especially aromatic compounds may offer excellent stability to applied consolidants.

Both thermal degradation and degradation by decay seem to be caused by different mechanisms than the degradation in buried wood [20](p. 41). Unfortunately, this means that the best way to test a consolidant is to wait for it to degrade in a museum. Accelerated ageing tests at elevated temperatures (and possibly known atmospheric compositions) become the best way to investigate the durability of polymers. In such cases, it is vital to test the impregnated objects, rather than a pure polymer mix, as ions or acids in degraded wood may affect the degradation pathways of treated artefacts.

5.2 Ideal consolidant requirements list

An important aspect of designing new materials for treating archaeological wood is to specify exactly what qualities are desired in future consolidants. Discussions with the people in the project (and the Department of Conservation) resulted in a list of desirable properties. While all involved understood that it was unreasonable to expect all of these point to be met, the list at least served as a focus point for selecting possible materials for further study. The following list has been rearranged in an attempt to prioritise the requirements contained within. The order is mainly based on considerations relevant when developing new materials. Once it comes to implementing an actual product in conservation, all are of vital importance.

1) Re-treatability (airy structure): The only practical way to make something last forever is by treating it whenever it begins to show signs of weakness. Thus it is vital that objects may be treated again in the future. In order to ensure that future treatment is possible, open pores must exist throughout the treated material to allow future treatments to fully penetrate the artefact. As such, an 'airy structure' is a vital requirement.

2) Good penetration: Since the alum treatment demonstrates how fragile objects can be if only supported by a crust of consolidant, any new materials must thoroughly penetrate the wooden matrix to properly support the core.

3) High durability: As cultural heritage should be available for future generations, a consolidated item should ideally last forever. With 'forever' being impossible, it is at least important to consider ageing and structural strength a couple of hundred years into the future. One should note that the museum climate is quite stable and polymers might be less prone to degradation here than for example outside.

4) No size alteration: As the polymer cures or penetrates, it is vital that it does not distort the wood. This does not mean that the polymer itself cannot expand or shrink slightly but the effects must not be noticeable on the treated objects.

5) Surface interaction with remaining wood: Since much of the alum-treated wood from the Oseberg find is barely coherent, a consolidant should interact with the wood sufficiently to prevent it from further warping out of shape. One easy way to achieve this is through chemical bonding to the degraded wood but other kinds of bonds may be sufficient to prevent distortion of the artefacts.

6) Non-poisonous solvent & materials: As conservators may have to re-treat some objects directly in the museum environment, it is vital that they (or visitors) are not exposed to de-gassing carcinogen compounds. As such both the solvent used and the polymer components should ideally be non-toxic. While this is of vital importance in actual application, toxic materials are acceptable during development of new methods.

7) Non-warping solvent: Most solvents – especially polar ones – warp wood. While it is possible to treat newly excavated wood with water as a solvent, it will not be possible for the more degraded alum-treated objects (see chapter 6.4.1 'Imaging of PF-treated samples' beginning on 100 for more on what solvents do). This requirement is significantly less important for methods which will be applied to fresh wood as such material will most likely be freeze-dried in order to prevent warping during drying. Thus the choice of solvent will often be dictated by health and safety concerns or compatibility with earlier treatments.

8) Wood-coloured: The texture and colour of a consolidant must not ruin the impression of the objects for museum visitors. While slight colour changes may be acceptable, white or yellow colours are preferred as they will simply make the dark archaeological material look more like fresh wood. This requirement is less important if applied to stabilise the core of fragmented items – such as alum-treated material – since the visible surface should remain unaltered.

9) Wood-friendly pH: The effects of the alum-treatment clearly demonstrate that extreme pH ranges degrade the remaining wood over time (see chapter 2 on page 7 and chapter 4.1.3 on page 54) and that future treated materials should ideally have pH values in the 4-6 range. This requirement has been assigned relatively low priority since a composite solution can introduce a different compound with the capacity to neutralise whatever acid might be generated inside treated objects. Furthermore, some finds may already have extreme levels of acidity. This applies to the alum-treated Oseberg wood, for example.

10) Cost: Expensive materials is no barrier to research and testing of new materials. Still, it is unrealistic to assume that a museum will be able to afford a new and superior treatment which costs 20 times as much as an existing alternative. From a chemical perspective, various ways to synthesise the desired product – or a number of similar products – should be considered.

As can be seen, the ideal consolidant has to live up to real-life requirements and as such the tests described in this thesis can be said to be a mix of theory and practice, constantly compromising between the possible and the desirable. With the many new disciplines emerging in science, collaboration between different fields is sure to yield the theory, materials, and expertise needed to develop truly new and promising consolidants for archaeological wood.

6. Phenol-formaldehyde

The search for future polymers began by going back to the very beginnings of polymer chemistry to Bakelite. While this was not envisioned as the ideal solution in itself, the results generated would help dictate likely avenues of approach.

Polyphenols are the reason plant species were able to colonise land so effectively. The basic phenyl-propanoid pathway used by plants for lignin construction today was already present in plants 400 million years ago [26]. For this reason, it is logical to try to reinforce degraded plant matter with simple phenolic compounds, and one of the simplest is phenol-formaldehyde (PF), the first widespread plastic. A fully cured PF can withstand most solvents (only boiling with concentrated sulphuric acid will break it down) and can be heated to 300ºC before charring [112].

6.1 History and use of PF

In relation to conservation history specifically, the use of PF has been covered in chapter 4.1.5 'Phenol-formaldehyde treatment' on page 59. From a more general perspective, the history behind PF is covered here.

As far back as 1859, Butlerov managed to create a poly-formaldehyde (although this was not identified until the 1920's). Work on phenolic resins made from aldehydes was reported in 1872. Even though a polymer was formed from phenol and formaldehyde, it was not researched very well as it was found that the product could not crystallise. An insoluble cross-linked PF resin was described by Kleeberg in 1891 and Smith gained a patent for PF and proposed that it could be used to substitute wood and ebonite (a highly cross-linked rubber). He also stressed the insulating properties of the material. With this focus, the research into PFs gained renewed interest. The Louis Blumer Company gained a patent for production of PFs in 1902 and Luft introduced the use of plasticisers in resins. Henschke produced a non-soluble product upon reaction between phenol and formaldehyde in the presence of sodium hydroxide. A significant change came with the invention of Bakelite, however [6].

It has been slightly more than a century since Leo Hendrik Baekeland (1863-1944) applied for a patent on the 13th of July 1907. Baekeland was trying to produce a synthetic product with insulating capabilities to meet the increasing demands put forth by the electrical industry. What he proposed was a phenol-formaldehyde polymer which is now considered the first fully synthetic plastic [6].

Baekeland was born in Ghent, Belgium, and attended university there. After graduating, he patented a way of developing photographs in water, but this never became a commercial success. Possibly to start anew, Baekeland moved to the United States where he continued to develop Velox, a fast-copying photographic paper. Eventually, he was able to sell the factory producing this product and gain economic independence in 1900. While drawing upon the knowledge of fellow chemists, Baekeland started researching phenolic resins in 1905. Although he was not the first to produce phenolic formaldehyde, Baekeland managed to describe an inexpensive way of producing it on a large scale. This allowed it to replace shellac, which was needed for insulation by the electrical industry at the time. Motivated primarily by making money, Baekeland was quick to exploit this need [6]. In 1907 Baekeland was well aware of others making products similar to phenol-formaldehyde. He used these in his own research. He also divided the polymers into two classes. The first was a 'shellac substitute', which was not fully cured, and can be transformed into the second class, which is a fully cured polymer. The second type can also be formed directly [112].

Baekelands breakthrough was to let the polymerisation take place at 100ºC or more. This eliminated most of the release of formaldehyde gas, enabling commercial use of the polymer [6]. He knew that gas (primarily formaldehyde) may escape due to the high temperature [112]. Baekeland tested a variety of acids and bases while producing the PF, but did not find any major differences between polymers formed by different organic or inorganic catalysts or the finished products [6], [112]. He eventually divided the production into three stages and three products [6]:

A: A soluble and meltable product.

B: What is gained when heating product A. It may swell in different solvents but is a non-meltable solid. It softens when heated and may be moulded under pressure.

C: What is obtained when heating B under pressure. It cannot be melted or dissolved and does not thermally degrade at temperatures lower than 300ºC.

Use of Bakelite, as Baekeland named the polymer, became very widespread. Production companies were set up in Canada, Europe, and Japan. Baekeland was often willing to work with competing companies rather than fight them. The Bakelite was mixed with fillers such as wood flour or asbestos. Although the material was at first used for electrical insulation, development of coloured resins made Bakelite a natural substitute for ivory or rubber. Cars, telephones, jewellery, and radio sets used Bakelite components. Thomas Edison even chose Bakelite to construct gramophone records from. Baekeland recognised the potential for a Bakelite layer to replace lacquers on for example kitchen utensils. That Baekeland eventually held over 400 patents speaks of the diversity of the material, which could be used to produce everything from doorknobs to billiard balls [6].

After the the second World War, Bakelite was used less and less. The odour of Bakelite became associated with times of despair and poor quality materials. It was probably more important, though, that the production of Bakelite was expensive when compared to new plastic materials like PVC, polystyrene, and nylons. Not only were they cheap, but their thermoplast qualities often made them superior to Bakelite. Baekeland's legacy is very much alive despite this. Is not just the material named after him, but rather the fact that plastics were used in new ways (such as for insulation, jewellery, and structural materials). In this way Bakelite paved the way for the innumerable plastic products surrounding us today [6].

A quick search on the internet will reveal that phenol-formaldehydes are still produced today. PFs are used as adhesives for fresh wood and can even improve the mechanical stability of plywood boards [113]. In fact, the slower curing time of the polymer in wood might be due to monomers penetrating into the cell wall material. The question is whether the PF cures normally or actually substitutes wood polymers [114](p.111 & 192). Low-molecular PF seems to penetrate slightly into the wood cells while high molecular PF does this to a lesser extent [114](p. 156 & 160). Phenol-formaldehyde can be mixed with waste lignin to produce adhesives for wood [42]. Incorporation of lignin into PF novolac polymers has already been successfully done [115], [116].

It is thus logical to attempt to incorporate the lignin-rich archaeological wood into a polymer network in order to reinforce it.

6.2 Chemistry of PF

The purpose of this chapter is mainly to give those without previous polymer knowledge some insight into how phenol and formaldehyde react. Notes on novolac reactions will be given as most of the experiments were carried out using acid catalysts.

Even though mixing phenol and formaldehyde with a catalyst is relatively easy, the cross-linking of PFs is a complex process. As such, the structure of the resulting polymer is difficult to elucidate. As such it was not until after 1945 that significant progress was made in determining their structural properties despite the fact that PF had been in use for decades at the time [119]. In fact, the polymerisation process might not be fully understood even today [120]. As condensates are formed, many complex structures may result, making it hard to model every possible reaction even though only two reactants are involved. In one study, no less than 89 reactions between 13 compounds were considered, distributed as "7 addition reaction of formaldehyde to the phenol ring, 77 condensation reaction of monomers with the phenol or other monomers, 4 addition reaction of formaldehyde to the aggregate dimers, 1 condensation reaction of dimers with monomers." [117].

The polymerisation of PF can be catalysed by sufficiently strong acids or bases. The resulting thermosetting structure is amorphous. PFs catalysed by acid are called *novolacs* while those catalysed by base are called *resols* [118]. The structure of the prepolymer depends upon the pH of the solution [6]. Th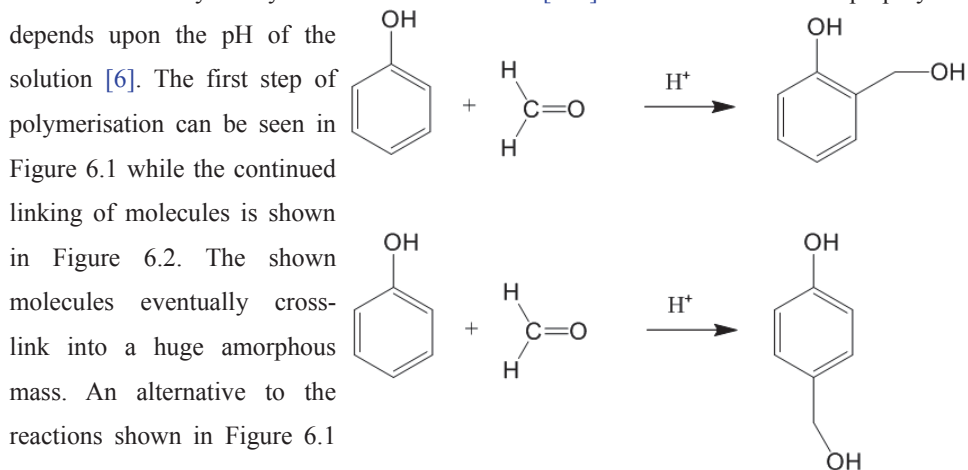e first step of polymerisation can be seen in Figure 6.1 while the continued linking of molecules is shown in Figure 6.2. The shown molecules eventually cross-link into a huge amorphous mass. An alternative to the reactions shown in Figure 6.1 can be seen in Figure 6.3 below. While this reaction is

Figure 6.1: Initial reaction between phenol and formaldehyde.

unlikely to be very common, it is shown since the kinetics measurements try to evaluate which initial reaction is the more likely (see Figure 6.6 on page 98 for more information).

Today the PF reaction is divided into three steps [6]:

1) addition of formaldehyde to phenol,

2) synthesis of prepolymer, and

3) cross-linking of prepolymer.

Adding increasing amounts of formaldehyde relative to phenol creates more bonds between phenol molecules and thus a stronger product – but the average degree of polymerisation is reported to increase with increasing reaction time even if no additional formaldehyde is added [113]. Since phenol has a functionality of one to three, and formaldehyde has a functionality of two, a formaldehyde:phenol (F:P) molar ratio of 3:2 should theoretically yield a completely cross-linked polymer – although this does not happen in practice . It is also hard to generalise the results as polymers cured for shorter times sometimes show a higher degree of cross-linking than a similar polymer cured for a longer time [119]. This is surprising as it would be logical to assume that the finished polymer has a statistically predictable distribution and that
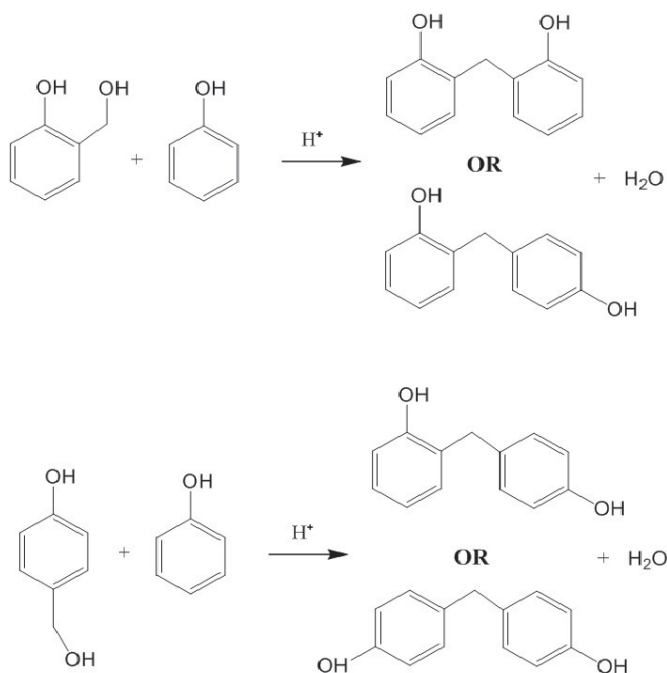

Figure 6.2: Second step of the condensation reactions between phenolic pre-polymers, phenol, and formaldehyde. The shown reaction is for novolacs. Resols have ether bonds in the structure as well as the above kind of oligomers.

additional curing would enhance cross-linking. One can speculate that results might be different for polymers cured a relatively low temperatures and pressures where the individual molecules have more time to change orientation and fit into the existing polymer structure.

What is noteworthy about the initial polymerisation is that formaldehyde may react at both the meta and para positions. This means that the resulting polymer becomes amorphous, lacking a recognisable repeatable structure. Rather than a single coiling chain (which is common for most other polymers used in conservation) the resulting PF network is reinforced throughout its structure, rendering it less flexible but more resistant to decay.

Since the reaction between phenol and formaldehyde is exothermic, PF reactions have the unusual ability to self-heat at any pH if sufficient acid or base is added (the heat of reaction is roughly 2800 J/g). Regardless of F:P ratio, the tendency to cause runaway reactions is very small in between pH 2 and 7, but much higher more extreme levels of pH [121]. This means that boiling is not only possible but likely at elevated temperatures and may cause significant damage to archaeological wood should it occur.

Under basic conditions, formaldehyde in at least 1.5 times the molar mass of phenol is used, forming a hydroxymethyl phenols called resols. These can again be heated and further cross-linked (typically at 120°C). The temperature controls the degree of polycondensation. Polymerisation under acidic conditions forms a novolac. These thermoplastic products contain less formaldehyde than phenol. Adding hardeners (for example hexamethylenetetramine)
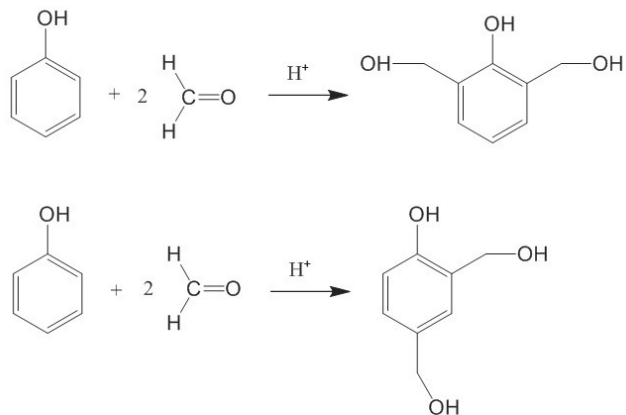

Figure 6.3: Hypothetical reaction between phenol and formaldehyde used for the kinetic models.

84

may result in later cross-linking. They are used as powders for injection and compression moulding [6].

As novolacs are often sold as uncured pre-polymers, some references state that all novolacs have F:P ratios of less than one while all resols have ratios greater than one. In the following text, however, the term 'novolac' is used for any acid-catalysed PF even if said polymer contains more formaldehyde than phenol. The effects of varying F:P ratios will be further discussed in chapter 6.3.2 Pure polymer experiments on page 89).

What makes novolacs particularly durable is the mix of ring structures and lack of ether bonds. This means that while the OH groups on the phenol rings may oxidise (possibly explaining the colour change which happens as the polymer is exposed to oxygen), the covalent bonds linking the polymer itself will not normally be broken. In this way the strength of the material will not be drastically reduced by oxidation, and objects treated with it may be stored in normal atmosphere (for example while on display in a museum).

It is possible to fully cure a pre-polymer by adding more formaldehyde or a molecule which breaks down into similar parts. Hexamethylenetetramine (HMTA) is used as a source of 'anhydrous formaldehyde' but often at elevated temperatures such as 130-250°C. The polymer still takes more than 24 hours to cure below 175°C [118], [119]. In fact, it has been reported that the addition reaction does not occur until about 90-95°C [121] although adsorping water into the mix accelerates cross-linking through plasticisation so that it may occur at temperatures as low as 70°C [122]. This may be due to the limited duration of the experiments as PF test polymers did seem to cure at significantly lower temperatures (this is described in chapter 6.3.2.1 on page 89). HMTA crystals can be found in pores of PF polymer even after curing for 24 hours at 170°C. This indicates that HMTA is not soluble in the polymer melt[3] [122]. HMTA cures polymers with a high amount of ortho-ortho linkages more effectively [120]. It also seems that conversion rates for the pure resin is actually higher at lower temperatures as high temperatures quickly fuse part of the structure and thus hinder mobility. The investigated temperature range was 105-155°C so what happens at only slightly elevated temperatures was not determined [123].

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3 Note that the word 'melt' is often used about (pre)polymers in the liquid state even if said polymer is incapable of melting in the chemical sense because it cannot form a crystal structure (such as for example the amorphous phenol-formaldehyde).

Although the reaction between phenol and formaldehyde may not be fully investigated, it is possible to modify the bonds in the resulting polymer. The most effective catalysts in promoting ortho-ortho linkages are reported to be zinc acetate, magnesium acetate, manganese acetate, boric acid, and copper acetate (in that order) at about 4% weight compared to phenol. All of these catalysts resulted in more than 80% ortho-ortho links when reacted for 5 hours at 125ºC. Prolonging reaction times meant that the ortho-bonded molecules started to react at the para sites. The ratio between phenol and formaldehyde also modifies the ortho-ortho frequency, with 18-30% molar excess of phenol being optimal [120].

6.2.1 Mixing PF with other consolidants

In the same way as Kauramin method (see chapter 4.1.6 'Kauramin and melamine-formaldehyde treatments' on page 60) started with pure melamine formaldehyde and modified it to produce a more flexible polymer, it may be possible to modify PF in a similar fashion.

PF has been modified in several ways already. A blend of two or more polymers may result in an inexpensive way to create a product with superior properties. Since most polymers are immiscible, block or graft polymerisation is usually needed to make a polymer blend. Mixing poly(propylene) and phenolic resins results in a 'thermoplastic phenol formaldehyde' made from high molecular weight novolacs. Using more formaldehyde than phenol results in a thermoset product while using less formaldehyde than phenol results in less cross-linking and thus a thermoplastic product [124]. Adding Bisphenol-A to novolacs allows them to form denser networks than usual due to the increased functionality of pure phenol. This increases both stability and resistance to chemicals. This may be done merely by cross-linking the bisphenol-A with formaldehyde without the need for further added phenol [125].

Carbohydrates (especially glycerol) were originally added to phenol-formaldehyde polymers to alter their physical properties. During resin formation, the aldehydic functionality of compounds like xylose is rapidly destroyed, preventing incorporation into the polymer system. Sucrose, on the other hand, can be incorporated despite lack of

aldehydic functionality as it is non-reducing. In fact, results indicate that any alditol derivative gives better results than resins modified with reducing sugars. The alditol version of xylose, namely xylitol, gave the best results. Adding 1,3-propanediol results in extremely strong resins with high dry- and wet-shear strengths. More 1,3-propanediol than phenol (on a molar ratio) could be added to the resin and was usable as a modifier [126]. In the cited investigation, it was not determined if the carbohydrates were chemically incorporated into the polymer itself or merely served as filler material.

Actual lignin does not contain very much phenol. Using $NaIO_4$ titration, it is estimated that there is less than one phenolic hydroxyl group per five C_9 units [29]. Despite this, PFs (both novolacs [115] and resols [116]) have been reacted with lignin to form a coherent polymer. This is primarily interesting because it is more environmentally friendly to use bio-renewable wood components than petrochemical phenol for the production of said polymers [36], [115]. Temperatures were relatively high in one study; the phenol:formaldehyde ratio was 1:0.7 and the mix was heated to 80^0C for one hour and then raised to 110^oC for two hours. Six to eight hours after this, there was less than 1% free formaldehyde left and the reaction was stopped [115].

PF resols have been mixed with waste lignin in order to produce resins. Although such waste lignin is fairly sulphonated [42], it still means this could be a valid method for stabilising archaeological finds which consist of highly deteriorated lignin and would be an interesting avenue of research for future investigations.

The most obvious solution for a very durable polymer which will harden at room temperature is probably a novolac oligomer linked through epoxy links to an aliphatic chain [111]. Due to time constraints, such experiments were not initiated as part of this work.

6.3 PF experiments

Unfortunately, it is difficult to utilise Baekelands breakthrough of high-temperature polymerisation to eliminate some of the escaping formaldehyde since wood will blacken and age at temperatures above 100^oC. Thus the first goal was to determine how easily PF would polymerise at low temperature (preferably room temperature but temperatures up to 80^oC or so should be possible to implement).

Despite the vast amount of published material on PF, all available information on novolac was obtained at elevated temperatures and so-called 'low-temperature studies' were still carried out at 140-150°C (and were on HMTA-cured resols) [127]. For this reason, the initial steps were more time-consuming than originally envisioned.

6.3.1 Experimental procedures for PF

The experimental procedure for most of the experiments described in *Paper 2* are detailed there but most of it is repeated in the following for ease of reference.

Phenol, 37% watery formaldehyde solution, and the assorted polymers tested in Chapter 6.4.2, were all purchased from Sigma-Aldrich. Unless specified otherwise, pure HCl was used as a catalyst for novolac experiments while NaOH was used for the resol experiments.

The pure polymer experiments were performed by mixing the reactants and catalyst in 30 ml plastic beakers with which the PF did not react. This made it easy to push the finished product out of the beakers after curing. Typically, 6 g phenol was used and formalin added to reach the desired ratio (5 g formaldehyde solution results in a 1:1 ratio). The beakers were typically sealed with parafilm to prevent evaporation during polymerisation.

The wood used for the majority of these investigations was from the 'Drammen' sample (since these were initial experiments and quantity of sampling material was a concern). Some actual Oseberg material was used to test the PF approach (this material is described more thoroughly near Figure 6.12 on page 106). The monomer mix was dripped onto sample pieces and polymerisation was initiated by dripping concentrated HCl onto the soaked sample. The 'lost' sample piece was sealed in a glass vial with a F:P 1.4 monomer mix, left to impregnate for three days, and heated to 70°C for a week to initiate curing. The sample was then rinsed with water and wrapped in parafilm to slow down the drying process.

Free formaldehyde content in samples was determined using the ISO 9397 standard. This is a potentiometric titration where hydroxylamine hydrochloride is added to convert the free formaldehyde to acid which is then neutralised with NaOH. Solid sample material is

dissolved during the first step of the procedure to free any formaldehyde trapped inside partially cured polymer bits.

6.3.2 Pure polymer experiments

The first experiments were designed to simply understand how PF cures under various conditions. Actual experiments began by mixing monomers and catalyst in 30 ml beakers. To fully cure the polymers, they were placed in an oven at 70ºC for at least three days. Some samples were left in the oven for about a week. As the polymers hardened before this time was up, increasing the time might ensure that any excess formaldehyde would evaporate.

While both acids and bases are available as catalysts, this work has primarily focused on acid-catalysed PFs, namely novolacs. There are two main reasons for this. Firstly, the archaeological wood is normally more resistant towards acids than bases (see chapter 3.5.2 'Properties of waterlogged wood' on page 38). Another reason is that resols tend to form some ether bonds in the structure, which may be undesirable as it can reduce the durability of the polymer (see chapter 5.1 'Practical considerations' on page 72).

Despite the theoretical advantages of novolacs, it is also important to get an idea of how the two different types of PF differ and react. One primary reason is that much of the investigated literature from actual industrial production focuses on resols. If there are differences, it could mean that the novolac will react differently from previously described experiments.

6.3.2.1 Colour and curing

Initial experiments simply focussed on trying to get low-temperature curing going as well as evaluate how PF might change the colour of treated wooden pieces.

A mixture of phenol and formaldehyde has been reported to have a pH value of 3.2 before catalyst is added [121]. Actual measurements gave a much lower value, namely 2.14. This level of acidity might damage the wood if left for extended periods of time so it is quite fortunate that PF seems to penetrate rapidly into the degraded structure of archaeological wood.

Choice of acid or base should not affect the curing process. The resols were made using solutions of NaOH. The novolacs were primarily made using HCl as the catalyst if not specified otherwise. Tests with H_2SO_4 indicated that concentrated acid is not recommended as it immediately cures the polymer when a drop enters the prepolymer mix. The H_2SO_4-cured PF turned a very dark red immediately (much like HCl-cured PF after months of accelerated ageing). Using HNO_3 resulted in an almost black monomer solution and subsequently an almost black polymer. Due to the effects of accelerated ageing tests, it is assumed that the oxygen content in these acids makes them unsuitable for the production of bright PF polymers. For this reason, further tests were carried out using HCl only as a catalyst. On a smaller piece of "Drammen" test wood, pure HCl was added. The acid alone had no noticeable effect on the wood (except wetting) and did not colour the surface. This does not mean that such concentrated acid will not affect the wood over time – or could affect hardwoods more severely than the tested softwood.

Since runaway reactions are considered a problem in the industry, this was tested. Using 1.5 g of phenol and 5 ml 37% formaldehyde per cup, a series of four cups (and a test) were set up. Using the Fibonacci series, 5, 8, 13, and 21 drops of HCl was added from a plastic pipette. Only in the 21 drop container did the solution become cloudy and would proceed to boil unless stirred. Note that a lot of excess formalin was present in these initial runs (F:P-ratio 4) which would both provide more formaldehyde for the reaction but also more water to cool it. During the experiments it was observed that acid drops to the bottom of the cup and starts a chain reaction. It is thus important to stir the contents to avoid mishaps. Stirring or swirling the sample after adding HCl prevented bumpy boiling at all F.P ratios (unless the pH was significantly below 0) both at room temperature and when the sample was heated to 70°C after swirling it.

Samples at very low F:P ratios did not cure and even remained liquid after more than a year and a half of storage in a sealed flask at room temperature. At an F:P ratio of 0.6, the polymer cured enough to prevent flow after extended storage but the product could still be easily redissolved in acetone. At higher F:P ratios, like 1.4 to 1.6, the polymer cured and became solid. Most sample 'discs' polymerised in the bottom of 30 ml beakers could easily be dropped on the floor repeatedly without any visible damage. Samples with F:P ratios of 1

were incredibly brittle and shattered if treated so roughly. Samples with an F:P ratio of 0.8 did not harden fully and could easily be deformed if handled. Thin edges could be crushed even at high F:P ratios. This demonstrates that the cured PF is fairly brittle. With higher formaldehyde contents, the breaks were often less severe, however, and a piece would only break into two or three fragments. This means that it should be possible to glue objects treated with PF back together if they behave in a similar way.

The finished polymer samples looked different at similar F:P ratios. The novolacs were transparent and not fully cured at F:P ratios of 1 or below (even though an F:P ratio of 1 theoretically allows every molecule to be bonded). At F:P ratios above 1, the polymer fused into a solid mass with a pink or orange colour which became more red or brown the longer the PF was heated. The fully cured samples were opaque – possibly due to escaping gasses forming minute bubbles in the structure as thin layers seemed to be transparent after curing (the bubbles may be seen in Figure 6.4 on page 92). As long as the prepolymer was kept in a sealed bottle, it would remain colourless or very faintly pink. Thus the red/brown colour was likely caused by oxidation and will eventually become apparent in museum objects treated with novolacs.

One sample of novolac with a F:P ratio of 1.4 was kept in the oven to evaluate how the colour and possibly consistency of the polymer would change. Even after a year at 70°C the PF was still strong and resistant to minor blows although the beaker it had originally been kept in had all but disintegrated, proving the relative resiliency of PF. Even after a year at 70°C, the novolac sample had not become completely black but retained a dark red tone. The sample in question reached this state after about three months and then stayed fairly unaltered.

Resols were only prepared in F:P ratios of 1 or greater to ensure that they would fully cure. Even at high ratios, such as F:P = 1.8, the polymers remained mostly opaque. Sometimes a transparent top could be observed on an opaque bottom. Both were usually brown, with the transparent part looking slightly more red and the opaque part looking like tea or coffee with milk in it. An explanation for this difference in a single piece of polymer is that the top layer cures to the point where air cannot easily penetrate it and this traps escaping water and formaldehyde in the layer below, where they form tiny bubbles which makes the polymer opaque.

Resols had a more uniform appearance then novolacs and changed less during accelerated ageing experiments. Some of them turned very dark during curing, however, so the end result was not consistently different. A few resol samples had cloudy layers like the novolacs described above.

Some samples were examined in a was examined in a Leitz Diaplan microscope using a Phaco 1 160/- lens and with a Imaging Source DFK41AU02 USB colour camera attached . An example of a seemingly smooth surface can be seen in Figure 6.4 below. This confirms that gasses escape during the curing process and indicate that the PF will most likely only look transparent if cured in very thin layers. Of course, such thin layers will also maximise oxygen exposure and thus the speed at which the polymer turns darker and degrades.
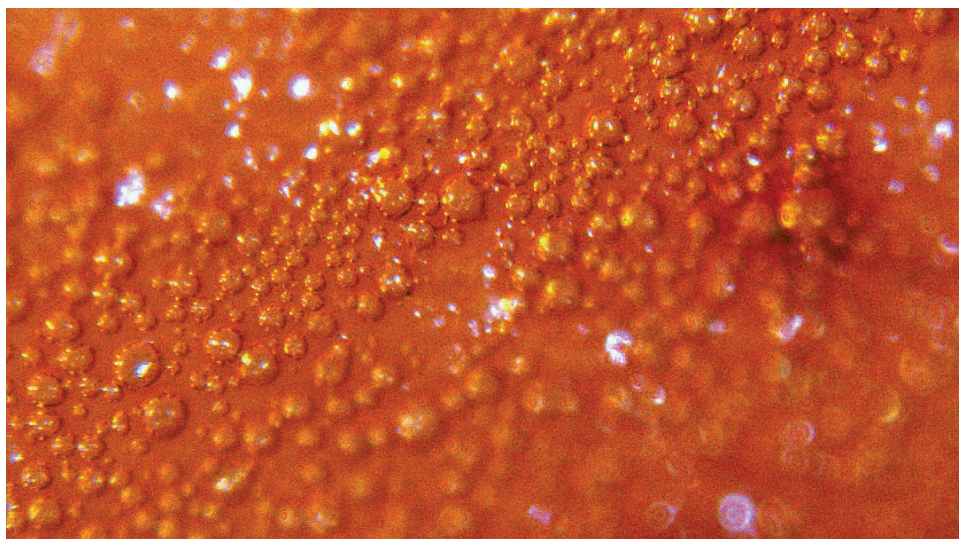

Figure 6.4: Image of the bottom surface of a novolac sample. Although the slight curvature of the surface makes it difficult to focus the microscope, note the numerous bubbles in the structure.

6.3.2.2   PF phase separation

One important difference between novolacs and resols is that the novolacs separate into a watery and an organic phase much earlier than the resols. A likely explanation for this is that the oxygen-containing ether bonds found in resols make them more water-soluble. This phase separation was always observed with novolacs – even when the mix was allowed to

evaporate during polymerisation – but rarely with resols – and then only during the final stages of curing. Due to the desirability of an open structure in treated objects (see chapter 5.2 'Ideal consolidant requirements list' on page 75) this phase separation means that the organic phase is pushed towards the wooden walls rather than randomly filling the remaining matrix (see Chapter 6.4.1 'Imaging of PF-treated samples' on page 100). This is a very desirable quality which can possibly be taken advantage of in other polymers which show a similar phase separation behaviour during polymerisation.

At first, the novolac mix would simply become opaque as the two phases formed. Given time, the mix would form a distinct bottom phase with a clear phase on top. Over time, the bottom phase would become opaque and later pink. In order to study this more thoroughly, tests were made in enclosed vials to prevent evaporation of the watery phase. An example of this phase separation is seen in Figure 6.5. The initial phase separation happened overnight at room temperatures with high amounts of acid (pH below 0) but took a week at the same

temperature when mixed in 0.1 M HCl. This means it is possible to delay the process when treating wooden artefacts with PF (possibly by adding acid after the prepolymer mix has had time to fully penetrate into the wood).

Since the two phases have vastly different affinities (one being highly polar while the other is composed of aromatic oligomers which are fairly non-polar), one might suspect that the phases would interact with the wooden matrix in different ways. This was found to be true (as seen in Figure 6.11 and the following tomographies, starting on page 105).
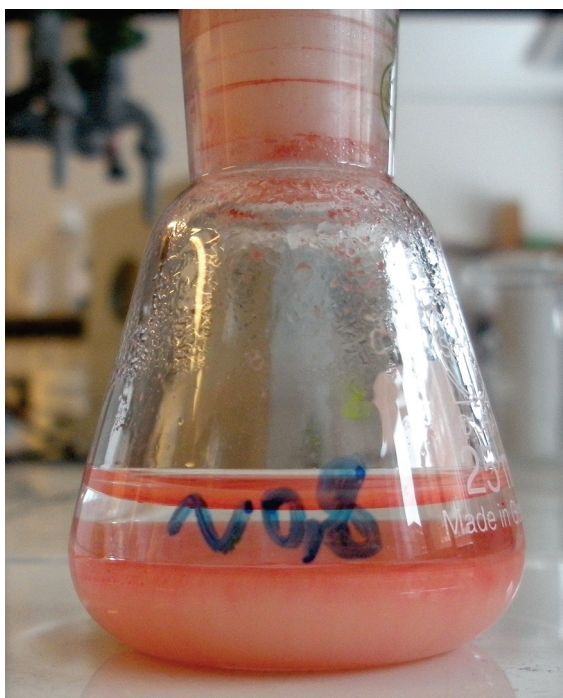

Figure 6.5: Photograph of phase separated novolac with a F:P-ratio of 0.8. Note that the upper phase is completely transparent and the lower phase opaque.

The free formaldehyde content was determined using the ISO 9397 standard. The concentration of the pure formaldehyde was measured as being $39.5\%^w/_w$ (rather than the $37\%^w/_w$ claimed by Sigma-Aldrich) and this result was used for all further calculations.

It should be added that this free formaldehyde determination was also used on oligomer novolacs made with an F:P ratio of 0.8. It showed that free formaldehyde content in the watery phase is less than 1.5% and even lower in the organic phase. Considering the formaldehyde content in most wooden products, such as fibreboard, this means that it should be safe for conservators to handle such oligomer molecules.

6.3.2.3 Solvents and alternative cross-linkers

Glyoxal (OCHCHO) has been used to cross-link wood – although at 130-150°C while adding a suitable catalyst [128]. Due to the toxicity of formaldehyde, it was attempted to create a polymer from phenol and glyoxal. A sample was polymerised using pure glyoxal and left for several months at 70°C to determine whether it would eventually polymerise. The polymer did eventually become solid rather than liquid. Unfortunately, it was extremely brittle and could be easily broken into smaller fragments by pressing into it with a metal spatula.

Using a mix of formaldehyde and glyoxal resulted in a cured polymer which looked much more brown than a pure reddish novolac made from formaldehyde. While brown will more closely match the colour of treated objects than red, the colour is much too dark to give a satisfactory wooden appearance. For this reason, glyoxal cannot be recommended in any significant amounts as a replacement for formaldehyde.

As HMTA has been previously reported to be a good cross-linking agent, this was also tested on the novolacs. Various amounts of HMTA were added but were difficult to dissolve in the pre-polymer and did not seem to affect the curing in any noticeable way. Based on this, the reaction did not seem to take place in the novolac mixtures at room temperature. It might be possible to add additional catalysts to initiate the process at low temperatures. Since the possible effect of such catalysts on the degraded wood is unknown, investigation of catalysts would require a lot of time-consuming analyses. For this reason, the idea of

replacing formaldehyde with HMTA for the final cross-linking of oligomer molecules inside treated wood was not tested during this work.

Since water seems to dissolve at least the most damaged parts of the alum-treated wood ([11] and see chapter 6.4.1 'Imaging of PF-treated samples'), a couple of other solvents were tested. Two common solvents used in conservation are acetone and propanol. Both may dissolve a novolac prepolymer – given time and stirring. The finished solution is almost colourless for the acetone and slightly yellowish for the acetone. When dried, it should be noted that the resulting polymers look very different – whether excess formaldehyde is added to ensure curing or not. Prepolymers dissolved in acetone end up very dark red. The colour is so dark that it may be mistaken for black at a glance. For this reason, acetone should probably be avoided as a solvent if treating archaeological objects with a PF-prepolymer. Propanol, on the other hand, causes the polymer to become much lighter and somewhat more yellow. The polymer also becomes more transparent than novolac polymerised under water and possibly more flexible. If so, it seems like the propanol might introduce flexible chains into the PF structure. An image of the treated polymers in shown in *Paper 2* in the appendices. The effects on durability are not currently known. Should it become important to know more about the structure of these polymers, vibrational spectroscopy might give sufficient information to understand them better.

At F:P ratios below one, the novolac prepolymer does not fully cure. This results in a viscous mass which can be shaped and even flows given sufficient time. It may be dissolved in solvents like acetone and propanol for impregnation (this happens after phase separation so water is no longer a suitable solvent). In the dissolved state, the prepolymer does not seem to further polymerise as no visual changes occurred in a month or so. This would indicate that such a pre-polymer has a relatively long shelf life and might be suitable for impregnation of waterlogged wood.

6.3.2.4 Oddy corrosion tests

In conservation science, degassing is extremely important as fumes might affect not only the treated objects and visitors but also other artefacts on display. This is clearly seen in

many museums where the shelves and display cases were constructed from MDF (medium density fibreboard) which emitted acids which resulted in most lead objects being covered in a thick layer of lead acetate [11]. In order to evaluate whether similar reactions might occur due to formaldehyde or acids generated from PF, an Oddy test using lead coupons was performed. This test is an accelerated corrosion test developed in the early 1970s by Oddy and his co-workers [129].

The procedure from Ref.[129] was followed for the actual experiments. When preparing the sample, each piece of PF was weighed to ensure that roughly the same mass was used for each lead coupon. Sample polymers were smashed with a hammer to allow them to pass into the test tubes as well as maximise surface area. Somewhere between 2.0 and 2.1 g sample material was weighed for the first eight samples. The last sample, which consisted of actual Viking Age wood, only weighed 1.4 g. The sample material was placed at the bottom of a test tube along with a smaller test tube filled with a few drops of water to ensure high humidity. A small piece of lead was scrubbed using a plastic brush to remove corrosion. It was then suspended inside the tube on a thin plastic line. The test tubes were sealed with glass plugs but since the plastic line went into the tubes, parafilm was added as well. In addition to the tubes with samples, a control tube with just the lead coupon and water was also set up. The vials were put into the oven at 60°C and left for exactly 28 days. The parafilm melted and the tubes might not have been entirely airtight but the results seemed consistent despite of this. The results are summarised in Table 3.

The results clearly show that the cured PF does it emit any volatile compounds which can tarnish lead. The only PF sample which caused corrosion to occur was the one containing lignin. Since the other samples were not likewise affected, it seems likely that degradation of the lignin powder caused the corrosion. The same applies to the actual piece of treated Viking Age wood where the wood might also have affected the lead irrespective of the polymer used to consolidate it. 2-propanol might affect this corrosion process slightly but not alarmingly. Furfural and furfuralcohol both generate significant amounts of corrosion on lead coupons.

Table 3: Oddy test samples and results

Sample number	Sample description	Notes	Result
1	Phenol-furfural 1:1.2.		A flat layer of brown/red corrosion. The line attached to the lead coupon was also coloured reddish. The sample itself also acquired a reddish tint.
2	pure furfuryl alcohol (HCl polymerised)		Extreme dark orange corrosion in a thick layer.
3	2-propanol novolac cured in oven	Sample had a clear outer layer with an opaque core after the test.	Not significantly more corroded than the control – but possibly slightly.
4	2-propanol novolac (FP 1.4?) cured in the fume hood	It was noticed that this sample was particularly tough and difficult to smash with the hammer.	Slightly more corroded than control (but more black than white). Sample itself had become slightly darker and was a clear amber.
5	Novolac FP 1 with lignin	Very brittle (powdered almost completely)	Faint layer of white corrosion. The sample melted and could not be retrieved.
6	Resol FP 1.6 with less NaOH catalyst	Clearly opaque beneath a shallow transparent surface	Coupon as control. Sample seemed unchanged.
7	Novolac FP 1.6		No change (as control).
8	Novolac FP 1.4 + SDS	More pink than the other PF samples	No change (as control).
9	Viking age wood prepared with FP 1.4 novolac in propanol then precipitated with water and cured before drying	Sample weighed only 1.4 g (rather than about 2 g)	Some faint reddish corrosion (possibly also due to wood in the sample?)

6.3.2.5 Kinetics experiments

The behaviour of curing kinetics have been studied previously using a variety of methods such as DSC [130] and rheology [131]. Specific studies have even been carried out on novolacs [132]. and resols [133]. Since the literature found only describes kinetics at higher temperatures, a series of potentiometric titrations (using the ISO 9397 standard) was carried out to elucidate the initial reaction between phenol and formaldehyde on a water

bath set to 25ºC. More on the experiments, including the theory behind the kinetics, can be found in *Paper 2* in the appendices.

The curves for the various models may be seen in Figure 6.6. Most of the shown curves assume the initial reaction happens as shown in Figure 6.1 on page 82. Model IV in Figure 6.6, however, assumes that the initial reaction happens as shown in Figure 6.3 on page 84 where each phenol molecule reacts with two formaldehyde molecules. As can be seen, all of the proposed models correspond well to the experimental data although models III and IV are the best. These correspond to second order reactions with two reactants. The reaction where one phenol molecule reacts with two formaldehyde molecules gave the best fit although all the models gave good fits in the plotted region.
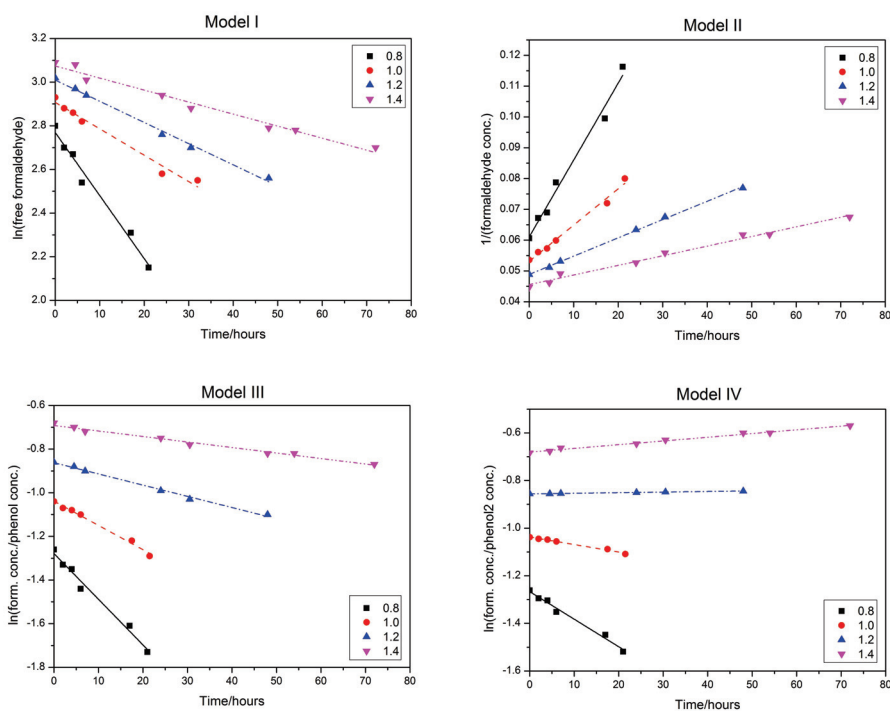

Figure 6.6: Results of kinetic experiments plotted as graphs in Origin 8.1. The stated values denote different F:P-ratios.

The kinetics experiments show that it takes about a day for the phase separation to occur at pH 0 or below. Note that the phase separation at this early stage simply means that the mixture goes cloudy. The formation of two distinct phases takes longer. The pH value is based on a worst case scenario for the actual alum-treated items and reaction times may be extended by raising pH or shortened by adding catalyst. Adding more formaldehyde also extends the time to phase separation (so while it takes about 20 hours for F:P ratio 0.8 samples it takes more than 70 hours for F:P ratio 1.4 samples). This means that the monomers will have sufficient time to penetrate smaller pieces of wood before the phase separation occurs under these conditions.

6.4 Impregnation experiments

Archaeological wood was treated with PF. As these were some of the first experiments carried out, choosing plentiful sample material seemed important. For this reason, most of the experiments were performed using the 'Dokka' wood sample rather than more degraded wood. In the first attempts, the wood was simply filled with the monomer mix and concentrated HCl was dripped onto the piece in order to catalyse the polymerisation. The mix hardened in a minute or less, leaving reddish or even pink fragments which turned more brown with age. The speed of polymerisation meant that it would most likely cause warping of the wood. Additionally, concentrated acids are not very safe to work with – or conductive to the lifetime of the remaining wooden material.

The approach was modified slightly to slow down the rate of polymerisation. Only a little acid was added and the wood was kept in a closed container to prevent collapse due to evaporation. It was still dripped onto the sample so no impregnation bath was used. This is the approach tested on a few pieces of Oseberg wood described in *Paper 2*. Although these pieces were small, the one with the least alum content seemed to preserve its shape during this treatment (while the one with high alum content lost its shape almost immediately after the monomer mix was applied). The results are further evaluated in the following chapter 'Imaging of PF-treated samples' on page 100.

A final step was attempted where the piece was kept wet in an attempt to see if the polymer would cure effectively under water. Given time, the polymerisation does progress but the curing process takes more than half a year without evaporation. It seemed that the

pre-polymer mix only penetrated into wet wood slowly. 2-propanol was used to replace water in the 'lost' sample. The piece was dried in a paper towel and kept sealed with the prepolymer mix in the oven over the weekend. After the phases had separated, the piece was taken out of the prepolymer mix and wrapped in parafilm to prevent rapid evaporation. The polymer does seem to cure in the fume hood but the wooden piece collapsed over the course of the next week. This means that it will likely be necessary to extend the reaction time in the oven – possibly while removing the prepolymer mix and adding more formaldehyde – in order to stabilise the degraded material sufficiently.

6.4.1 Imaging of PF-treated samples

Computer tomography (CT) is most famous for its medical applications. Images from different angles are recorded and the information is used to transform the data into a 3D structure (often viewed in tomographic slices – such as the images in this chapter). Synchrotron radiation increases spatial resolution to the micrometre scale on smaller samples. Not only are synchrotron storage rings effective when producing x-rays but the energy distribution is continuous rather than distributed around characteristic energy levels. The source brightness (photons at a given angle) is also higher when using synchrotron radiation [134]. Due to these advantages, it is not surprising that synchrotron radiation and its use in archaeometry has already been discussed [135]. Especially when checking the penetration of potential new consolidants, CT is an excellent tool. For this reason, it was attempted on a series of samples treated with various polymers.

Imaging was performed at the Paul Scherrer Institute near Villigen, Switzerland[4]. Neutron imaging and tomography as well as synchrotron x-ray computer tomography were both employed. It should be noted that neutrons are particularly interesting for investigating archaeological finds as they are sensitive to other elements than traditional x-rays. In neutron imaging metals are generally transparent while anything containing hydrogen (such as water) will block the transmission. This allows neutron tomography to examine metallic

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4 Rajmund Mokso from the PSI is acknowledged for instrumental guidance during the stay while the actual imaging was conducted in collaboration with Susan Braovac and Hartmut Kutkze from the Museum for Cultural History at the University of Oslo. Eberhard Lehmann, also from the PSI, is acknowledged for his assistance with the neutron experiments and knowledge of the method.

statuettes or similar objects for filler material. Despite this advantage, larger samples were examined with the neutron source and most of these were not treated with PF. Due to this, only the x-ray results are discussed in detail in this thesis (an example neutron image can be seen in *Paper 2*).

Since synchrotron time is precious, there was no easy opportunity to go back and run more samples based on existing results. In stead, as many samples as possible were run while at the PSI, resulting in a diversity of studies samples. Most of the run samples related to new consolidants are presented in the following.

In preparing the samples for the x-ray investigation, it became painfully obvious that synchrotron imaging requires small samples. Most of the samples reported on in this work were a maximum of 1.5 mm in width/depth as this was the size of the recorded images. An ideal sample is circular. Cutting fragile alum-treated wood to these specifications was
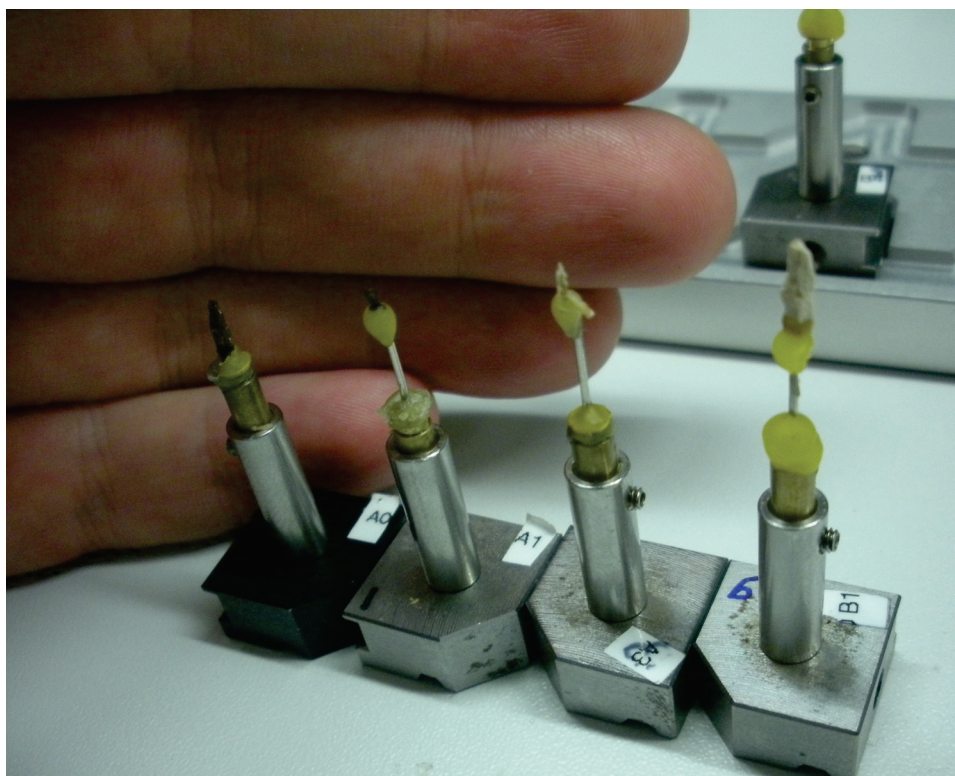

Figure 6.7: Samples of archaeological wood for synchrotron x-ray tomographies mounted with bee's wax on sample holders. Note the diminutive size of the samples themselves.

impossible and the samples ended up being whatever shape they fractured in. Several even powdered during the investigation. The small samples were mounted using bee's wax – which incidentally penetrated the alum-treated wood much more efficiently than most consolidants and was often sucked several mm into the samples before hardening. Examples of the samples can be seen in Figure 6.7 above.
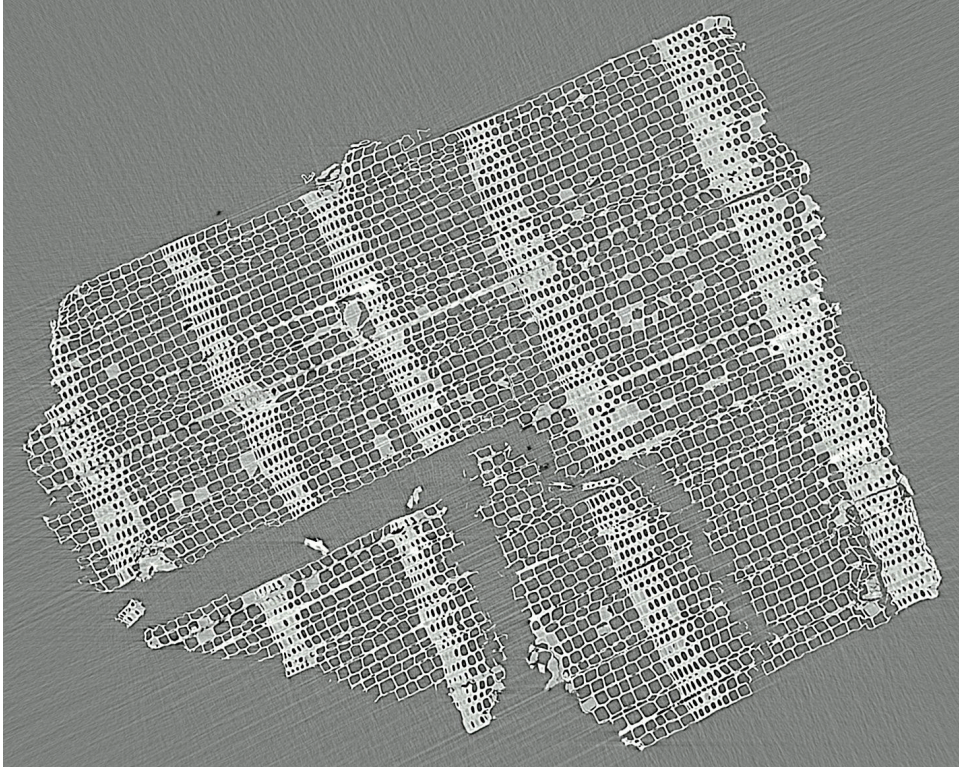

Figure 6.8: Reconstructed x-ray tomography slice of 100 years old untreated archaeological wood (sample 'Drammen'). Note that most of the cell wall material is gone.

In order to understand the distribution of consolidants, reference samples are needed. As most tests were carried out on roughly 100 year old wood from Drammen, this was examined and is shown in Figure 6.8 above and is further described in chapter 3.5.3.1 'Samples used in these investigations' on page 44. Unless mentioned otherwise, this is the wooden material presented in this chapter. It was found that the wood itself had maintained its overall structure although relatively large cracks had formed. Most of the cells are empty

but some seem to be filled with a fairly uniform material. Apart from several observed large cracks, the structure of the wood does not seem to be significantly damaged.
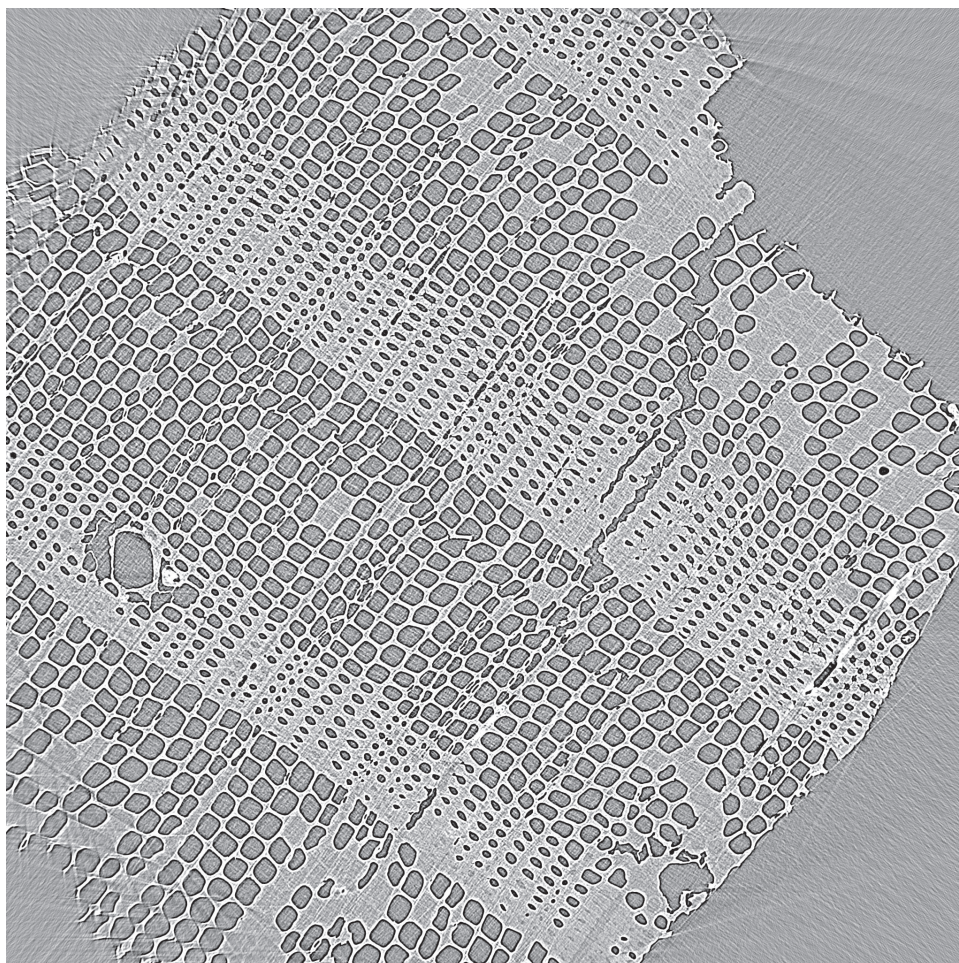

Figure 6.9: Reconstructed x-ray tomography slice of a piece of 100 years old archaeological wood (sample 'Drammen') treated with PF polymer. Note the uneven distribution.

A sample treated with PF is seen in Figure 6.9 above. The wood was soaked in PF monomer solution and then cured using concentrated HCl. The tomography investigation clearly shows a very uneven penetration of PF. As such, it will not be enough to simply drip the consolidant onto an item for proper treatment. The archaeological wood should be completely immersed in impregnating solution to ensure a proper distribution of

consolidant. While this is hardly surprising, it does add an extra complication to treating existing museum objects – particularly the alum-filled objects from the Oseberg find.
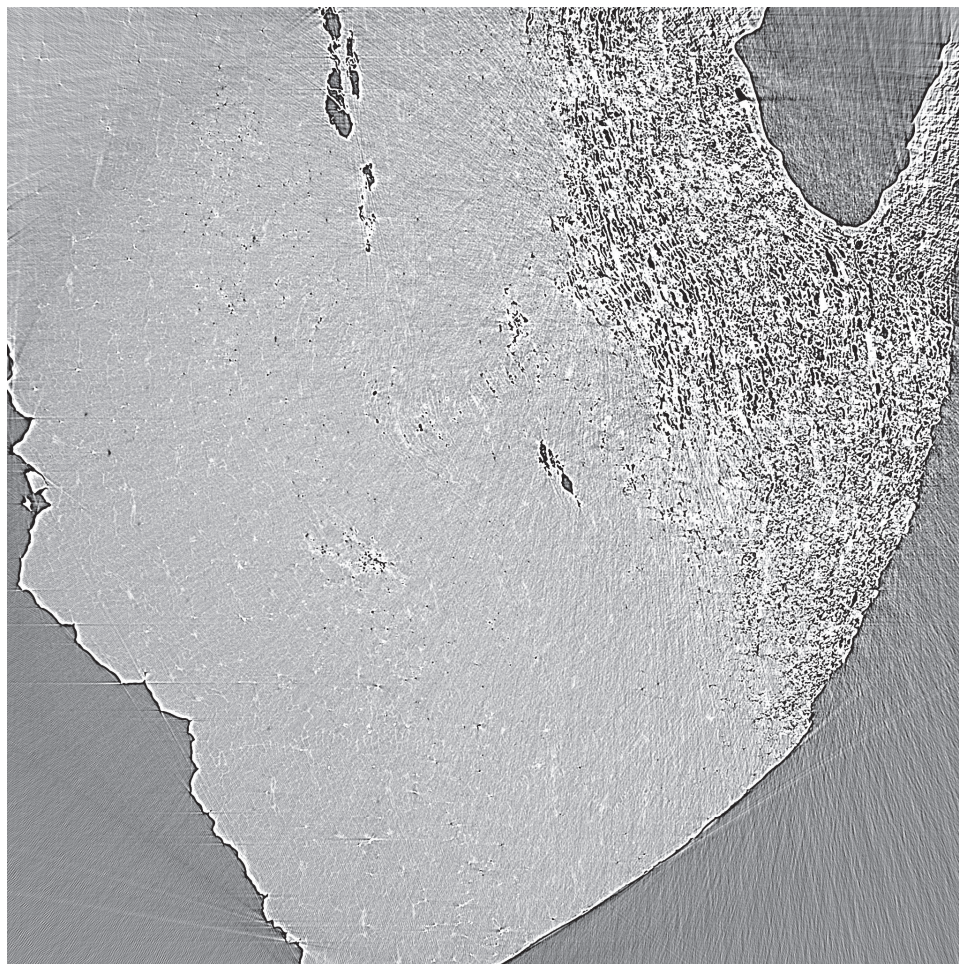

Figure 6.10: Reconstructed x-ray tomography slice of a piece of Viking Age wood treated with PF (sample 'lost'). Note that the structure has collapsed.

A small piece of 'lost' Viking Age wood was treated with PF. The F:P ratio was 1.4. A bit of the piece was also investigated as shown in Figure 6.10 above. The polymer clearly penetrated into the wood but unfortunately bulked most of it. What remains of the wooden structure seems to have collapsed. This likely happened during the drying process as water

was simply allowed to evaporate in the initial samples as they were placed into the oven for curing.
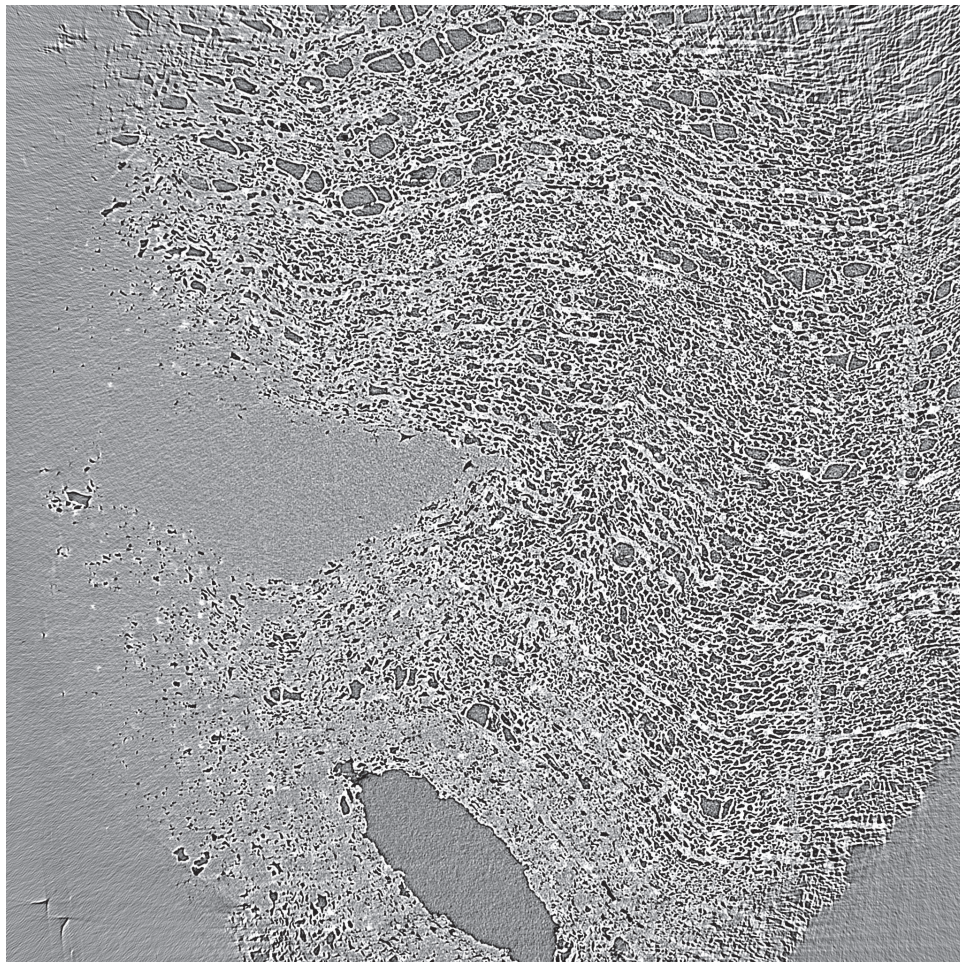

Figure 6.11: Reconstructed x-ray tomography slice of a piece of Viking Age wood (sample 'lost') treated with PF. Note that less polymer seems to leave more of the wooden structure intact but still fills some of it completely.

A similar piece was treated in a simiar way but using less PF. A tomography slice from this sample is shown in Figure 6.11 above. The wooden structure is obviously better preserved in this sample, suggesting that finding the proper concentration of PF monomers

to coat the wood without filling all pores will be critical if this method is ever to be developed further.
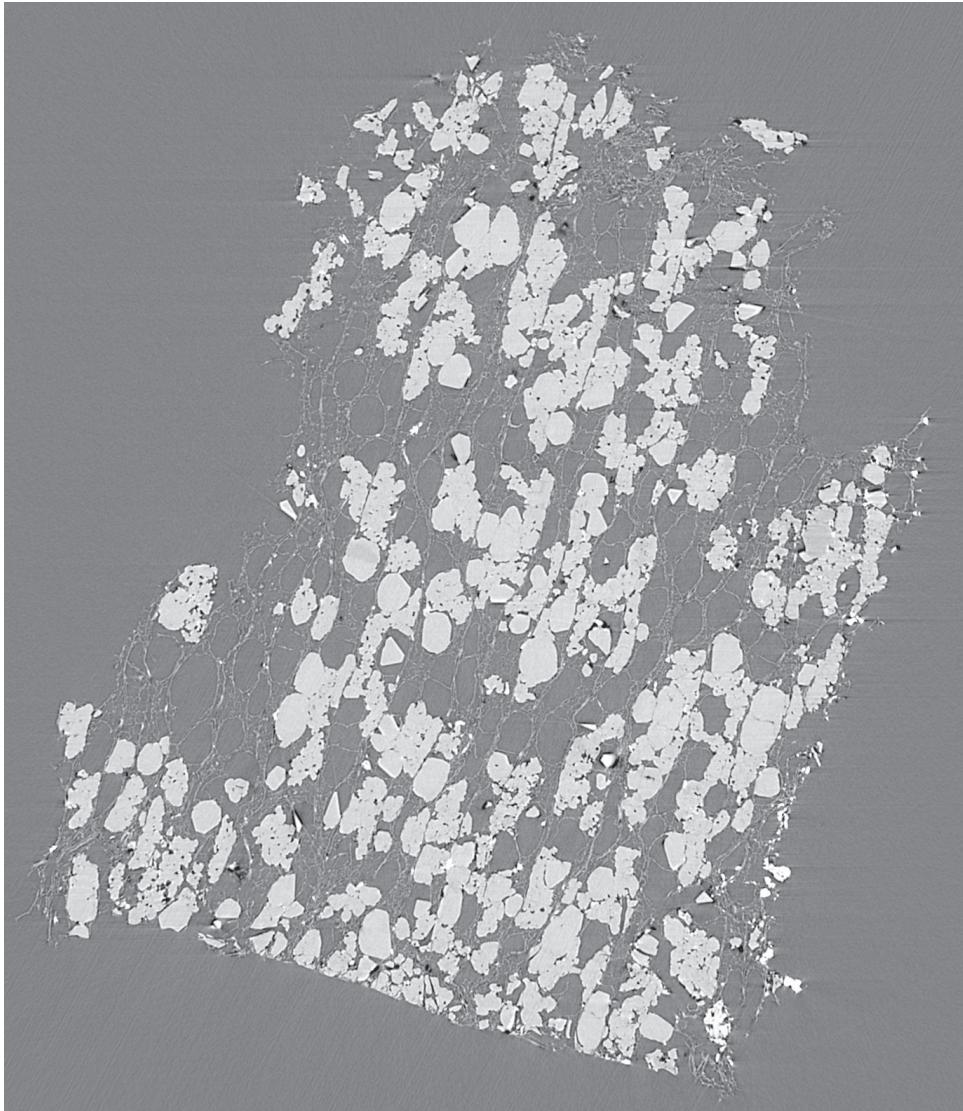

Figure 6.12: Reconstructed x-ray tomography slice of a fragment of alum-treated Oseberg material. Note that the white/grey alum patches seem to exist in two different densities (one grey and one white).

106

Figure 6.13: Photograph of the samples from the Oseberg find after treatment with PF. The ruler shown at the bottom of the images has a cm/mm scale. The left sample retained its wooden structure while the one to the right 'melted' during treatment. Note the shining crystals which have formed on the degraded piece to the right.

Two pieces from the actual Oseberg find were also treated with PF. They were identified as either birch (*Betula*) or alder (*Alnus*) but no further identification could be performed due to thei In order to understand the effects of the polymer on these samples, pieces of alum-treated wood without and added PF were also investigated. A typical example is shown in Figure 6.12 above. As can be seen, the alum crystals seem to have two phases with different densities. It is not known whether this happened during the original treatment or is something which has developed over time. More worrying, it is clear that the alum is not evenly distributed and that several of the vessels are not filled. This means that the remaining wooden structure is not properly supported and thus likely to fracture in places. Based on this, it is not surprising that several of the treated objects seem to be powdering.

Sample 1 was light brown which indicates that it had a relatively low alum content. It was marked C55000/250 1904.27 but the piece had broken off in 2008 during re-packaging. The solution penetrated this test piece of wood much like fresh wood, not penetrating well across the grain. Two tests were made on this wood with different amounts of PF relative to wood.

Sample 2 was dark and had high alum content. It was marked 1904-229-232 (ref. x-ray 23/10/01 Fragment 1). This fragment was degraded enough that the solution seemed to get sucked into the piece no matter where the solution was dripped onto it.
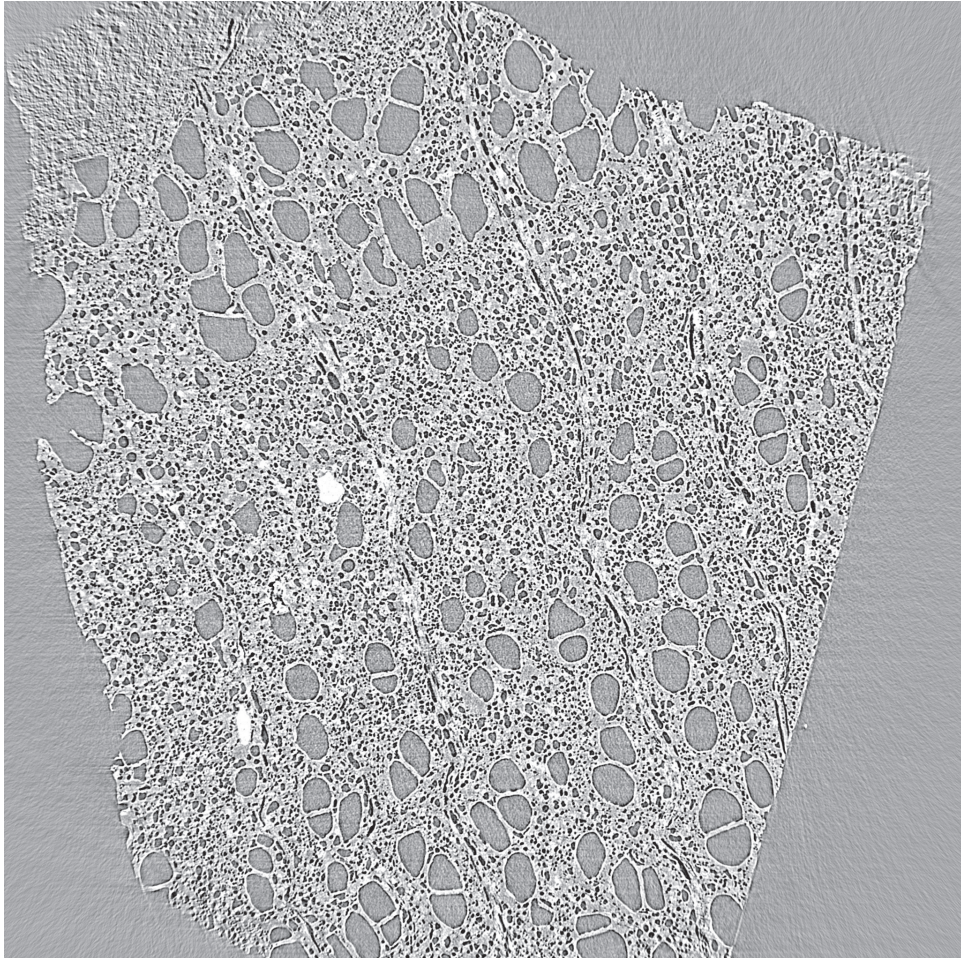

Figure 6.14: Reconstructed x-ray tomography slice of alum-treated Oseberg wood treated with a surplus of PF.

Both samples were treated with a standard solution of 6 g of phenol to 7 ml formaldehyde solution (F:P ratio 1.4). The mix was split into three beakers and 3 drops of concentrated HCl were added to each. The solutions were applied to the test pieces using a glass pipette and the samples were sealed in glassware in order to prevent evaporation and

subsequently left in the fume hood to polymerise. After three hours, the 'melted' appearance of Sample 2 was observed first. The samples were put into the oven for four days in order to cure the polymer. Shortly after the containers were opened, a whitish coating (most likely of minute alum crystals) was observed on the surface of Sample 2 (especially at the bottom of the sample between it and the glass container). The samples were left in the fume hood until dry enough to be handled by tweezers. Sample 1 had acquired a reddish cast from the PF but seemed to have retained its structure. Both pieces can be seen after impregnation in Figure 6.13 above.
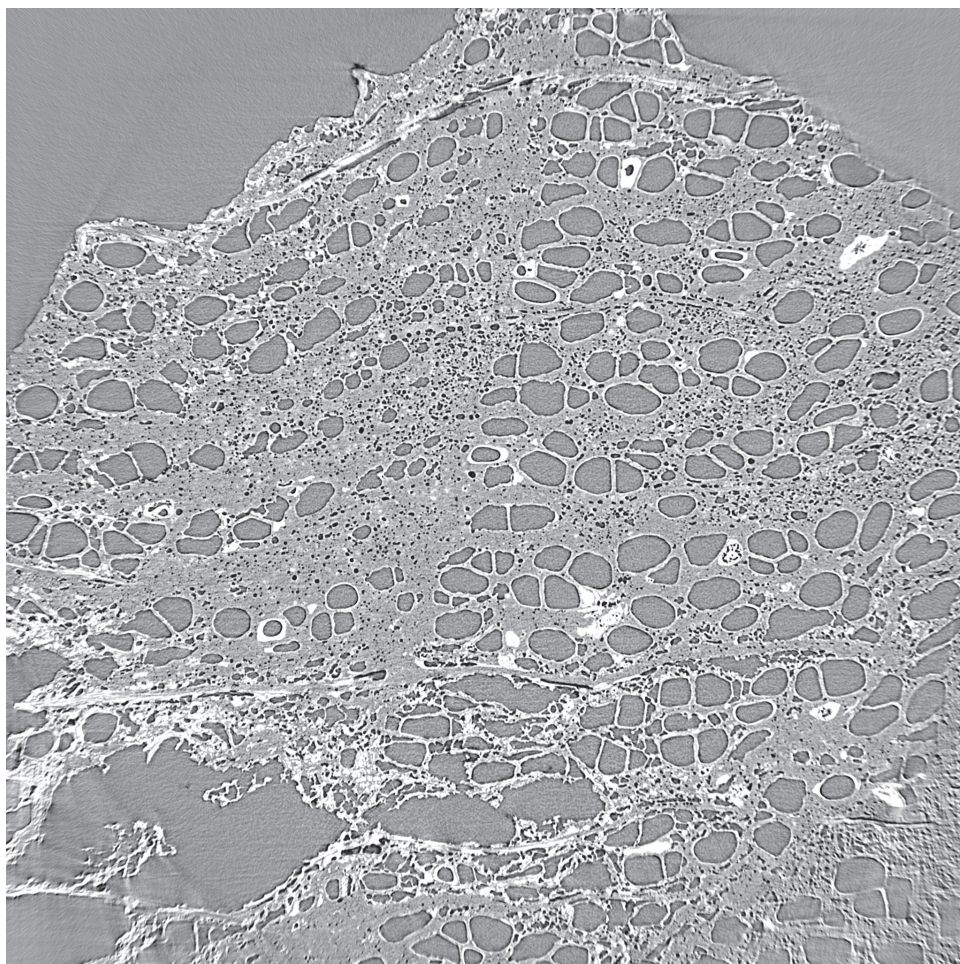

Figure 6.15: Reconstructed x-ray tomography slice of a piece of alum-treated Oseberg wood treated with less PF.

The impregnated Oseberg material was a fairly successful story considering that no piece had been thoroughly examined before the x-ray study and that standard PF – rather than a mix optimised for treatment – was used. In samples treated with varying degrees of PF, the wooden structure was largely intact although the smaller cells were mostly filled with cured polymer. These results are shown in Figure 6.14 and Figure 6.15 above. It should be noted that the results for the two tests with varying amounts of PF are virtually identical, meaning that it would have been preferable to make a greater separation between the amounts of pre-polymer added.
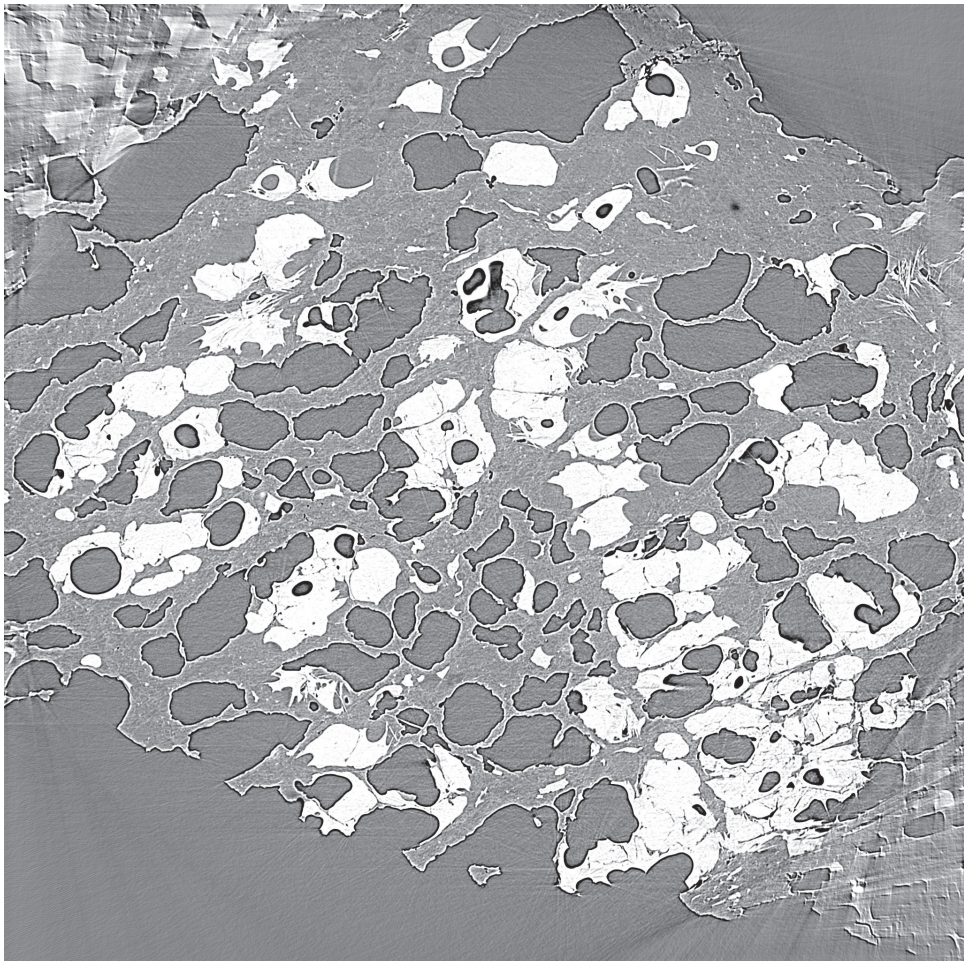

Figure 6.16: Reconstructed x-ray tomography slice of Oseberg wood treated with PF. Note that the structure of the treated sample is amorphous - unlike wood.

Sample 2 was very dark – an obvious sign that it had been severely degraded – and likely contained a relatively high amount of alum. The 'melted' appearance is likely due to alum crystals in the sample recrystallising due to the water content of the formalin used. As can be seen in Figure 6.13 and Figure 6.16 above, all signs of wooden structure were lost on both a macro and micro scale. The sample had been transformed into an amorphous mix of polymer cavities and crystal-rich regions. This obviously means that existing alum-treated objects cannot be treated with PF monomers as tested (or for that matter any stabilising agent dispersed in water) as the solvent itself will destroy the object.

6.4.2   Tests of polymers similar to PF

Since it is desirable to have more flexible consolidants than the results yielded by pure novolac, a few similar polymers have been tested. Some of these have already been used to treat/conserve wood or similar materials. Again, mainly the 'Dokka' sample material was used for the initial tests to ensure that sample material was plentiful.

6.4.2.1   *Water glass*

Water glass is chemically very different from PF but it might stabilise the wood by adhering to the remaining structure (see chapter 4.1.8 'Silicon oil treatment' on page 66 for more information). The main advantage of water glass, however, is that it is extremely easy to work with.

Water glass was purchased from Sigma-Aldrich (sodium silicate solution, $Na_2O_7Si_3$). The used water glass was not thinned significantly as it seemed to seep into the archaeological wood without problems. Appearances can be deceptive, however, as the polymer only coated major cracks and failed to distribute itself evenly throughout the test sample. One tomography slice is shown in Figure 6.17 where it is quite clear that the polymer completely bulks cells and mainly fills cracks. While it is possible that longer impregnation times at lower concentrations might alleviate this problem – and further experiments should be carried out before the method is dismissed completely – the sample at least shows that water glass cannot be applied to archaeological wood as easily as it can to fresh flowers.
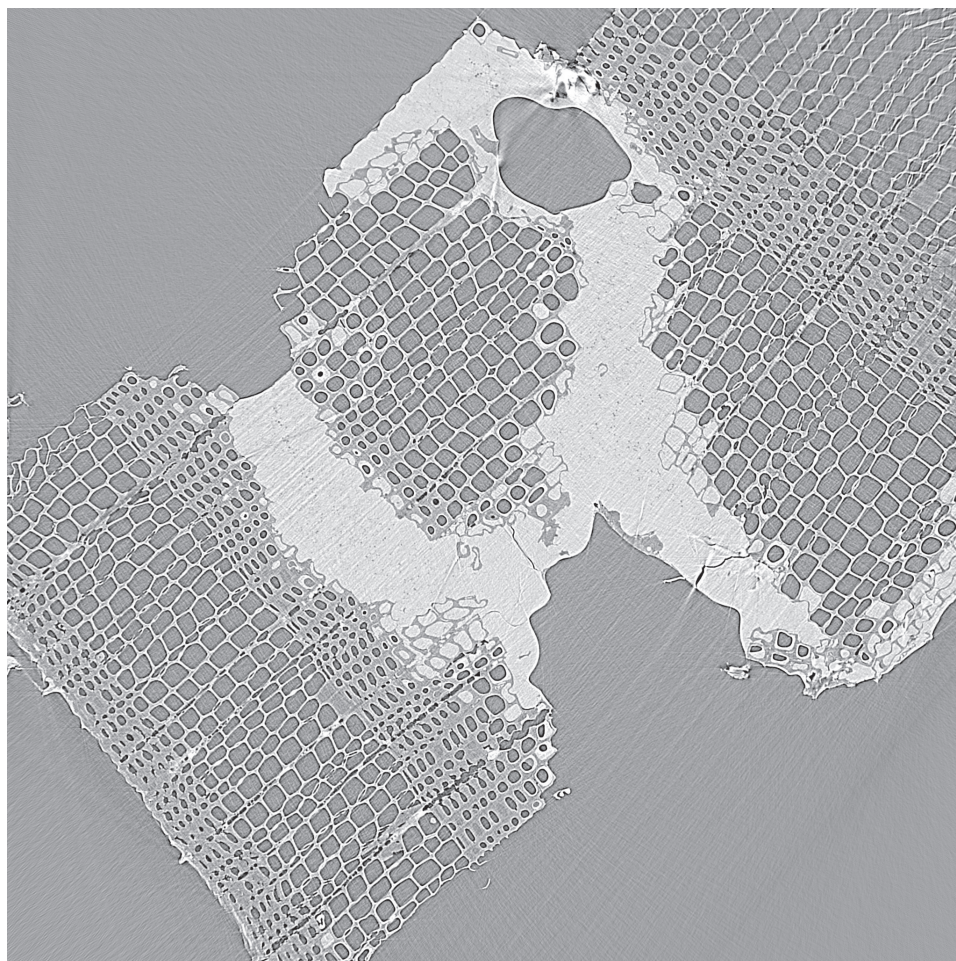
Figure 6.17: Reconstructed x-ray tomography slice of a piece of 100 years old archaeological wood (sample 'Drammen') treated with water glass. Note the uneven distribution.

6.4.2.2 Melamine formaldehyde

The Kauramin method (described in chapter 4.1.6 'Kauramin and melamine-formaldehyde treatments' on page 60) utilises a melamine-based polymer. As the colour of this polymer is white, it affects the appearance of the archaeological wood less than PF. Pure melamine formaldehyde (but not Kauramin) was tested on wood using the novolac procedure described above. Unfortunately, the material did not fully cure under these conditions and the resulting white mass could be broken apart simply by squeezing it

between two fingers. It may be possible to obtain suitable results at higher pH but as wood is generally more resistant to acid than base (and the alum-treated wood is already highly acidic). Because of this problem with polymerisation – and because a melamine formaldehyde designed specifically for the conservation of archaeological wood already exists – this approach was not pursued any further.
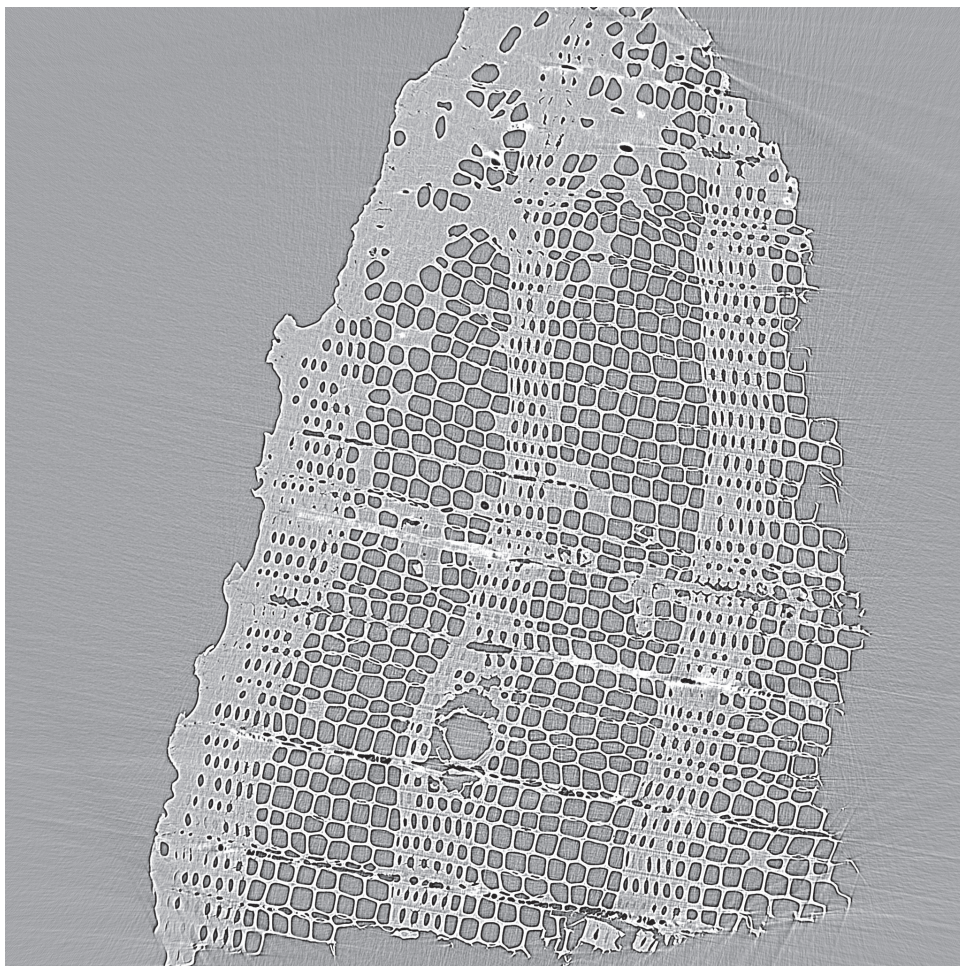

Figure 6.18: Reconstructed x-ray tomography slice of a piece of 100 years old archaeological wood (sample 'Drammen') treated with phenol, formaldehyde, and melamine.

A mix of melamine and phenol formaldehyde was also tested. It cured but given earlier experiments this could simply be the PF curing with the melamine acting as a filler. It was tested on 100 years old archaeological wood from Drammen but did not penetrate properly. As can be seen in Figure 6.18 above, the distribution is very similar to that of pure PF seen in Figure 6.9 on page 103.

6.4.2.3 Furfuryl-related products

Furan resins can be made by substituting phenol with furfuryl alcohol. The reaction is very similar to that of phenol and formaldehyde, including the possibility to polymerise it at any pH. The self-heating rate of the reaction is fairly low in the range from pH 3 to pH 12 [121].

These polymers have ring structures and although five-sided rings are weaker than six-sided ones, they should still prove more durable than linear ethers. Since these polymers may self-polymerise without the need for formaldehyde to cross-link them, they were initially considered interesting alternatives to PF.

Both furfuryl alcohol and furaldehyde were purchased from Sigma-Aldrich. They were polymerised simply by adding a drop of concentrated HCl to the pure polymer. Unfortunately, both of these products self-heated to the point of boiling during polymerisation, making them difficult to work with. Furthermore, the fused polymers were almost or completely black and thus a bad choice of consolidant. Significant shrinkage also occurred during polymerisation. In the worst cases, the pure polymer shrunk to have only half the diameter of the plastic cup it was polymerised in.

Synchrotron x-ray computer tomography also showed that the furfuryl products mainly filled the outer layer of the wood and failed to fully penetrate the structure of 100 years old archaeological wood from Drammen. The results for furfural in Figure 6.19 below show how similar the distribution is to pure PF or PF with melamine (see Figure 6.9 on page 103 and Figure 6.18 on page 113).
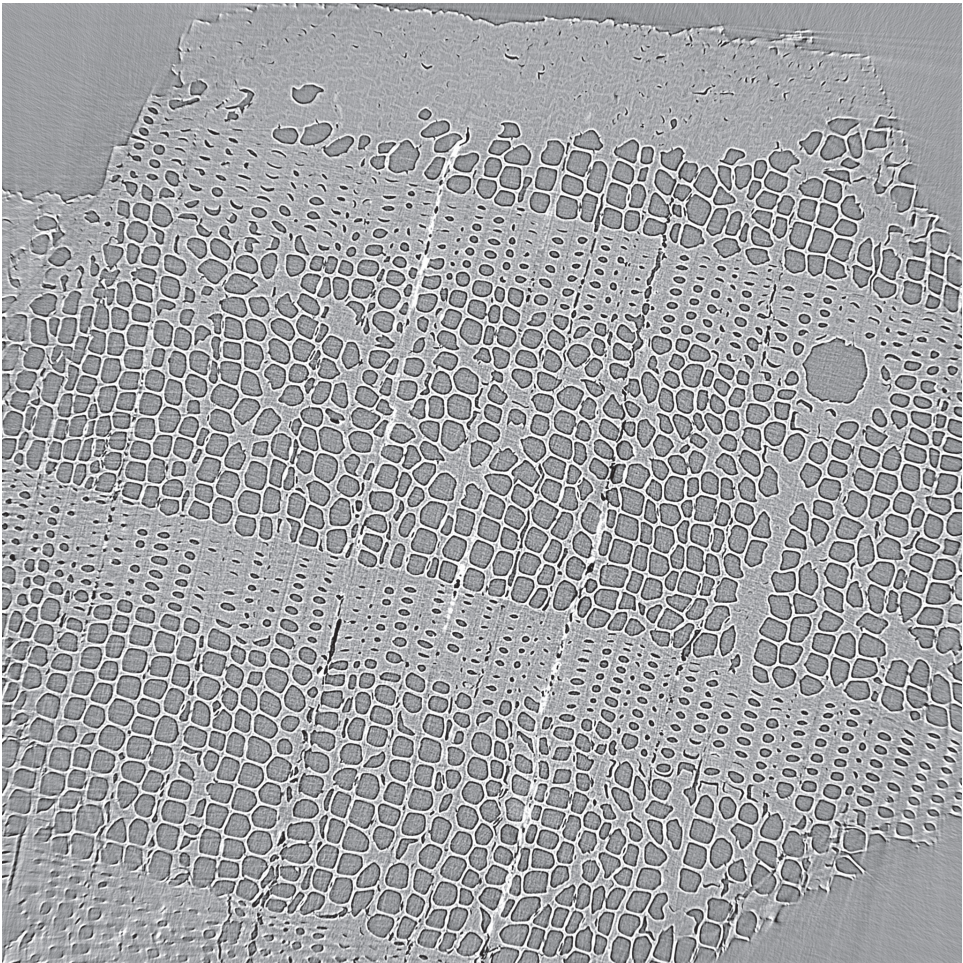
Figure 6.19: Reconstructed x-ray tomography slice of a piece of archaeological wood (sample 'Drammen') treated with phenol furfural.

6.4.3 Discussion of PF as a consolidant

Bakelite items are some of the most well-preserved plastics and one of the very few synthetic polymers where some items have endured more than a hundred years worth of real-time ageing [136]. This means that they are better suited for conservation purposes than many other polymers. Since many conservators agree that Bakelite was used to treat both bones and wooden objects, it is surprisingly difficult to find published information about the methods and polymer composition used. In one case, Bakelite was considered for the

treatment of a wooden bucket but the actual polymer in question was supplied by the Bakelite company (see chapter 4.1.5 'Phenol-formaldehyde treatment' on page 59). This makes it more difficult to determine how many of the Bakelite-treated items were in fact treated with PF. As such, it may not be meaningful to compare the real-time ageing of such objects with the ageing of newly PF-treated wood. Additionally, one must remember that most industrially produced PF objects contain substantial amounts of filler (often saw dust) in order to make the polymer cheaper. Furthermore, Bakelite was normally made with a base as a catalyst (since it was cheaper than acid). This may affect treated wood since especially lignin is much more easily broken down in a basic than in an acidic environment. Although PF filled with saw dust might be a good model for wooden items treated with PF, it is also possible that the composition of the archaeological wood is sufficiently different from fresh wood to affect the actual degradation significantly. These factors combine to make it very difficult to actually judge the long term affect PF will have on treated items.

Since bumpy boiling did not occur above pH 0 at temperatures up to 70ºC, it should not affect the actual treatment of archaeological wood which will most likely be treated at significantly higher pH values – provided the catalyst is properly dispersed. Additionally, the amounts and concentration of polymer needed in conservation cannot be compared with industrial PF manufacture. For these reasons, runaway reactions are unlikely to be a concern if PF is applied to archaeological wood.

Speaking of acidity, it would be interesting to apply the treatment to more archaeological hardwood samples. Much of the treated wood was fairly recent softwood, which is probably fairly resistant to acid.

The Oddy corrosion tests demonstrated that pure PF catalysed by HCl does not affect lead coupons. While it would be ideal to repeat this test using other kinds of metal as well, the result makes it unlikely that PF will significantly corrode surrounding metals. For this reason, it should be safe to display objects treated with PF along with other objects in a museum.

The accelerated ageing experiments at 70ºC demonstrated that the polymers tend to redden and darken with age – eventually becoming so dark they almost look black. While

this colour is much too dark to be desirable, it is no darker brown than many examples of treated archaeological wood. It is darker than the alum-treated objects, however, and means that pure novolac should not be used in this form for the treatment of restored surfaces. As was found with the solvent tests, mixing PF with other reactants might dramatically alter the appearance of the polymer. This means that it is possible to add a certain amount of phenolic groups to a consolidant without affecting the appearance of treated objects significantly. This in turn means that the increased chemical stability obtained by having aromatic rings in the structure can be achieved.

In certain cases, the appearance of the polymer might not matter. For example in the case of the Oseberg material, PF might be a better solution than on previously untreated wood. Since the alum-rich surface of treated objects may have to be left alone, PF can be injected into the core of degraded fragments and cured inside them. Provided the phase separation can be achieved in way which does not warp the objects, this would allow the powdery cores of the artefacts to be strengthened. Since the PF would not be applied to the surface of the objects, any colouration would not be seen by museum visitors.

While the colour might not be a problem for alum-treated material, the solvent is. As water was demonstrated to simply 'melt' certain degraded fragments of Oseberg material, it is imperative to find another solvent if PF is to be implemented as a strengthening agent. Since the objects from the Oseberg find likely have to be treated directly where displayed, severe measures must be developed to prevent conservators and visitors from coming into contact with the fumes emitted by the pre-polymer mix (more on this below).

The importance of the phase separation occurring during novolac curing should be stressed. It is vitally important that this phase separation seems to distribute the polymer so that voids in the lumen remain open but the walls are reinforced (as seen in for example Figure 6.15 on page 109). Since access to the synchrotron facilities was limited, it was not possible to return with a series of samples with different water contents, F:P ratios and pH values. Doing this might well lead to an optimal ratio where the remaining wooden cell material is reinforced without thickening the cell walls needlessly.

Regardless of whether novolacs themselves will be used, the usefulness of the phase separation means that it should be kept in mind and, if possible, copied with other consolidant systems.

The kinetics experiments demonstrated that the polymerisation reaction happens at a sufficiently slow rate to allow the monomers to penetrate into archaeological wood. Unfortunately it also means that the wood will have to be enclosed during this time to prevent evaporation of water and formaldehyde. While this should not be a problem when treating new artefacts, it will make it very difficult to apply the method to the existing alum-treated pieces (in addition to problems with water as a solvent).

When evaluating the penetration of PF, most of the test wood was from the sample from Drammen. This means that the wood was not very degraded and this might affect the final distribution of the polymer. Ideally, some of the experiments should be performed again if/when given access to sufficiently high resolution x-ray tomography equipment.

One of the main concerns about using PF in conservation is that both phenol and formaldehyde act as carcinogens and exposure to these monomers should be limited. This is especially important since large pieces of wood will have to be treated in vats, meaning that large amounts of monomers have to be handled. On the bright side, formalin should prevent biological attacks during the impregnation.

Glyoxal and HMTA were tested in attempts to lower toxicity but did not sufficiently cross-link the polymer without additional heat and catalysts. In addition, glyoxal resulted in extremely dark samples. For this reason, glyoxal cannot be recommended as a suitable substitute for formaldehyde in conservation studies. This does not mean that it is not important to replace phenol in the future but rather that systematic work on suitable low-temperature catalysts is desirable if phenolic polymers are ever to be used in conservation.

If phenol and formaldehyde can be pre-polymerised into oligomer molecules, the toxicity drops dramatically. Since such oligomer tests showed a concentration of 1.5% or less free formaldehyde, this level is acceptable when compared to other formaldehyde-emitting products (such as fibreboard). It should be remembered that the 1.5% formaldehyde was only found in the watery phase of the oligomer, which would be disposed of during initial production. This means that novolac pre-polymers should be safe for museum use. The primary drawback when considering pre-polymers is that larger molecules interact less well with the cell wall material. Whether this actually makes a noticeable difference must be tested.

Developing the pre-polymers, however, would require the testing of both suitable solvents (isopropanol and acetone were both tested but seemed to react with the pre-polymer) and a procedure for successfully cross-linking them once they have penetrated the archaeological wood. It may not be worthwhile to develop such procedures for new finds to be treated. On the other hand, the novolac oligomers are the most successful consolidant tested on alum-treated material during these investigations (more on this in the following).

Since the x-ray tomographies of alum-treated wood showed that PF adheres to the wooden structure and reinforces it, wooden items which are not completely degraded may be reinforced with PF while preserving the larger pores and openings of the wood. Unfortunately, the same investigation showed that severely degraded alum-treated wood cannot be treated with watery solvents as these dissolve the alum crystals maintaining the frame of the wood. This makes the polymer suitable for less degraded waterlogged wooden pieces (likely to include most newly excavated ones) or for stabilising the non-visible core of objects. In fact, the durability and acid-resistance of PF might make it one of the more attractive theoretical possibilities when evaluating which materials could be used to reinforce the core of the alum-treated fragments of the Oseberg find. In such a case the reddish PF composite would not be visible on the surfaces of treated objects, preserving their appearance while strengthening them.

Larger pieces of wood – especially freshly excavated pieces which are less fragile than the alum-treated material – should be immersed in an impregnation bath to ensure thorough distribution of the monomers. The amount of PF in the sample suggested that the concentration was a bit too high to preserve the open structure of the wood. For this reason, it is recommended that the prepolymer mix be diluted with water (but note that this will cause earlier phase separation unless the formaldehyde concentration is also increased). If this avenue is to be pursued further, it is also important to choose more diverse kinds of sampling material. The 'Dokka' sample used for the majority of these tests is not degraded enough to give a proper evaluation of how typical archaeological finds might behave. On the other hand, tests on the 'lost' sample and actual Oseberg material does give enough information to make a number of useful observations.

Based on the above, we can evaluate the suitability of using PF for wooden finds. The polymer has several advantages including good penetration in monomer state, long durability, resistance to acids and solvents, as well as chemical compatibility with the degraded wood. The disadvantages are brittleness, red or brown colouration occurring due to oxidation, high acidity required during polymerisation, and above all that the monomers are toxic.

The disadvantages probably outweigh the advantages if we consider PF as a solution for an untreated piece of wood. Despite this, PF might be developed in order to stabilise the core of severely degraded artefacts on display – such as the alum-treated objects from the Oseberg find. For any kind of wood, utilising phase separation qualities similar to those observed for the novolac could prove essential in maintaining the open structure of treated wood.

As for the non-PF polymers, some conclusions can also be drawn here. The water glass seemed to penetrate well into the wood – and would most likely distribute itself properly if thinned with water (provided the wood was properly immersed in an impregnation bath). The unfortunate tendency to completely fill cells means that the distribution of the polymer is unsuitable for use without further modifications. A simple possibility might be to freeze the treated wood after impregnation, allowing the forming ice crystals to push the polymer into the degraded cell material. It might be better to design a Si-based molecule specifically for wood conservation rather than simply use water glass, however (see chapter 8.6.2 'Silicate compounds' on page 186 for further ideas).

Melamine is less toxic then phenol, making melamine-formaldehyde a better choice than PF. On the other hand, melamine did not react as willingly as phenol and may be difficult to implement at low pH values. This is a significant drawback since archaeological wood is less resistant to bases than to acids. It also makes it impossible to simply inject melamine formaldehyde into alum-treated wood and let the natural acidity of the artefacts serve as a catalyst for the polymerisation.

Both furfuryl alcohol and furaldehyde could be thinned with water to prevent self-heating. Most likely, a suitable procedure for implementing them could be developed fairly easily. They would be less durable – but also less toxic – than pure PF. Their main disadvantage is their dark colour and extreme shrinkage during polymerisation. A further

complication is the fact that they caused severe corrosion of lead coupons, making it tricky to display furfuryl alcohol-treated objects along with other objects in a museum. These traits make them unsuitable as consolidants for archaeological wood.

6.4.4 Possible treatment procedure for PF

Due to the problems with toxic fumes, the following procedure uses sealed storage tanks. While it is certainly possible to polymerise the monomers in open air, the requirements regarding health and safety in such a case are left for others to assess. It is possible to do both impregnation and curing in a single bath. The following procedure uses two. The reasoning behind this is two-fold. Firstly, pre-polymerised molecules in the impregnation bath reduces toxicity. Secondly, using two baths means both impregnating and curing solution can be recycled, reducing costs.

Prepare a solution of phenol in formalin (37%wt). Using a ratio of 1 g phenol to 1 g formalin gives a F:P ratio of 0.8 and ensures that virtually all the formaldehyde will react. As long as pH is not lowered, the solution can be kept for some time (months – more if a non-watery solvent is added) before it is added to the wood.

Place the wooden item in plastic bag in an airtight container. Wait until the solution has penetrated evenly throughout the artefacts (further testing is needed to determine this point). Rinse the object with warm water or acetone/isopropanol to get rid of whatever pre-polymer might be attached to the surface of the object (and may later ruin its appearance). Then quickly transfer the impregnated items to another sealed bath containing 4:1 water:formalin mix. Using separate impregnation and curing baths would allow the solutions to be reused as long as a loss of formaldehyde content is accounted for. The additional formaldehyde will now react with the oligomers. Adding water ensures that the the prepolymer molecules will not dissolve in the formalin or meander throughout the wood as they are insoluble in water. Add HCl to the formalin solution. The exact amount of HCl should be varied to achieve a suitable curing time. Temperature and catalysts may be adjusted as well. A ratio of 0.0125 g HCl per g phenol was used for the kinetics experiments. This gives a very low pH (around 0) without causing runaway reactions. Actual treatment should be carried out at much higher pH in order to avoid damaging the objects.

Leave the container until the polymer has cured. The exact time is extremely temperature-dependant. It is possible to postpone the heating to allow the solution to thoroughly penetrate into every pore of the wooden object. The mix can be left longer without hardening but is very acidic.

Place the sealed bag and container back into the oven. Cure for five days at 70ºC. Curing at room temperature is not efficient when the final curing is taking place (the polymer may not harden completely). At the end of this phase the polymer (and thus object) should have hardened fully. Note that some formalin may be left in the water even after thorough reaction.

At this stage the object should be cured but needs to be neutralised and dried before it is put on display. It is possible to use a weak base or a buffer solution to neutralise the acid. While it is theoretically possible to simply dilute the acid in water, it would have to be diluted about 100.000 times to reach pH 6 (provided the pH of the solution is roughly 0 as in the kinetics experiments) and the time required for pH to stabilise throughout the pore system is not known.

Drying is the final phase and the PF should be more durable than for example PEG, making the treated wood able to withstand drying under more rough circumstances. Tests have shown that the wood may still warp if simply left in a fume wood, making it a better solution to freeze-dry it despite added costs.

Note that this approach would have to be modified for alum-treated objects on display. These will have to be injected with the prepolymer mix, most likely using syringes to penetrate the surfaces of the objects. It is also vital that the watery solutions be replaced by solvents which will not harm the alum crystals. Toluene might be a possibility.

If this method is ever to be implemented on a larger scale (meaning more than simply to treat an object or two to compare the results with those of other methods) some optimisation could be attempted.

The pre-polymer may be dissolved in acetone or isopropanol but beware that tests indicated that acetone gives it a very dark colour whereas isopropanol turns it more yellow. Unfortunately, the exact reaction happening has not been thoroughly investigated and it is not known to what degree it might affect the properties of the finished PF. In the month or

so that test solutions have been kept, there is no sign that the prepolymer beings to agglomerate. In this state, the prepolymer also penetrates wood well and the penetration step may be carried out without further acidifying the solution (and thus threaten the stability of the wood).

As above, the treated object would need to be neutralised and dried before being put on display. One possibility would be to treat the object with nanoparticles in dispersion before the drying phase. Notes on more about acid-neutralising $CaCO_3$ experiments will be given in chapter 7.4 'Calcium carbonate nanoparticles' on page 169.

7. Biomimetic materials

When the toxicity of phenol and formaldehyde put an end to experiments with phenolic polymers, the project launched off in a different direction. The goal was to find a field associated with so-called 'green' chemistry and non-toxic solvents. Preferably, it should be at the cutting edge of modern research and offer high compatibility with the degraded wood.

In an age where bio-technology becomes increasingly more popular due to environmental concerns, wood conservation still relies on petro-chemicals for safeguarding national heritage. Most conservators will probably agree that it is more important to treat historical artefacts well than worry about issues like bio-renewability – although low toxicity is a definite bonus. There is another reason for looking into bio-science; namely that wood was once a living material and mimicking the way it is constructed might lead to the discovery of very efficient consolidants. If non-toxic components and renewable materials are added bonuses, why not implement bio-science into conservation science?

7.1 The concept of biomimetics

Being inspired by nature was pioneered by D'Arcy W. Thompson who published the book 'On Growth and Form' in 1919. Long before that, Leonardo da Vinci looked to birds when designing his flying machines and Galileo Galilei studied how body mass affected bone structure in various species [137], [138]. In fact, the ancient Chinese tried to make artificial silk and similar intentions can be found numerous places in literature from the past few hundreds of years [137].

The term 'biomimetics' was coined by Otto Schmitt who used it as the title of a paper in 1969. The word 'bionics' was first used in 1960 by Jack Steele. However, Steele claimed in 1963 that he had come to prefer the word 'biomimetics' [137]. Eventually a significant number of words related to materials mimicking nature arose, such as biomimetics, bionics, biomimicry, biognosis or bio-inspired. Often, the exact distinctions between these concepts are blurred [139] or even considered synonymous [137], [138]. In fact, the whole field is somewhat undefined or, as Vincent et. al. put it; "No general approach has been developed for biomimetics, although a number of people are currently developing methods for searching biological literature for functional analogies to implement."[137]. The word

'biomimetic' will be used throughout this text to refer to the practice of adapting or become inspired by structures and/or materials found in nature.

Many materials and technologies have been inspired by nature. As such it is often easier to give examples of biomimetic materials than to explain all the possible implications of biomimetic collaborations.

Interesting plant surfaces include superhydrophobic and superhydrophilic constructions which interact with water in unusual ways due the surface structure of said plants. The most famous – and well studied – example is probably the lotus plant which cannot get wet or dirty (although this property is found in many other plants as well). Several examples are given in Ref.[140]. Plant surfaces may also adhere via burrs – they may for example stick to dogs when you take them for a walk – a fact which led to the development of Velcro [137]. It is quite likely that future materials will focus on the self-healing aspects (for example by including pockets of bacteria inside building walls which awaken and seal the crack if moisture penetrates into their area) [141]. Biological discoveries of interesting mechanisms lead to those mechanisms becoming available for engineers [137]. Robots are being developed which use the dry adhesive qualities of gecko feet for climbing [142]. The possibility of surrounding ourselves with adhesives pads based on gecko feet and self-cleaning surfaces inspired by plants is now common enough to have made it to Wikipedia [143].

A related field is biomineralisation. While this has not been put to great use in the experiments carried out during this project, it might still be important for future conservation treatments. For this reason, a brief explanation of the concept of biomineralisation follows.

Minerals have been used in organisms for at least 3500 million years. Complexity of structures and applications expanded until at least until about 540 million years ago when skeletal formation came about. Mineralisation is seen in all five animal kingdoms and specialised to the degree where biological materials are likely to outperform engineered ones. The mineralisation in living organisms is usually controlled by macromolecules, such as a combination of polysaccharides, which forms a framework which is then filled with minerals (like collagen is a framework in bone). The properties of formed crystals are

usually not taken advantage of but rather used purely for mechanical purposes (a notable exception being the magnetic properties of some Fe structures). If a crystalline phase is formed, it might simply be induced by supersaturation and not possess much long-range structure. Crystals may be reinforced with small amounts (as little as 0.02%wt) of proteins which help deviate or absorb fractures. The most famous probably being the plywood-like layering of nacre (mother of pearl). Such proteins may also promote nucleation and thus spur growth [144].

7.1.1 Hierarchical structuring

Nature grows rather than fabricates. This means the way materials are structured differs from engineered materials. The range of components is also very different [138]. Biological systems are usually structured at the nano, micro, and meso levels. The structure and design are intimately connected – unlike engineering where they have traditionally been divided into two different disciplines [145].

Self-assembled polymers and composites provide control over the structure at all levels of hierarchy. This allows for a more dynamic approach as the end result is obtained by an algorithm rather than by pure duplication of an existing design [138]. Although more than 300 different polymers have been produced, proteins and polysaccharides can be considered both more versatile and more responsive [137]. Additionally, bio-materials provide multiple functions (for example human bone offering support and blood cell formation or a chitinous exoskeleton offering protection and points for muscle to attach). Despite the numerous advantages, it should also be remembered that most biological materials have poor high-temperature performance and are fairly weak when compared with synthetic materials [145].

Another extremely important aspect of bio-materials is self-healing. While it is difficult to implement in engineered materials, self-healing can allow failed surfaces or materials to fuse. One way to create a self-healing material might be to incorporate hollow glass tubes in the polymer. Fractures will break the tubes and release a catalyst which promotes polymerisation and cross-linking [141].

7.1.2 Using biomimetic materials in conservation science

Biomimetics have already been applied in the field of conservation. Weathering weakens the structure of exposed stone due to both chemical and biological issues. Bio-inspired growth of calcium carbonate has been tested as a way to reinforce such stone. A thin solution of organic matrix molecules (OMM) extracted from for example shellfish was tested along with the much cheaper polyaspartic acid sodium salts (2 mg/100 ml). Both enhanced the growth and structure of calcium carbonate crystals from supersaturated calcium bicarbonate solutions. Test pieces and historical buildings were both treated and the mix penetrated about 8 mm into the stone. Colour change was only observable through instrument measurements for some treatments but the stone is not significantly reinforced by the method [146].

With the growing demand that renewable materials and 'green chemistry' be used across fields, biomimetics can be considered is very interesting from an environmental perspective no matter what field it is applied to. The approach is, however, particularly relevant in conservation science.

Conservators perform treatments of archaeological finds. This means that treatments are usually carried out without any standard chemical facilities or chemical safety measures. Especially the latter point makes it vital to investigate harmless materials and our bodies have evolved to tolerate a large number of naturally occurring polymers.

A significant disadvantage of bio-materials is their lack of the strength associated with engineered materials. Since most archaeological materials are already fragile, they can be reinforced using relatively flexible polymers. Thus this is less of a concern in the field of conservation.

Many biological materials are hybrid materials. If a material already incorporates both organic and inorganic parts, it might make it easier to mix and match materials with especially desirable qualities for conservation purposes. If a polymer easily incorporates inorganic material, for example, it might be easy to incorporate inorganic nanoparticles for acid neutralisation purposes.

Wood is a bio-material. Since wood is made up of several bio-polymers, similar bio-polymers might easily adhere to the surfaces of the wood and thus strengthen it. Furthermore, the bio-polymers will likely degrade under similar conditions as the wood,

meaning that the degradation of the remaining material is not accidentally accelerated. Even if the polymers used do not occur naturally in wood, building blocks like chitin in insect carapaces are very similar to cellulose in structure. Several bio-materials are light-weight, like bone, and thus offer excellent support. Finally, many biomimetic materials might self-assemble or 'grow' inside the objects, enhancing strength and penetration. With such excellent possibilities, it is essential to evaluate the possible application of biomimetic materials for the treatment of archaeological wood.

7.2   Cellulose whiskers

The chemestry and function of cellulose in wood is described in chapter 3.2.1 'Cellulose' on page 18 while its molecular structure can be seen in Figure 7.16 on page 156. From a bio-inspired perspective, cellulose is the most common renewable polymer in nature, making up 40-50% of wood and 90% of cotton fibre, with more than $7.5 \cdot 10^{10}$ tons produced yearly [147], [148]. In addition to wood and other plants (particularly hemp, flax, jute, ramie, and cotton), bacteria and tunicates may also produce cellulose [149]. While not ordinarily considered very strong, cellulose molecules can form a structure so tight that even water cannot enter. It is this crystalline structure which is highly concentrated in the so-called 'cellulose whiskers' [149]. Since normal cellulose already exists in archaeological wood, these resilient whiskers were chosen as a field of further study.

7.2.1.1   Chemistry of cellulose whiskers

Cellulose is very stable due to a network of hydrogen bonds which prevents melting and dissolution with many solvents [149]. Adjacent cellulose chains can thus fit together in crystalline regions. There are essentially four different forms of cellulose (simply labelled I, II, III, and IV) with I being the native cellulose. The I_α lattice is found in cellulose from algae and bacteria and has a triclinic unit cell while the I_β lattice is found in cotton and ramie and has a monoclinic unit cell. The hydrogen bonding in the crystalline regions is so tight that most common solvents cannot penetrate into the crystals and dissolve the cellulose. Crystallinity thus affects swelling and absorbtion of the fibres. The less dense amorphous regions, on the other hand, can be dissolved using acid (the type, temperature and treatment

time affects the properties of the finished product). Whatever remains after such dissolution is often referred to as 'whiskers' although the highly crystalline cellulose is known by many names such as 'cellulose nanocrystals', 'microcrystals', 'nanocrystals/particles', 'microcrystallites', and 'nanofibres' [147], [148]. Technically, 'whiskers' refers to rod-like nanoparticles with a high crystalline content while 'nanofibrils' should be used to describe long flexible nanoparticles with both amorphous and crytalline regions [149]. Most whiskers from plant sources have lengths of 100-300 nm while those from tunicates or bacteria can be up to 3000 nm long. Diameters range from 3 to 70 nm with typical values around 15-20 nm [148]. This means that whiskers from plants are better than those from other sources when treating archaeological wood as the dimensions of the fibres should be kept small to enhance penetration.

Cellulose was first isolated in 1832 but has been thoroughly studied since then. That cellulose fibres can make stable suspensions in water after degradation with sulphuric acid was reported in the 1950s [148]. H_2SO_4 in particular can produce whiskers which do not flocculate due to electrostatic repulsion. Sulphur content can therefore be used as a measure of properties. H_2SO_4-treated fibres contain some weak acids (sulphate ester and carboxyl groups) which are less common in fibres treated with HCl (26 mmol/kg compared to < 18 mmol/kg) [147]. It is possible to reverse the surface changes in H_2SO_4-treated fibres under mildly alkaline conditions, or to modify HCl-treated fibres by adding sulphatic groups [148].

At a certain concentration, the whiskers form a chiral nematic phase which is ordered enough to display macroscopic birefringence – similar to that of cholesterol. It can be seen through crossed polarisers or by optical microscopy. In solution, the whiskers have a natural vertical alignment which can be optimised by placing them in a strong magnetic field. When under flow, they in stead align in the flow direction. The structure tends to be preserved even if the fibres are covered in surfactants. The chiral twist power can be increased by adding monovalent electrolytes like HCl or NaCl. H^+ counter ions induce ordered phases at the lowest concentrations. The critical concentration increases as follows: $H^+ < Na^+ < K^+ < Cs^+$. NaCl concentrations as low as 10^{-5} M may screen the electrostatic interactions [147]. The equilibrium between isotropic and anisotropic phases is sensitive to the sulphate content, the presence of electrolytes, and the kind of counterions used [148].

Due to the hydroxyl groups on the surface of the CNs, both chemical modification and various surfactants can affect the whiskers [148]. Stearic stabilisation has been attempted before by grafting PEG-NH$_2$ chains onto the whiskers. This allowed them to be dispersed in organic solvents. A method based on sililation has also been proposed [147]. Actual polymer grafting onto the surface of the whiskers has been successfully been implemented [148]. In addition to ionic species grafted during acid-treatment, whiskers may also be kept in suspension by stearic repulsion between poly(oxy ethylene) chains grafted onto the rods. Surfactants may be used to obtain dispersions in organic solvents as well [150]. The use of surfactants is of course especially attractive as they potentially allow whiskers to keep remain suspended even in water with a high ion concentrations (tests are described in chapter 7.2.4 'Coagulation by iron ions' on page 148).

Cellulose also provides high axial stiffness, which is particularly advantageous when using fibres to reinforce other polymers. Even adding water can dramatically alter the modulus of cellulose composites (a reduction from 800 to 20 MPa for a sample containing 19%^{v}/$_v$ nanowhiskers has been reported) [149]. Note that this means it is vital that cellulose fibres in museums are kept at constant RH.

Cellulose nanowhiskers have thus been incorporated as fillers into a number of polymers including siloxanes, oxyethylene, styrene, vinyl alcohol/acetate, ethylene/propylene and urethanes. Bio-polymers like starch derivatives, soy protein, chitosan, and regenerated cellulose have also been tried [148]. Crack lines are frequent in urea formaldehyde (UF) without cellulose. Upon successful introduction, cellulose whiskers prevented cracking in UF polymer bond [149]. Due to the hydrophilic nature of many cellulose whiskers, it is often simple to mix a watery dispersion into the prepolymer while nonpolar solvents usually require a solvent exchange (and even then some aggregation usually occurs). Most often, incorporating whiskers into polymers does not affect the glass transition temperature of said polymers – unless the polymer is moisture sensitive. For semicrystalline polymers, the melting temperature is unaffected as well – unless the whiskers are chemically modified [148].

Cellulose whiskers were combined with another tree component as part of a triblock copolymer. The plant matter used was xyloglucan oligosaccharides from tamarind kernels and the polymer a xyloglucan-oligosaccharide-poly(ethylene glycol)-polystyrene (XGO-

PEG-PS) triblock copolymer. A diblock copolymer of XGO and PS was tested but precipitated and could not stabilise the whiskers in watery dispersions [151]. This is the only reference found which describes an attempt to approach a true wood structure by mixing cellulose whiskers with components which resemble hemicelluloses.

Cellulose fibres have been used to produce films when combined with various other polymers since pure cellulose does not have acceptable thermomechanical properties. In stead the whiskers are incorporated into thermoplastic matrices. When mixed with latex, it was found that 6% cellulose improved the elastic mechanical properties of the polymer 500 times [147].

7.2.1.2   Uses of cellulose whiskers

Cellulose whiskers have been used commercially for as varies purposes as emulsions in foodstuffs for at least 35 years [152].

Cellulose and cellulose whiskers has been chemically modified with the specific purpose of making consolidants for archaeological wood. The solubility of cellulose modifications in water or organic solvents is modified by degree of substitution as well as functional groups. Due to high stability and low toxicity, cellulose ethers are being used in a wide range of products from cosmetics to building materials. Some have been previously tested as consolidants for archaeological wood where high molecular weight has led to poor penetration. On the other hand high molecular weight is desirable in order to confer better strength and stability to treated items. One solution is to polymerise smaller molecules and cross-link these inside the wood by heating the treated sample. On the other hand, carboxymethyl and *n*-hydroxypropyl groups are particularly suitable for making cellulose water-soluble [153]. Cellulose whiskers have been prepared with HCl. SAXS (Small Angle X-ray Scattering) as well as FTIR (Fourier Transform Infra Red) and NMR (Nuclear Magnetic Resonance) spectroscopies were used to determine the properties of synthesised polymers and the degree of penetration. Capillary viscometry was used to determine the degree of polymerisation of the products. Klason lignin was also synthesised in order to test

affinity with degraded wood (although it can be debated if the leftover wooden matrix is identical to Klason lignin). Actual archaeological wood was also used [153].

Polymers synthesised were: allyl carboxymethyl cellulose and allyl *n*-hydroxypropyl cellulose in various degrees of substitution and with varying degrees of polymerisation. Allylic groups allow for cross-linking at 60°C but makes it difficult to dissolve the modified cellulose in water – although it may be dissolved in chloroform or DMSO, replacing water and the toxicity of these solvents is a problem in conservation. Thus carboxymethyl was introduced in order to make the polymers more water-soluble and resulted in stable colloidal systems in cold water [153].

IR spectroscopy revealed that a significant portion of the cellulose ether could simply be washed out of the wood if of a type which does not cross-link. After being kept at 60°C for 6 hours the samples treated with allylated polymers could no longer be dissolved in water. This was taken as an indication of successful polymer cross-linking [153].

A test on actual archaeological wood kept in the dispersion for 20 days at room temperature showed that even the low molecular weight polymer did not penetrate fully during this time [153].

7.2.2 Experimental procedures for cellulose whiskers

The experiments in this chapter were carried out in collaboration with the Max Planck Institute for Colloids and Interfaces in Potsdam, Germany and several of the experiments were performed there[5].

'Fibrous cellulose, long' as well as H_2SO_4, acetic acid, and acetic anhydride were purchased from Sigma-Aldrich.

Three different SEMs, all located at the Max Planck Institute, were used for these experiments. One was an ESEM (Environmental Scanning Electron Microscope), specifically an FEI FE-ESEM Quanta 600 (FEI Company, Oregon, USA) used in low vacuum mode with a large field detector. Samples were used without sputtering. Recordings

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5 Ingo Burgert is gratefully acknowledged for arranging the stay and useful discussions during the trials while Anayancy Osorio demonstrated the use of the tip sonicator and discussed the production of cellulose whiskers.

from this instrument are referred to as "ESEM" images. The second was a LEO 1550 FE-SEM equipped with a Gemini detector (LEO Elektronmikroskopie GmbH, Oberkochen, Germany). Images from this instrument are simply noted as "SEM images". The final instrument was a JEOL JSM-7500F FE-SEM using a secondary electron in-lens detector (JEOL, Eching, Germany). Images from this instrument are referred to as "Cryo-SEM images". Acceleration voltages used (usually 5, 2, and 3 kV, respectively) along with magnifications and working distances are noted on the individual images.

The freeze-dried samples were carefully cut with a razor blade into slices before mounting them on sample holders. No coating was applied for the ESEM samples but others were sputtered with 5 nm Au/Pd before being placed in the respective instruments.

Acetylation of cellulose whiskers was carried out by dispersing 0.248 g of the freeze-dried fibres (treated for 30 minutes) in 15 ml glacial acetic acid. They were then acetylated by being stirred at 60ºC in roughly 10%$^w/_w$ acetic anhydride in acetic acid (with a catalytic amount of added H_2SO_4).

Experimental procedures and theory for Zeta potential measurements is found in chapter 7.2.3.2 on page 147.

7.2.2.1 Producing cellulose whiskers

Whiskers were prepared using the following procedure: 5%wt. fibrous cellulose was put into a 66%wt. H_2SO_4 solution. The mix was stirred vigorously and heated to 60ºC for either 30 minutes or one hour. After heating, the mix was poured into plastic tubes and centrifuged at 10.000 RPM (rounds per minute)

Figure 7.1: Photograph of newly collected cellulose whiskers in watery suspension.

for ten minutes. After this the transparent supernatant was discarded and the vials filled with deionised water, shaken and centrifuged again. These steps were repeated about five times until an opaque phase could be seen in the supernatant. This was collected and used for further experiments. If only a few whiskers were present in the supernatant, the vial was refilled and centrifuged once again to maximise the yield. An example of prepared cellulose whiskers collected from the cloudy supernatant after centrifuging can be seen in Figure 7.1.

7.2.3   Testing cellulose whisker impregnation

Viking Age wood was impregnated with cellulose whiskers in watery suspension. The initial tests showed that cellulose whiskers attach and form a kind of fluffy structure seen in Figure 7.3 below. They seemed to adequately fill the cracks in the archaeological wood but agglomerate too fast to fill the vessels. These filled cracks can be seen in Figure 7.2. This means that they could potentially be used to create a kind of porous 'scaffolding' for further stabilising agents to attach to. The downside is that this would likely require double treatments, at first an impregnation with cellulose, followed by freeze-drying to stabilise the cellulose matrix, then another impregnation cycle with a different consolidant to strengthen the material.

It was observed that the cellulose sometimes degraded upon immersion in acid, turning the mix dark brown (rather than the yellow-white or ochre colouration normally observed) and ruining the whiskers.

Figure 7.2: Freeze-dried piece of Viking Age wood (sample 'Box 7') impregnated with cellulose whiskers. Note how the freeze drying causes some of the whiskers out of the wooden structure. Also note that the larger cracks are filled with whiskers.

Affected whiskers were also dark brown after freeze-drying and the procedure caused them to shrink dramatically during the process. The most likely explanation is that the metal ions catalyse the degradation process somehow, rendering the whiskers unfit for further use. This was probably due to either impurities in the equipment or the use of metal spoons when handling the cellulose fibres.

This is particularly important if metal ions inside the wood can affect the whiskers in a similar way – although this process might explain why so little cell wall material remains in archaeological objects. At any rate, it is recommended that only plastic tools be used to handle the cellulose fibres when making whiskers and that any affected batches of whiskers are discarded rather than used.

Figure 7.3: Freeze-dried Viking Age wood (sample 'Box 7') in cellulose whisker suspension. Note that the whiskers form a fluffy layer around the samples unless washed off.

Several solvents were tested in order to see if the cellulose whiskers were dispersible in other mediums than water. Note that this was H_2SO_4-treated whiskers. Another treatment method might result in whiskers which can be dispersed in nonpolar solvents. That this was not the case for the H_2SO_4-treated whiskers can be seen in Figure 7.4 below. Clearly, polar solvents like acetic acid and acetic anhydride were able to disperse this kind of whiskers much more evenly than toluene – in which the whiskers did not disperse at all.

Figure 7.4: Dispersion test for a number of solvents. From left to right: Toluene, absolute ethanol, acetyl, acetic acid, anhydride, acetic acid after overnight, and water. The water seemed to give the least flocculation.

7.2.3.1 *Imaging of cellulose whiskers*

The imaging presented in this chapter was carried out at the Max Planck Institute for Colloids and Interfaces[6]. Imaging was initially performed on an ESEM in order to minimise sample preparation. Since it was not possible to obtain images at magnifications above 12.000 times on this instrument, two others – which required sample coating – were used as well. One was a normal SEM while high magnification images were taken on a cryo-SEM.

The overall structure of the freeze-dried cellulose whiskers seems somewhat 'fluffy and flaky'. The structure is generally open and porous but some larger 'sheets' are formed. An example of this structure can be seen in Figure 7.5 above. Note that the dimensions of the
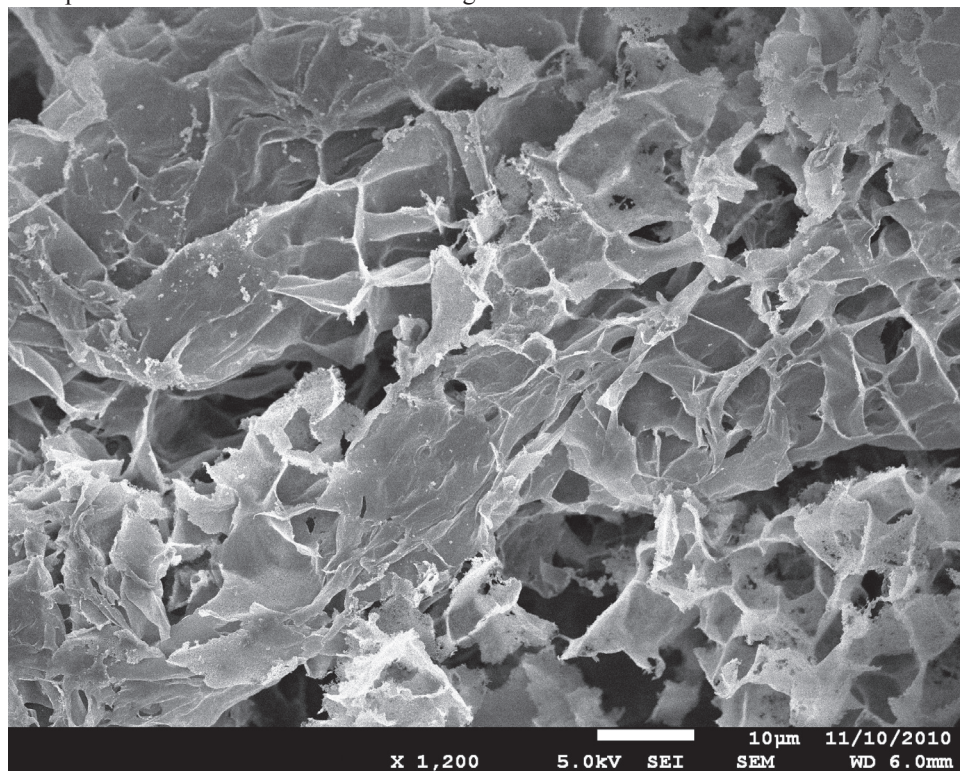
Figure 7.5: Cryo-SEM image of freeze-dried cellulose whiskers. Note that the whiskers arrange themselves in an open porous structure with some 'sheets' and 'leaves'.
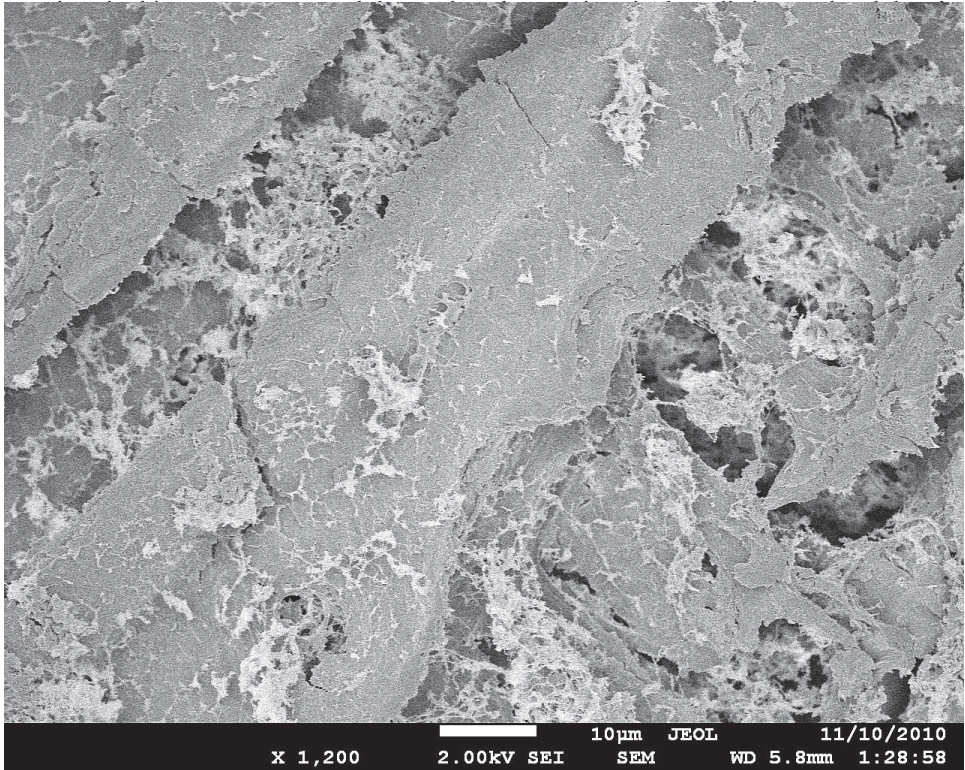

Figure 7.6: Cryo-SEM image of cellulose whiskers which have agglomerated inside a piece of Viking Age wood (sample 'Box 7').

Generally speaking, the cellulose whiskers did not penetrate properly into the wooden test pieces in watery dispersion. In stead, the whiskers tended to simply agglomerate and adhere to the surface of treated pieces. This was seen in Figure 7.3 on page 136 and can be seen at larger magnification in Figure 7.8 below. In one way it is advantageous that the whiskers adhere so well to the surface as it means that they will most likely also adhere quite well to the remaining wooden matrix and support the wood. Unfortunately, a white fluffy surface mars the visual appeal of objects on display and the whiskers adhere fairly well to the wood.
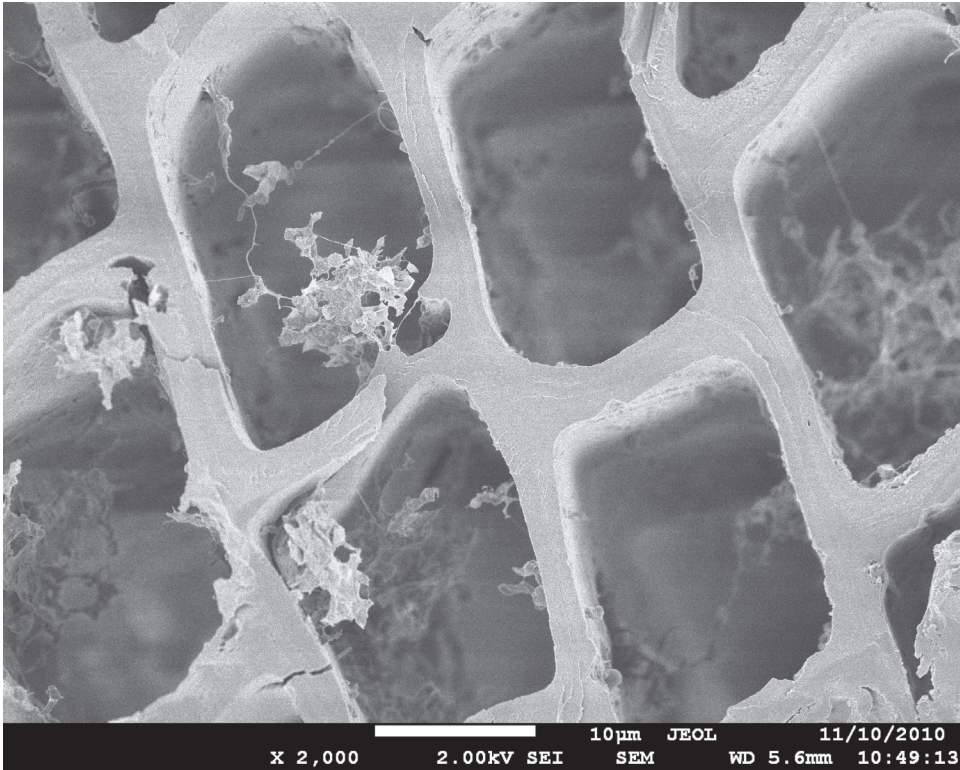
Figure 7.7: Cryo-SEM image of freeze-dried Viking Age wood (sample 'Box 7') impregnated with cellulose whiskers. Note how the whiskers agglomerate rather than attach to the remaining cell walls.

The fluffy structure of the cellulose whiskers can – at certain magnifications – look somewhat like a fungal attack. As fungi can theoretically grow inside the wood (especially when kept at room temperature during the impregnation procedure), it was important to compare a fungally infected piece to the ones treated with consolidant. During one of the chitosan impregnation trials, a sample was infected. Since it was likely that other samples would be infected by the same type of fungus (if they were infected at all), this sample was also imaged and is shown in Figure 7.9 below. As can be seen, a huge amount of fungal spores were visible in this image but were not found in any other examined sample. Therefore, it is assumed that the structures found inside the wood are indeed consolidant polymers and not the result of biological growth.
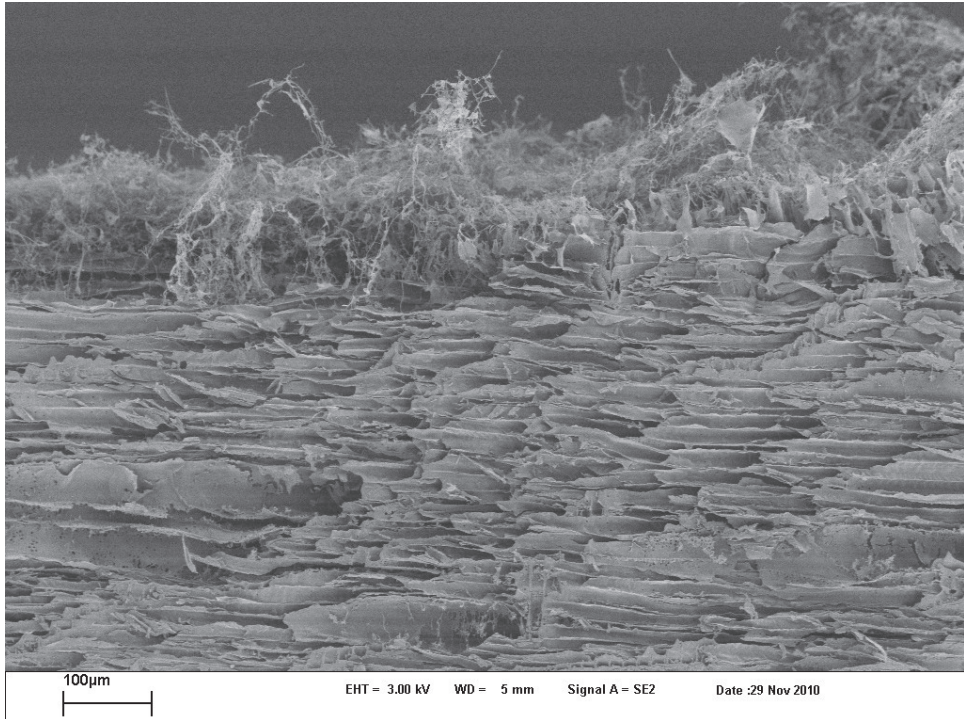
Figure 7.8: SEM image showing the edge of a freeze-dried piece of archaeological wood (sample 'Stokk 9 sjakt 7') treated with cellulose whiskers. Note that the whiskers form a fluffy layer on top of the wood (the upper third of the image) but that the wooden structure itself is relative free of whiskers.

Using the cryo-SEM made it possible to detect individual fibres at magnifications of x20.000-30.000 depending on how good the image quality was. An example of individual whiskers agglomerated into a leaf-like structure can be seen in Figure 7.10 below. This made it possible to determine that the typical whisker is about 300 nm long and around 15 nm in diameter. The size distribution is not very narrow, however, and some fibres seem to be almost twice as long as the average.
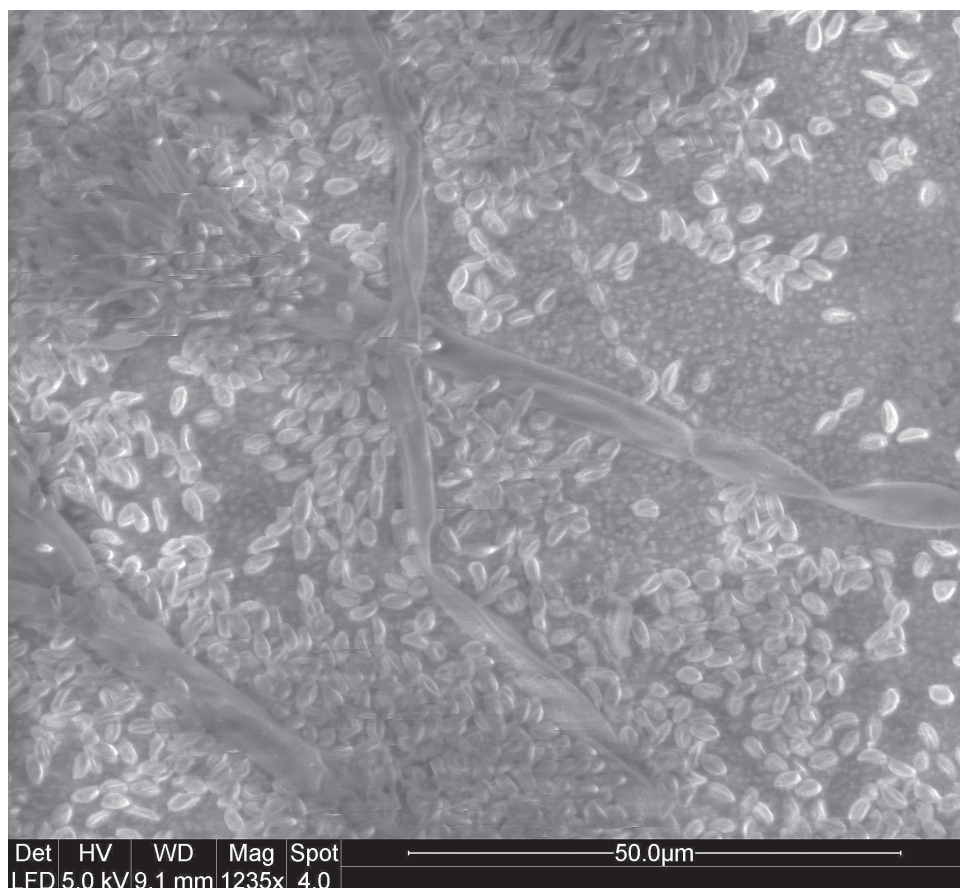
Det	HV	WD	Mag	Spot	50.0µm
LFD	5.0 kV	9.1 mm	1235x	4.0	

Figure 7.9: ESEM image of fungally attacked freeze-dried chitosan. Note the abundance of fungal spores.

These whiskers tended to agglomerate at the surface of wood and not penetrate well. PEG 1000 was added to the whiskers as it might act as a surfactant, preventing the whiskers from sticking together and thus enhancing penetration. An example of this can be seen in Figure 7.11 below. Close to the surface, even more material had entered into the wooden structure as seen in Figure 7.12. While this initial test successfully proved that the whiskers could be stabilised, PEG might not be the ideal surfactant.
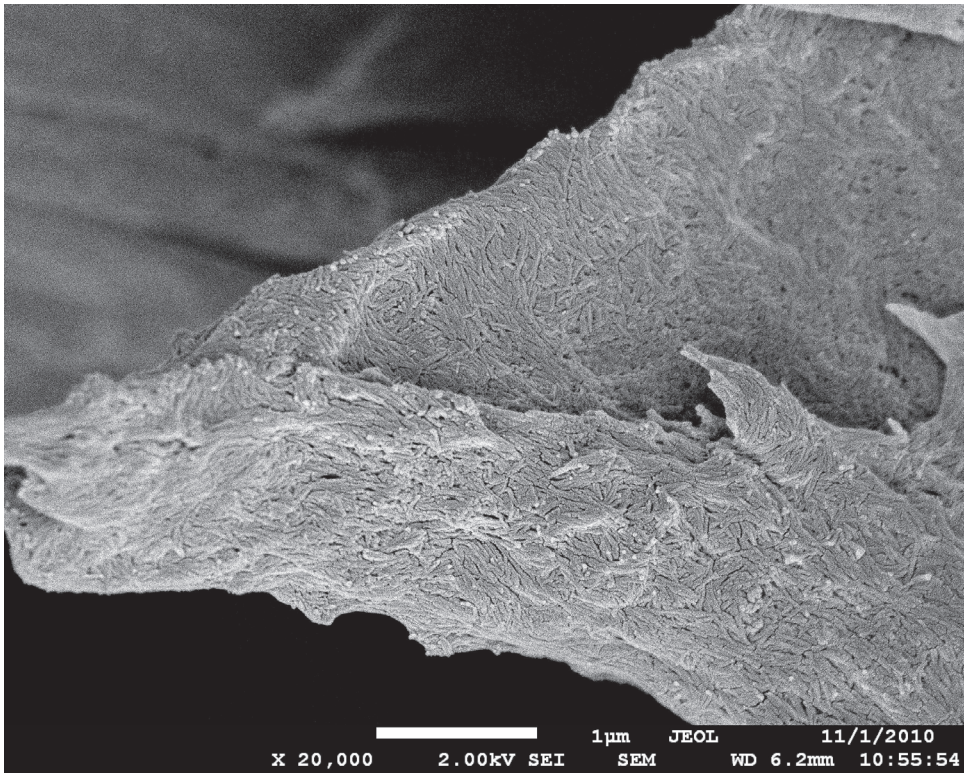
Figure 7.10: Cryo-SEM image of the freeze-dried cellulose fibres. Note that it is actually possible to see individual fibres at this magnification.
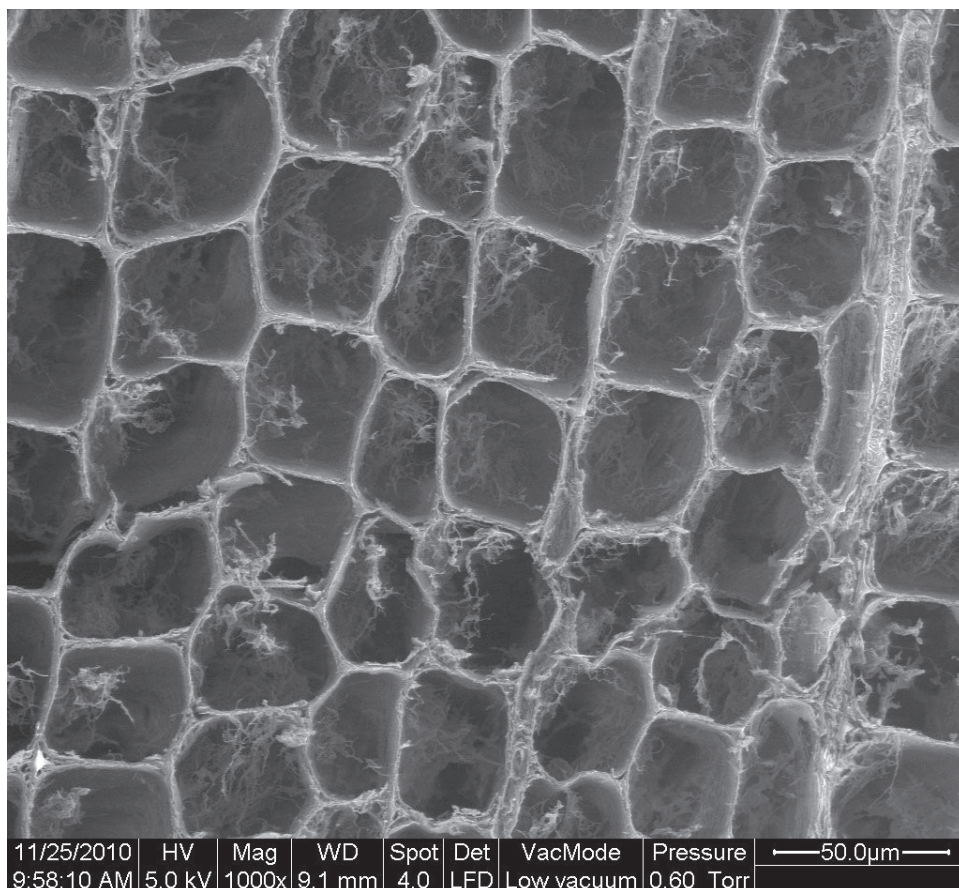
Figure 7.11: ESEM image of freeze-dried Viking Age wood (sample 'Box 7') impregnated with cellulose whiskers and PEG 1000. Note the fairly high amount of whiskers filling the voids in the cell structure.

Acetylation of cellulose whiskers is a standard procedure for modifying fibres [154]. Since acetylation changes the surface properties of whiskers, this was tested as well. It seemed that the whiskers were dispersed in acetic acid almost as well as in water. As acetic anhydride was added, the fibres seemed to dissolve.
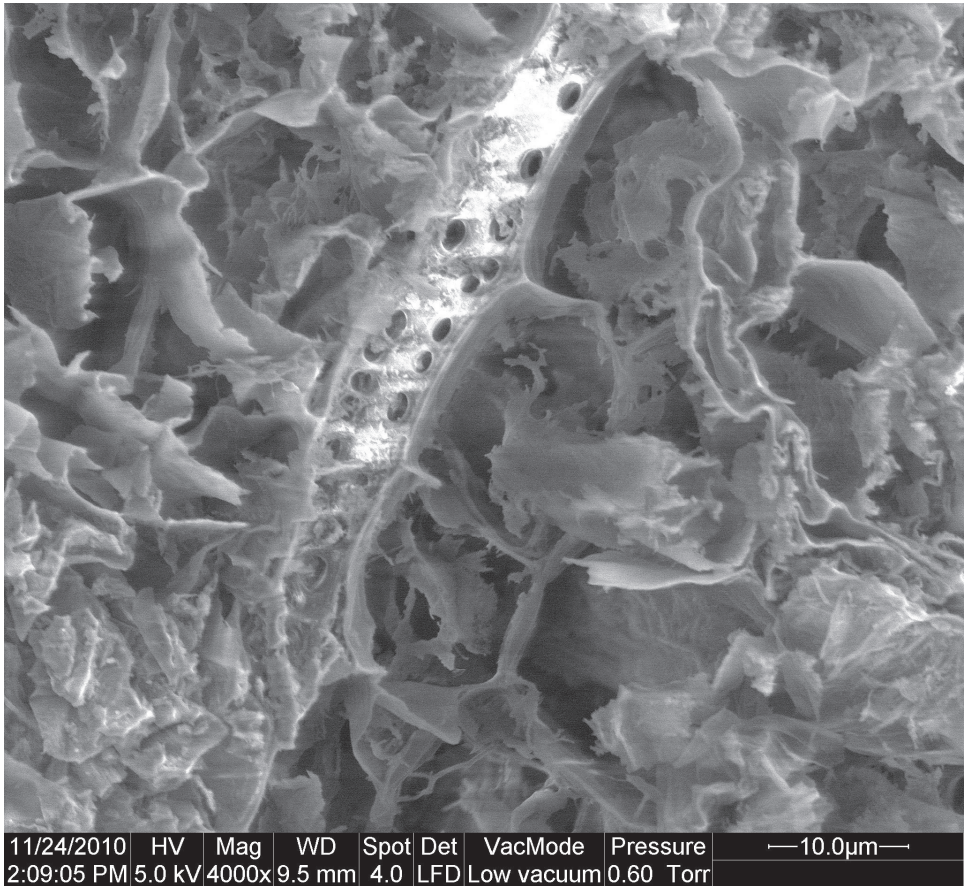
Figure 7.12: ESEM image of archaeological wood (sample 'Box 7') treated with cellulose whiskers and PEG 1000. Note that in these surface layers, significant amounts of material is deposited inside the wooden structure.

Adding sufficient acetic anhydride to make the solution completely transparent, impregnating wooden pieces with it, and then freeze-drying them resulted in massive amounts of material inside the cell structure. An example can be seen in Figure 7.13 below.
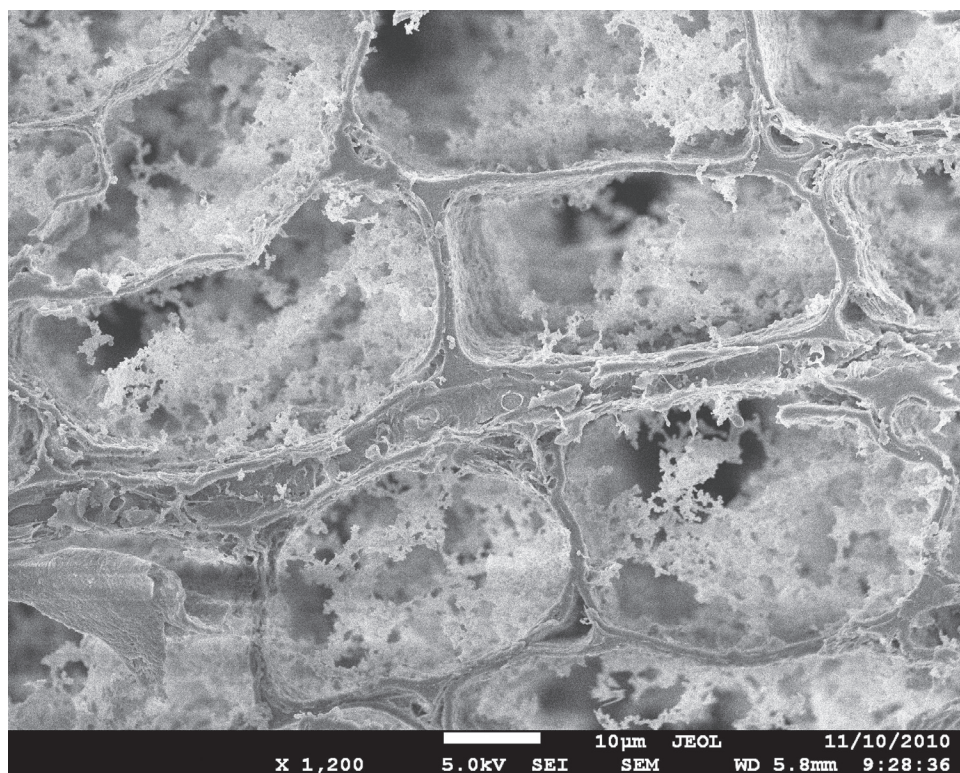
Figure 7.13: Cryo-SEM image of freeze-dried Viking age wood (sample 'Box 7') impregnated with acetylated cellulose whiskers (cellulose acetate).

Unfortunately, the structure of the whiskers had changed as seen in Figure 7.14. They had become a coherent web-like structure rather than being composed of distinct rods (compare to Figure 7.10 on page 143). The most likely reason is that the whiskers reacted with acetic anhydride to form cellulose acetate (a material well known in conservation circles for giving off acetic acid as it oxidises upon contact with air [136]). For this reason, acetylation should probably only be performed if it is essential to disperse the whiskers in non-watery solvents.
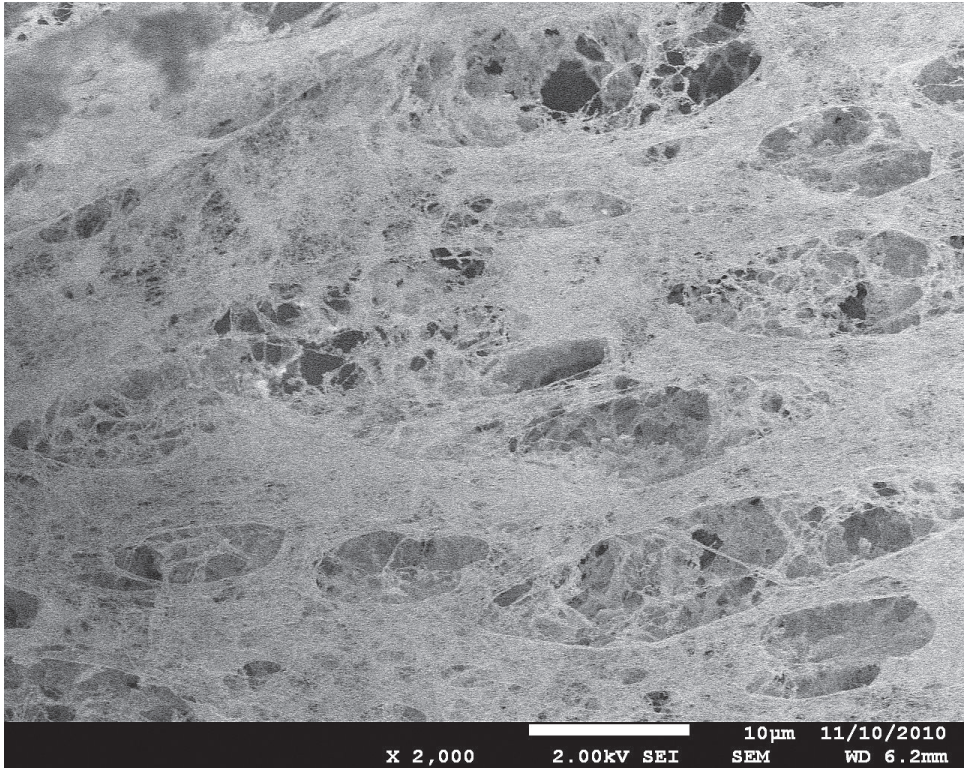
Figure 7.14: Cryo-SEM image of cellulose whiskers which were dissolved in acetic anhydride, reprecipitated, and freeze-dried. Note that the overall structure is much more 'fluffy' than the more 'flaky' untreated freeze-dried whiskers.

7.2.3.2 Zeta potential measurements

The Zeta potential is easier to measure than it is to define. It relates to the charged electrical field around a particle and as such gives an indication of electrostatic stability. A very high positive or negative Zeta potential means that particles in dispersion will repel one another and thus remain stable [155](p. 538+). A lower numerical Zeta potential, on the other hand, means that the particles will usually flocculate unless somehow shielded (note that the exact limits for stability depend on the particles but ±25-50 mV is usually enough to keep dispersions stable).

In order to determine if the fibres could be stabilised in a proper pH region, crystalline cellulose was dispersed in 0.01 M NaCl (by pulse tip sonicating them for 30 seconds at 30%

power) and a number of samples where made with varying pH values (adjusted using diluted H_2SO_4 and NaOH). A total volume of 1.5 ml of sample (at specific pH) was prepared for each measurement. 1 ml of each sample was injected into a flow cell on a Malvern Zetasizer Nano-Z instrument (with a HE-NE laser calibrated using a PS latex standard at 25°C). The flow cell was thoroughly cleaned using deionised water and pressurised air between measurements.

The results can be seen in Figure 7.15 below. The whiskers have the lowest Zeta potential in the pH 3-6 range and should thus be more stable at these pH levels. Since the differences in potential between various pH levels is limited, the stability of a whisker dispersion should not change much with varying pH.
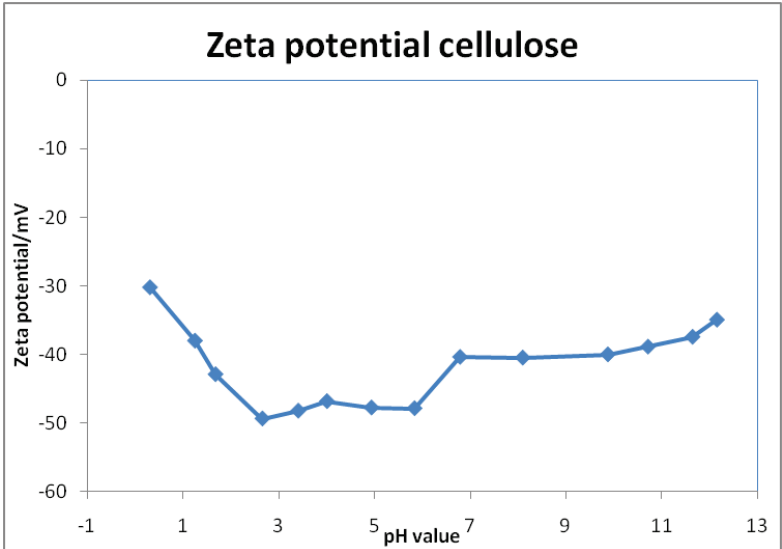

Figure 7.15: Zeta potential of cellulose whiskers at varying pH values.

7.2.4 Coagulation by iron ions

Since the flocculation of cellulose fibres was the primary reason why cellulose did not effectively enter the wood, it was attempted to estimate what kind of ion concentrations caused this flocculation ('coagulation' refers to the initial agglomerates formed by particles in suspension while 'flocculation' is a later stage where larger agglomerates are formed). If

very low concentrations of ions still result in flocculation, it will be effectively impossible to penetrate a piece of archaeological wood with cellulose whiskers.

The size of such particles can be measured using Dynamic Light Scattering (DLS). This technique measures the intensity and fluctuations of a laser beam shining through a dispersion and thus estimates the size of particles in the sample. To get accurate measurements you should know the liquid and the particles should be perfectly spherical [155](p. 236-242). Obviously, this is not the case for cellulose whiskers but the technique still gives information about the relative size of the whiskers (so if the measured diameter suddenly increases it is due to flocculation).

7.2.4.1 Critical coagulation concentration

The critical coagulation concentration, CCC, is the concentration at which dispersed particles follow the fast and irreversible flocculation rate. Normally, particles can be kept from flocculating due to electrostatic repulsion – meaning that identical particles have the same charge and will thus repel one another (see also chapter 7.2.3.2 'Zeta potential measurements' on page 147). Ions with opposite charges (also known as a counter-ions), decrease the effective thickness of the diffuse double layer around charged particles, reducing repulsion between them and thus allow them to stick together [155](p. 588). The study and modelling of such coagulation can be modelled using DLVO theory (named after the surface science pioneers Deryaguin, Landau, Verwey, and Overbeek) [155](p. 585). The relevant equation (for parallel surfaces at 25°C) is:

$$CCC = 3.86 \cdot 10^{-39} (\gamma^4 / A^2 z^6)$$

where CCC is the concentration of the coagulant, γ is dependant upon the surface potential (it is 1 for large potentials), A is the Hamaker constant (approximately 10^{-20} J for dispersions in water), and z is the valence of the counter-ions [156](p. 37).

Note that since z^6 affects the concentration for large potentials (it is related to z^2 for low ones), this means that the CCC should be directly related to $1/z^6$ in the case of the whiskers

(Shulze-Hardy's rule) [156](p. 37). Thus the type of ions in impregnation tanks containing archaeological wood becomes extremely important as a single Fe^{3+} ion causes as much coagulation as 11.4 Ca^{2+} ions or 729 Na^+ ions.

7.2.4.2 Experimental coagulation procedure

Two samples of whiskers were initially investigated using a Malvern 3000 HS_A Zetasizer. Both samples had much the same average size. However, the distribution was almost uniform in the first sample (200-400 nm) while the second had a wide size distribution (20-1000 nm). Both samples were produced from the same batch of cellulose fibres and the only difference between them is that the first sample contained the initially collected whiskers while the second sample contained the whiskers which went into dispersion after repeating the shaking and centrifugation process. This suggests that the collection stage of the production might be important as it could influence the size and/or stability of the produced fibres.

Since iron is common in archaeological finds, it was natural to determine the CCC of cellulose whiskers in Fe ion solutions. Since the effectiveness of an ion as a coagulation agent depends upon its valency, Fe^{3+} is much more potent in this regard than Fe^{2+} (see last chapter), this means that any experiments on pure Fe^{3+} ions will serve as a 'worst case scenario'. After all, the actual ion concentration in impregnation baths with archaeological wood should contain a number of different ion species. $FeCl_3$ was chosen as a source of Fe^{3+} ions and a 1 M solution of these was prepared. Note that as cellulose has a negative charge, the positive ions will affect the electrical layer around the whiskers and speed up coagulation. The Cl^- ions from the $FeCl_3$, or other negatively charged ions for that matter, will not influence coagulation time noticeably.

In total, 15 samples were prepared in 1 ml cuvettes. The concentration of Fe^{3+} was halved in each successive sample with the initial sample containing a final concentration of 0.167 M Fe^{3+} and the last sample containing $1.02 \cdot 10^{-5}$ M Fe^{+3}. In addition, two control samples without Fe^{3+}, one containing surfactant and one reference with only whiskers and water, were investigated.

Since cellulose whiskers eventually coagulate on their own, they would obviously also coagulate in the presence of ions. For this reason the experiment was not carried out using pure whiskers but whiskers to which a surfactant had been added. The chosen whiskers were ultrasonicated at 40% power output on a Misoni Sonicator 3000 for one minute. This made the dispersions visibly clearer. They were then mixed with a nonylphenol etoxylate (n=20) surfactant. The initial mixing concentration as 2 g/l so the concentration in the samples (where ion solution was also added) would be 0.33 g/g. A higher concentration is undesirable as the surfactant could be visibly seen after treatment in the SEM images at concentrations of 1 g/g. Thus a lower concentration was chosen for the stability test.

After three months, the experiment had to be terminated because some of the water had started to evaporate despite the parafilm seal on the cuvettes. Although this means that it was impossible to fully evaluate the long-term stability of the dispersions, it is still possible to make some valuable observations.

7.2.4.3   Results concerning whisker stability

Immediately following the initial mixing of the samples, the ones with the highest iron content flocculated visibly and formed a precipitate at the bottom of the cuvettes. The first sample where the whiskers did not flocculate immediately had a concentration of 0.62 mM Fe^{3+} (meaning that the sample with 1.2 mM Fe^{3+} flocculated). This means that the CCC lies below 1.2 mM Fe^{3+}. The samples below the CCC could be further analysed.

The results of the measurements show that the DLS gives very odd results from time to time. The standard deviation of signals sometimes came up impossibly narrow (for example 2.6 nm in a sample with a peak at about 150 nm). The whiskers might be arranged in a single distribution which the instrument interprets as multiple peaks – possibly because these particles are not spherical. For this reason, standard deviations are not presented in the data below and multiple peaks may not represent the actual distributions. Despite these sources of error, the estimated diameters can still be used to determine whether there are changes – particularly flocculation – happening in the dispersions.

The initial dispersed cellulose without any added surfactant or Fe^{3+} seemed to have an excellent narrow size distribution. Tip sonication reduced the average size from 200-400 nm to a narrow peak around 150 nm. This shows how essential tip sonication is to whisker dispersion. As time wore on, it became apparent that some flocculation occurred.

Table 4: DLS measurements of sample 0 (containing whiskers without surfactant).

Sample 0	Peak 1		Peak 2	
Time	Intensity 1	Diameter 1	Intensity 2	Diameter 2
0	96.8%	159 nm		
1 day	95.7%	141 nm		
6 days	100%	156 nm		
61 days	47.3%	199 nm	52.7%	482 nm
90 days	18.6%	390 nm	81.4%	1006 nm

Selected measurements from the sample without any added Fe^{3+} or surfactant can be seen in Table 4 above. While no major changes happened in the first week of measuring, some coagulation had happened after two months and that the average size increased significantly after another month of coagulation. This did not occur in the sample containing surfactants. As can be seen in Table 5, below the average size had increased slightly from the initial measurements to the final ones but no measurable flocculation had occurred.

Table 5: DLS measurements of sample 1 (containing whiskers and surfactant).

Sample 1	Peak	
Time	Intensity	Diameter
0	95.5%	138 nm
7 days	96.9%	116 nm
61 days	100%	144 nm
90 days	100%	159 nm

An example of measurements on a sample which contained Fe^{3+} ions which caused flocculation can be seen in Table 6 below. This shows how the positive ions affect the stability of the dispersion.

Table 6: DLS measurements of sample 11 (containing both surfactant and $1.62 \cdot 10^{-4}$ M Fe^{3+}).

Sample 11	Peak 1		Peak 2	
Time	Intensity 1	Diameter 1	Intensity 2	Diameter 2
0	88.8%	211 nm		
1 day	100%	128 nm		
61 days	45.9%	153 nm	54.1%	608 nm
90 days	42%	272 nm	57.6%	782 nm

After two months, all samples up to and including Sample 12 had begun to flocculate. Samples 13-15 still only gave a single peak with average sizes in the 132-167 nm range. Due to evaporation through the parafilm seal, it was not possible to test whether these samples were still dispersed after three months. Thus the sample with $8.14 \cdot 10^{-5}$ M Fe^{3+} flocculated while the samples with half this Fe concentration or lower did not.

The experiments thus show that flocculation due to positive ions will require the use of a surfactant to keep whiskers dispersed. Even though a surfactant is applied, however, the whiskers may flocculate before the impregnation is complete. After all, wooden artefacts may be treated for years in impregnation baths to ensure proper distribution of the stabilising agent – and several of the initially stabilised solutions still flocculated when left for a quarter of a year.

To proceed from these results, a number of surfactants should be tested. While a poly(oxy ethylene) might be a good starting point, various ether or alkyl groups could significantly influence results. Additionally, a combination of different surfactants may provide much better results than a single species.

7.2.5 Evaluation of cellulose whiskers as a consolidant

Although cellulose whiskers are made up of the most durable kind of cellulose, they do not form sufficiently strong support on their own to reinforce wooden artefacts. They are resistant to acids and most forms of degradation though, so whiskers might still bestow desirable properties if combined with other materials.

The initial experiments clearly showed that cellulose whiskers will fill larger cracks and voids in the wooden structure. They retain an open structure after freeze-drying which

allows any treated object to be re-treated either with further components or sometime in the future. This means that it may be possible to inject cellulose fibres into voids in wooden artefacts to construct a kind of 'scaffolding' for future consolidants to adhere to and reinforce.

Unfortunately, the fibres do not enter the smaller pores or lumens of the degraded wood as the time it takes to penetrate it is longer than the time it takes the whiskers to start flocculating.

The zeta potential measurements showed that the potential of the produced cellulose whiskers was fairly constant throughout the pH range. This means that the flocculation cannot be prevented simply by introducing the fibres in a buffer solution.

The DLS experiments demonstrated that Fe ions caused the whiskers to flocculate in most solutions. Since the results were for Fe^{3+}, this means that a solution might contain 11.4 times more divalent positive ions and 729 times as many monovalent positive ions. As such, actual impregnation baths might contain quite a bit of Fe^{2+}, Ca^{2+}, and Na^+ before the whiskers begin to flocculate (for example, you would need a Na+ concentration greater than 0.45 M – equivalent to more than 16 g NaCl per litre – in order to cause immediate flocculation). Because cellulose has a negative charge, such ions as SO_4^{2-} or Cl^- can be disregarded as they do not influence the stability of a whisker dispersion.

Since the impregnation of archaeological wood is likely to take several months, metal ions are still likely to cause flocculation unless a better surfactant than the tested ones can be found. Note that even if such hypothetical a surfactant allows whiskers to stay in dispersion, it might have certain chemical properties which could affect treated wood. Much worse, surfactant molecules might adhere to the surfaces of the degraded wooden matrix directly, possibly preventing stabilising agents from attaching – or adhere to the dispersed fibres and prevent them from attaching to the wood. In either case, more surfactants should be carefully chosen and tested if this method is further developed. Until such a time comes, it is more prudent to look towards consolidants which are easier to dissolve and get into the wood.

7.3 Chitosan

Cellulose is not the only sugar-like molecule which can be interesting for conservation purposes. From a chemical viewpoint, the shells of insects and crabs are very similar to the fibres in plants. Thus chitin is an interesting alternative to cellulose. A derivative of chitin, chitosan, is an even more attractive since it lacks most of the acetic groups in chitin, meaning that it is less likely to produce acetic acid upon degradation (which may harm metals on display in a museum).

Chitosan has been mentioned in conservation literature but mainly to point out that it cannot protect fresh wood against fungal attack – and with no comments about waterlogged wood [20](p. 244). It has been applied to paper conservation and seems to strengthen certain papers made from short fibres. If the chitosan is precipitated, the kind of alkali used will heavily influence the durability of the paper [157].

Chitosan is non-toxic and relatively easy to dissolve in weak acids. These qualities alone makes it worth testing as a wood consolidant.

7.3.1 Chemistry of chitosan

Chitin is a polysaccharide, specifically 2-acetamido-2-deoxy-β-D-glucose. It is identical to cellulose with a hydroxyl group replaced by an acetamido group. Chitosan is a derivative of chitin produced by alkaline deacetylation of the acetamido group into a primary amine group (see Figure 7.16 below). Chitosan can be obtained from crab or shrimp shells as well as mycelia. It is more biocompatible and biodegradable than typical synthetic polymers [158]. While chitosan films have been used for packaging material, the hydrophobic nature and relative weakness of the film means that petrochemical polymers are still more attractive for this purpose [159]. Chitosan has been investigated for drug delivery due to its low toxicity and biodegradability and may promote tissue growth and wound healing [158], [160]. However, the same qualities are beneficial for conservation science as it allows chitosan to be handled with minimal precautions.
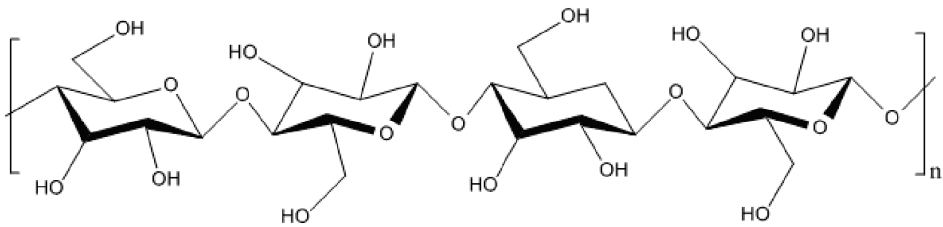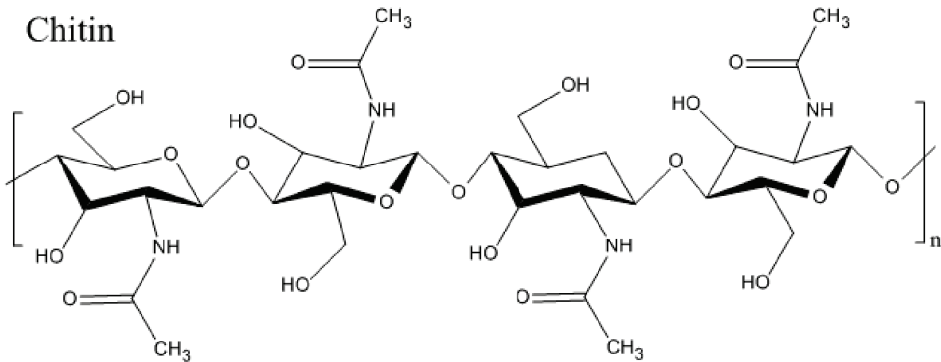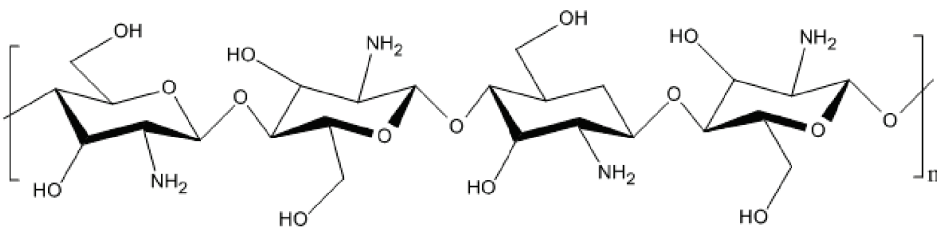
Figure 7.16: The chemical structures of cellulose, chitin, and chitosan (top to bottom) [158].

Gels made from chitosan may swell significantly in acidic (but not basic) solutions [158]. This led to the statement that "Most of the naturally occuring polysaccharides […] are acidic or neutral in nature, whereas chitin and chitosan are examples of highly basic polysaccharides." [158] Due to the chemical compositions of chitin and chitosan, this statement seems highly dubious and it does not fit with previously published results. Tests to determine the kinetics of binding Cu^{2+} to chitin also showed that this molecule is acidic with a pK_a value about 6.45 [161]. Potentiometric titrations proved that chitosan has a pK_a value

ion the range of 6.39-6.51 (inversely proportional to molecular weight) but can go as low as 6.17 for high degrees of deacetylation (94%) [162]. This means that both chitin and chitosan are slightly acidic in nature – like the other polysaccharides – and that the phrase "highly basic" should be avoided (this wording was unfortunately repeated in *Paper 1*).

At a pH of about 4, most amino groups in the chitosan chain will be protonated, causing electrostatic repulsion and enhanced swelling of the polymer network. Raising pH causes the charges to be screened and thus the chains to entangle more, increasing viscosity. In the pH range 5.8-6.4, an actual gel zone is formed (samples in test tubes can be turned upside down without running out of the tube) while even higher pH leads to phase separation. A very low pH, such as 0.5, also leads to phase separation since increased ionic strength also causes the chains to flocculate. This means that viscosity of chitosan solutions is at its lowest at pH 3-4 and rises on either side of this window [163]. As such this is the ideal pH for penetrating chitosan throughout archaeological wood.

Depending upon degree of deacetylation, chitosan might be soluble in both acidic and alkaline solutions (especually with a fraction of *n*-acetylated residues around 0.6) [164]. Since archaeological wood is more resistant to acids than base, only acids have been considered in the following. Chitosan is soluble in monovalent acids but not divalent ones. Acid concentrations of 0.1-0.15 M can dissolve $2\%^w/_v$ chitosan but generally not $2.5\%^w/_v$ (out of several tested acids, only chloroacetic acid could dissolve this higher concentration). Using HCl leads to a less viscous system than using carboxylic acids [160]. Acetic acid results in better fixation to wood than HCl [165].

Adding salt to chitosan solutions reduces the hydrodynamic volume of the molecules for both the hydrophobically modified and pure chitosan. In most cases, 10 mM NaCl was sufficient to eliminate the need for surfactants [166]. Since it is effectively impossible to remove salts from archaeological wood prior to impregnation, this effect might help to further disperse the chitosan inside the degraded wood.

Chitosan can chelate metal ions and this may be utilised in waste-water treatment (both industrial and otherwise) [158]. The adsorption is through the free electron pairs in N and O atoms. Efficiency is in the following order: $Cr^{3+} < Co^{2+} < Pb^{2+} < Mn^{2+} << Cd^{2+} < Ag^+ < Ni^{2+}$

$< Fe^{3+} < Cu^{2+} < Hg^{2+}$. The processes are influenced by the pH of the solution and concentration of ions as well as the size of the chitosan particles (with powder or microspheres adsorbing up to twice as much iron as flakes). The efficiency increases with increasing pH but takes place to some extent at pH levels at least as low as 2 [167]. This makes the chelation at least potentially viable for archaeological wood since treatment times are usually quite long.

7.3.1.1 Chitosan for wood impregnation

Chitosan has previously been tested on fresh wood in order to determine if its antifungal properties could be used to preserve wood used in buildings. Scots pine, beech, downy birch, and Norway spruce were impregnated with $2.4\%^w/_v$ chitosan solutions. The chitosan was treated with KNO_2 to depolymerise it. This resulted in four test solutions ranging from 129 to 18 kDalton in average molecular weight (MW). The viscosity decreased with decreasing average molecule size. This procedure also turns the chitosan somewhat brown depending upon degree of depolymerisation. In the longitudinal direction, the chitosan penetrated well into the beech and also acceptably into the pine and birch while the spruce only had very low uptake. Generally speaking, there was a visible difference between the uptake of the various solutions although this difference was not so dramatic as to make it improbable that the largest molecules would penetrate eventually. The uptake in the radial and tangential directions were limited by the structure of the wood [164]. In another study, wood samples were treated with 5, 2.5, and $1\%^w/_v$ chitosan. Both high (58 kD) and low (18 kD) molecular weights were used. The chitosan prevented burning although the high molecular weight was more efficient than the lower molecular weight. To achieve proper anti-fungal properties, a weight gain of $5\%^w/_v$ chitosan in water is required [169].

The pH value has been shown to be statistically significant for chitosan uptake in fresh wood, indicating that the amine groups actively contribute to the fixation. This might be due to hydrogen bonding to cellulose as well as an acid-base interaction with the phenolic groups in lignin. Lower pH values gave lower fixation rates. At pH 3.5 the fixation was about 44% lower than at pH 5.5. In the pH range 5.1-5.9, however, no change in fixation was registered and pH 5.5 remains the recommended acidity for treatments [165]. Note that

degraded wood could potentially react differently due to chemical changes to the surface groups during degradation.

Chitosan does not appear to affect the mechanical properties of fresh wood even when it mixes with the wooden matrix. Both the original and a somewhat depolymerised chitosan gave roughly the same mechanical test results [170]. It has been found that longer chitosan chains gives better fixation to the wooden matrix but the results are not consistent through the published literature [165]. Longer chains do seem to enhance the antifungal properties of the chitosan [171].

7.3.1.2 *Chitosan-cellulose film*

Combining the properties of cellulose and chitosan could be useful for both technical and medical purposes. Oligoethylene oxide diglycidyl ether (DEO) can react with the functional groups of both polymers. This decreases solubility dramatically while only substituting 3-4% of the groups with groups from the DEO. Films of cellulose-chitosan may be dry-spun and treated with NaOH or a plasticiser to modify their properties. Although films made from mixtures of the two polymers had lower mechanical strength than those made purely from one of the compounds, they still possessed sufficient strength for many purposes (breaking stress 15-20 MPa) and relatively high elongation (15-30%) [168].

A chitosan-cellulose film has been previously made. The substrate was dipped for 10 minutes in a $2\%^w/_v$ chitosan solution in 5% acetic acid, rinsed with deionised water and dipped for 10 minutes in a $1\%^w/_v$ cellulose whisker dispersion. Rinsing after each step, the procedure could be repeated until films of the desired thickness were deposited. After five minutes, very little change in layer formation occurred (although the time was kept at 10 minutes per cycle to ensure equilibrium) [159].

7.3.2 Experimental procedures for chitosan

Acids and KNO_2 were purchased from Sigma-Aldrich. Two types of chitosan were used, one from Sigma-Aldrich (chitosan, low molecular weight, from crabs) and one from Kitonor (also from crab exoskeletons). Solubility of chitosan was tested in 0.1 M solutions made by diluting concentrated monovalent acids in deionised water. Experiments were carried out in

0.1 M CH$_3$COOH using a chitosan concentration of 2%^{w}/$_w$ unless noted otherwise. The chitosan was dissolved overnight by placing the mixture on a magnetic stirrer.

Pieces of archaeological wood was cut with a razor blade and put into glass containers with chitosan solution. They were sealed with parafilm and left at room temperature for the duration of the impregnation (which was usually two weeks). After impregnation, the surfaces of the samples were rinsed lightly with deionised water, frozen in a normal freezer at -18°C and freeze-dried at room temperature.

Imaging was performed on an FEI Quanta 200 FEG-ESEM in low vacuum mode. This means that no coating was applied after cutting slices of the freeze-dried samples with a razor blade.

Full experimental procedures for the chitosan impregnation tests can be found in *Paper 3* while chapter 7.3.2.3 on page 164 summarises the methods used.

7.3.2.1 Initial impregnation experiments

Testing was carried out without many initial experiments. As soon as it was verified that chitosan was easily dissolved in monovalent acids, the objective was to get the chitosan into archaeological pieces of wood, freeze-dry them, and evaluate any strength and colour changes in the wood.

The literature suggested that acetic acid was one of the best solvents for chitosan. Since acetic acid can be a problem in museums, HCl was also tested for chitosan solutions.

Both HCl and CH$_3$COOH are suitable for getting the chitosan into solution and the choice of acid did not seem to affect viscosity. The solubility of chitosan is based on absolute amounts of acid added to the solution and not how much if it actually deprotonises. This means HCl solutions are significantly more acidic than solutions of CH$_3$COOH. Additionally, the HCl-containing samples started to precipitate after less than a month, forming thin white strands of chitosan. Even after half a year, there was no sign of precipitation in the CH$_3$COOH-containing samples. For this reason, 0.1 M CH$_3$COOH was chosen for all further impregnation experiments even though the acid is not desirable in a museum environment.

Initial experiments determined that while it is possible to dissolve chitosan up to $10\%^w/_v$, it is still very viscous down to below $5\%^w/_v$ and probably unlikely to diffuse into wood at concentrations above $2\%^w/_v$. Decreasing concentration to $1\%^w/_v$ significantly reduced viscosity but would result in less chitosan to reinforce treated items. Thus a $2\%^w/_v$ solution was used for all further experiments even though this consistency will realistically differ for various degrees of polymerisation (DPs) of chitosan.

In two impregnation trials, the chitosan was attacked by fungi (an image of the spores was shown in Figure 7.9 on page 142). Although this was not a general problem, it meant that further samples were cut and prepared while wearing gloves to minimise the risk of contamination. If the method is ever implemented for large-scale treatments, it will be important to add fungicide to the baths during the long impregnation procedure.

7.3.2.2 Imaging

Sometimes it is possible to measure the presence of a consolidant simply by looking at the thickness of the remaining cell walls before and after impregnation [73]. It was attempted to do this with the chitosan-treated wood. The chitosan investigations were carried out using an FEI Quanta 200 FEG-ESEM on low vacuum mode. This means that no coating was applied after cutting slices of the samples with a razor blade.

Without coating, it was difficult to get good quality images at high enough magnification to see individual cellulose whiskers but it was possible to determine how consolidants were distributed overall. Much like the cellulose whiskers, the freeze-dried chitosan could be found as a layer on the wood but did not fill the structure evenly.

The structure of the chitosan itself seemed fairly similar to that of the cellulose whisker 'flakes' and can be seen in Figure 7.17 below. Note that the structure of the chitosan somewhat resembles that of cellulose whiskers (as seen in Figure 7.5 on page 138). The chitosan structure is a little more uniform than that of the cellulose whiskers. It is likely, however, that these structures are formed as the polymers are being extruded from the freezing ice crystals, meaning that the way water freezes is more important for their shape than the polymers themselves.
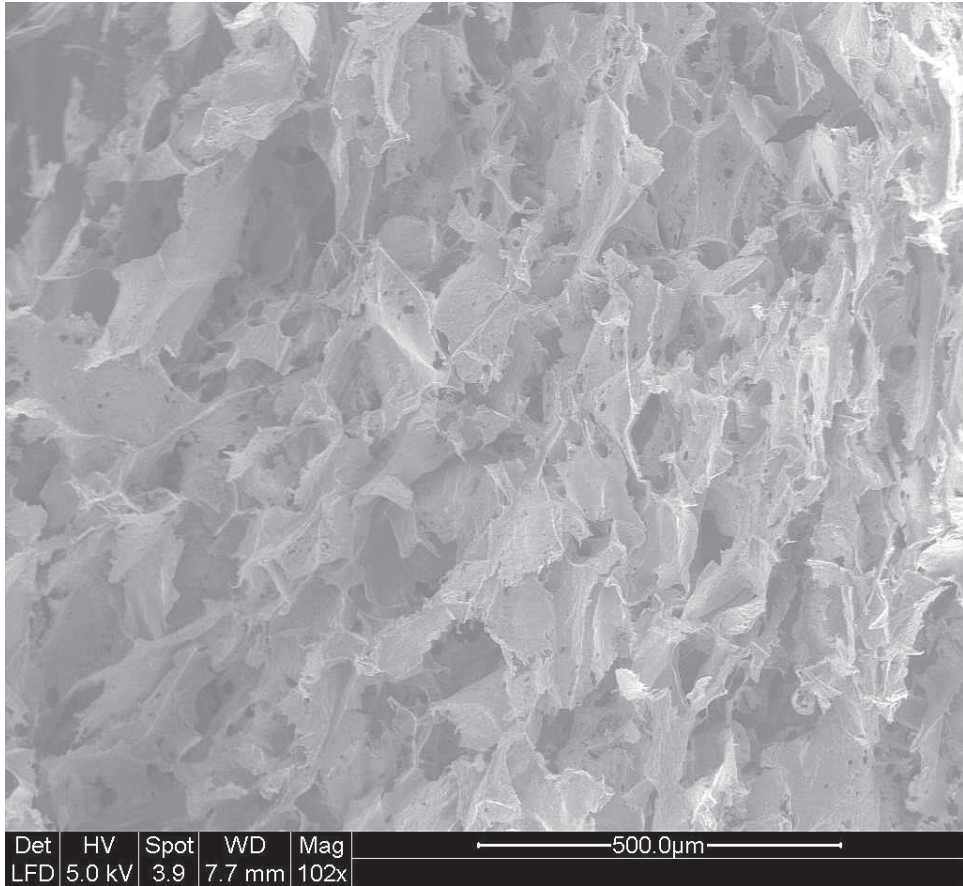
Figure 7.17: ESEM image of freeze-dried chitosan solution.

What was particularly interesting about the initial chitosan investigations was that the polymer – unlike the cellulose whiskers – did not seem to precipitate onto the remaining cell wall material. An example of the look of the wood after impregnation can be seen in Figure 7.18 below. While this might indicate that the chitosan does not penetrate at all, later investigations suggested that the chitosan simply adheres to the remaining wood, coating the degraded cell structure. This is an extremely desirable quality in a consolidant as it allows for further 'layers' to be added if/when the material starts to become brittle in the future.
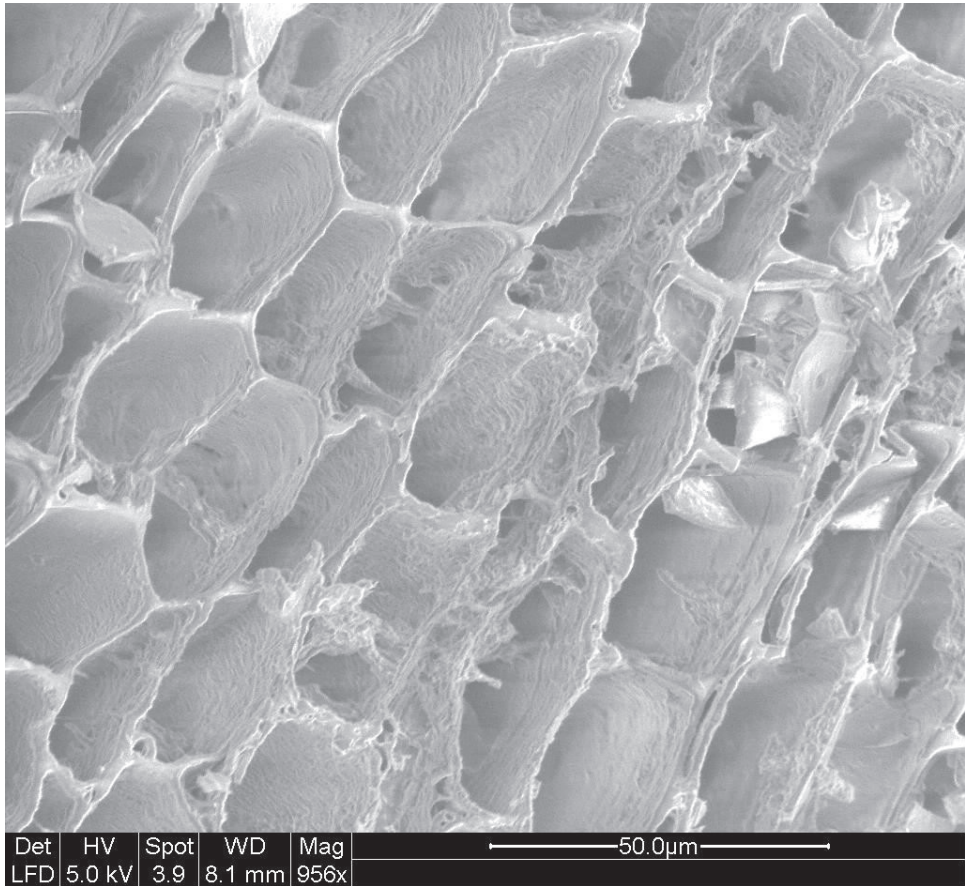
Figure 7.18: ESEM image of freeze-dried Viking Age wood (sample 'Box 7') treated with chitosan solution. Note that the remaining wooden matrix is relatively free of agglomerates.

A closer examination of the surface of the chitosan-treated wood revealed that it was fairly uneven. Although it was difficult to get sharp images at this magnification, an example of the 'lumpy' wooden structure can be seen in Figure 7.19. This structure is most likely due to an uneven coating of chitosan adhering to the wood.

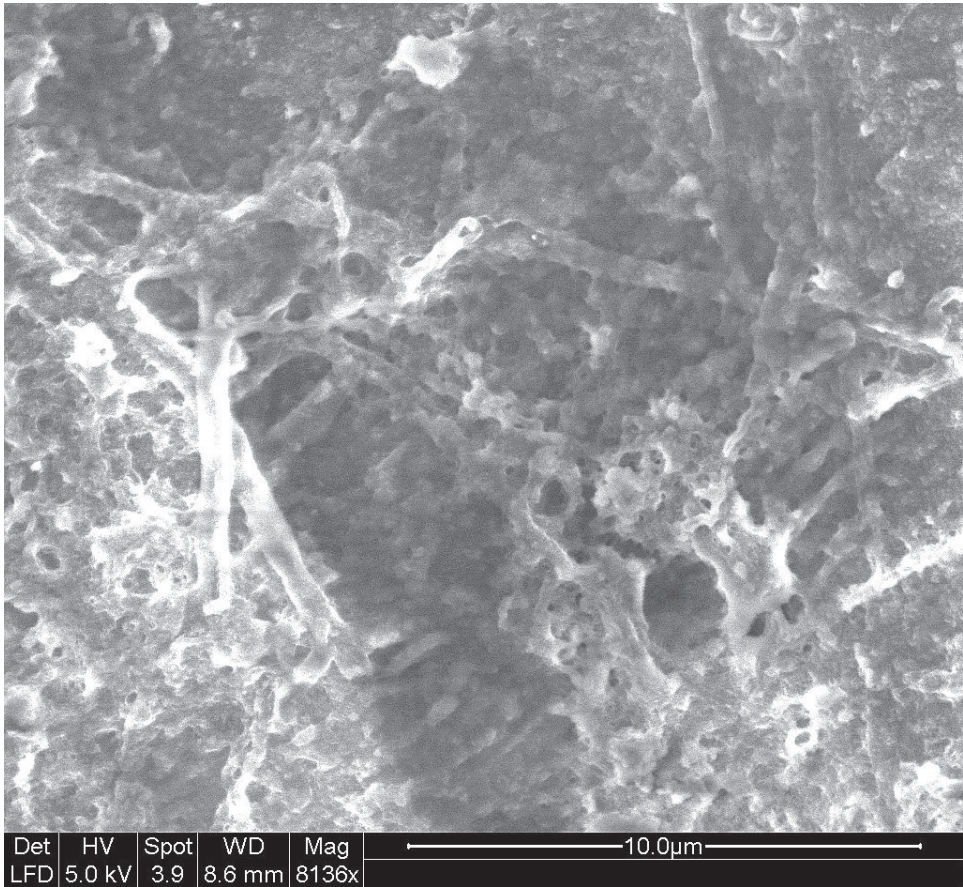| Det	HV	Spot	WD	Mag	
LFD	5.0 kV	3.9	8.6 mm	8136x	⊢————————— 10.0µm ————————⊣

Figure 7.19: ESEM image of freeze-dried wood treated with chitosan solution. Note how the surface seems uneven - likely as a result of chitosan conglomerating on it.

7.3.2.3 Determination of chitosan in test samples

The Norwegian Forest and Landscape Institute in Ås had experience with treating fresh wood with chitosan and generously offered to lend expertise in evaluating how effectively chitosan penetrated small test pieces of archaeological wood[7]. The results of this

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7 All impregnated and freeze-dried samples were analysed at the Norwegian Forestry and Landscape Institute by Monica Fongen, Eva Grodås and Erik Larnøy. Erik Larnøy also performed the statistical analysis and supplied the Figures shown in this chapter. Erik Larnøy and Gry Alfredsen also took part in the initial discussions concerning the experiments.

collaboration are shown in *Paper 3* although the results are also summarised below for increased accessibility.

The wooden pieces used were from the 'Stokk 3 sjakt 3' sample. This should be a fairly representative sample for Viking Age hardwood. As many samples as possible were cut from a single piece of wood. All impregnation experiments were carried out in triplicate to reduce the chance of non-significant results and outliers. The sample size cut was roughly 2x0.75x0.75 cm but due to the fragile nature of the wood, some samples fractured and an entirely even sample size was not obtained.

Most of the samples were impregnated with chitosan. A concentration of $2\%^w/_v$ in 0.1 M acetic acid was used to keep viscosity low. Treatments for the different series can be seen in Table 7 below. Some of the chitosan solution was depolymerised with KNO_2 (a $4\%^w/_w$ solution was added for 0.015 g or 0.022 g KNO_2 per g chitosan for series C and F respectively). The impregnation time was two weeks. Sample series F and G were heated for 24 hours at 60°C after impregnation (as this improved chitosan stability in fresh wooden samples [172]). The samples were rinsed with deionised water and subsequently frozen in a freezer. After a day, the samples were immersed in liquid nitrogen and freeze-dried. The dried samples were cut into an outer, middle, and inner part and ground before determining glycosamine contents.

Chitosan can be reduced to glucosamine monomer by hydrolysis. This means that chitosan contents can be estimated by grinding the samples and mixing them with HCl and an internal standard then heating them to 100°C for 48 hours. This degrades the chitosan. The samples may them be mixed with more acid and heated to 100°C once again for 24 hours. HPLC (High Performance Liquid Chromatography) analysis can then be performed where the glucosamine is detected using excitation at 340 nm and emission at 445 nm [173]. The main glycosamine contents can be seen in Table 7 below.

The results clearly showed that there was a vast difference in glycosamine content between untreated samples (about 10 µmol/g) and treated samples (324-735 µmol/g). There was a significant difference between the individual test pieces. This was expected due to the inhomogeneous nature of wood. An overview of the samples and their glycosamine content

can be seen in Figure 7.20. As can be seen, there is a significant difference between individual samples, although there is a noticeable difference between most of the sample series.

Table 7: Treatment of samples and average chitosan uptake.

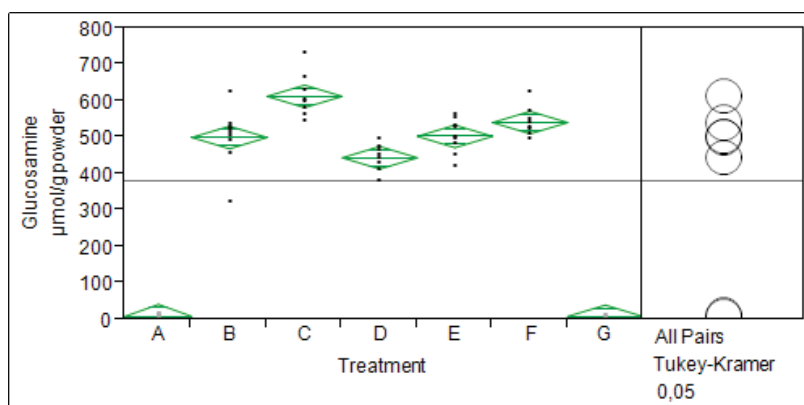| Sample series	Treatment	Mean glycosamine content/µmol/g	Average chitosan weight/kDaltons
A	Untreated (kept in acetic acid)	10.5	None
B	Chitosan (Kitonor)	502	12.25
C	Depolymerised chitosan (Kitonor)	615	6.25
D	Chitosan (Sigma-Aldrich)	446	222.5
E	Chitosan (Kitonor), heated after impregnation	505	12.25
F	Depolymerised chitosan (Kitonor), heated	543	Not measured
G	Untreated but heated	10.5	None

Figure 7.20: Glycosamine content of the various samples in the chitosan experiment.

Since series B and F are identical except for the heat treatment of series F, it is not surprising that these two series gave very similar results. Series D may contain less chitosan since these pieces were impregnated with chitosan from Sigma-Aldrich which may have a different composition from the others. This is likely because the average molecular size is larger in Series D, explaining why less material penetrates. It seems odd that series C

contains more chitosan on average than series F since slightly more KNO_2 was used to depolymerise the chitosan used for series F – meaning that the average molecular weight of the chitosan should be smaller than for series C. Since series C and F were cut from different wood fragments, an explanation might be that one fragment was more degraded and thus allows more chitosan to penetrate into it. This theory contradicts the results from series B and E, however, as these gave roughly the same result even though the samples were from different wooden fragments. The explanation might lie in the light rinsing of the surface of the treated samples, as a depolymerised chitosan would most likely be easier to wash out of the samples (leading to a lower result for series F than series C). Leaching might also have happened during the time series F samples were heated, so further experiments will likely be needed to confirm and explain this difference.
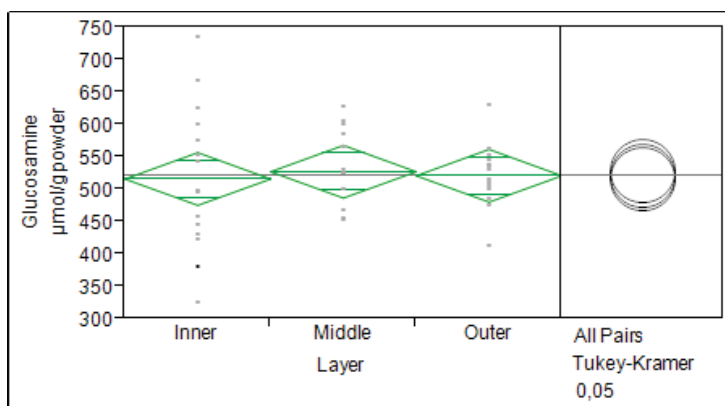

Figure 7.21: Glycosamine content of the chitosan-treated samples by layer. Note that samples A and G are not included since these were not treated with chitosan.

Since each sample was cut into an outer, middle, and inner part, an uneven distribution of chitosan would result in much higher average values in one category than another. As can be seen in Figure 7.21, there is no such consistent trend. While the samples from the inner part of the wood certainly have the largest spread, they contain higher as well as lower glucosamine than the middle part of the samples, so the average value is virtually identical for all locations. The spread might be due to cracks or partial collapse of the samples. Voids may fill with chitosan and thus give a high glucosamine weight content. On the other hand,

167

partial collapse, possibly having happened while the wood was in the ground, would make it more difficult for the chitosan to penetrate into the samples. It seems like the middle part of the wood seems to contain slightly more glucosamine on average – while the outer parts contain less. A possible explanation is that slight amounts of chitosan were washed from the surface when the samples were rinsed after the impregnation was complete. None of these differences are statistically significant so these trends may be completely accidental.

7.3.3 Evaluation of chitosan as a consolidant

With its cellulose-like structure, chitosan has some 'backup' carbon chains in case the oxygen in the rings gets severed. The oxygen links along the chain should also be more stable than aliphatic ethers without any ring structures (such as PEG). This means that chitosan should theoretically be stable enough to endure a while in a museum (at least compared with other flexible, water-soluble polymers). While fungal attacks can be a problem, adding fungicide to impregnation baths is already done for many consolidants.

One of the most interesting aspects of chitosan, is not purely its strengthening of the wood but its ability to bind metal ions and thus prevent their catalytic effect on degradation processes. This could significantly increase the lifetime of both the degraded wood itself and any other polymers potentially used to reinforce it. Unfortunately, it was not possible to evaluate how effectively chitosan chelated metal ions within this study.

When impregnating with chitosan, a pH of 3-4 results in minimal viscosity and thus potentially better penetration. On the other hand, a higher pH results in a much higher fixation rate (with an optimal rate at pH 5.1-5.9 provided degraded wood reacts the same way as fresh wood). Since the size of chitosan molecules is also affected by salt content, this effect will most likely counteract the slight swelling of chitosan at the increased pH. Due to the natural acidity of wood, a pH around 5 seems like a reasonable compromise which allows good penetration and fixation while minimising damage to the wood. Additionally, it was found that the 0.1 M solutions of CH_3COOH with $2\%^w/_v$ chitosan has this pH.

While the tests on fresh wood gives a good starting point, some of the considerations are not relevant for archaeological artefacts. For example, loss of chitosan due to weathering is not a problem in a museum environment. Several of the polymers used for conservation for future display in a museum environment, such as PEG, would not endure the conditions in outside buildings. This means that chitosan should be acceptable for museum use.

The initial study clearly shows that the $2\%^w/_v$ chitosan solution in 0.1 M CH_3COOH penetrated all the way into small pieces of archaeological wood in two weeks. Thus chitosan is potentially a good consolidant for archaeological wood.

It was difficult to see chitosan directly in the SEM images. The relatively low chitosan concentration ($2\%^w/_v$) might affect how readily it is seen. Even if an increase in width of the remaining cell wall material could not be measured, the treated wood cracked and powdered much less than untreated wood (or wood treated with cellulose fibres) when cutting the freeze-dried samples with a razor blade. Based on this, it seems that chitosan offers sufficient strength to keep smaller fragments together but it has not yet been tested on larger archaeological wooden remains.

7.4 Calcium carbonate nanoparticles

Although many types of nanoparticles might be interesting for conservation purposes (see chapter 4.1.10 'Nanoparticle treatments' on page 68 as well as Paper 1 in the appendices), time limitations made it impossible to fully explore the potential types during this project. Still, a few initial trials were carried out at the Max Planck Institute for Colloids and Interfaces in Potsdam, Germany[8].

Pieces of Viking Age softwood (samples 'Box 7' and 'Stokk 9 sjakt 3') were taken in the waterlogged state and immersed in solutions of concentrated $Ca(OH)_2$. After a week the samples were removed, freeze-dried, and examined on a LEO 1550 FE-SEM equipped with a Gemini detector (LEO Elektronmikroskopie GmbH, Oberkochen, Germany). The samples were sputtered with Au/Pd. $Ca(OH)_2$ was purchased from Sigma-Aldrich.

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8   Kuy-bock Lee was working on growing $CaCO_3$ matrices *in situ* and offered to help conduct a few experiments. He prepared the impregnating solutions and carried out the SEM imaging presented in this chapter.
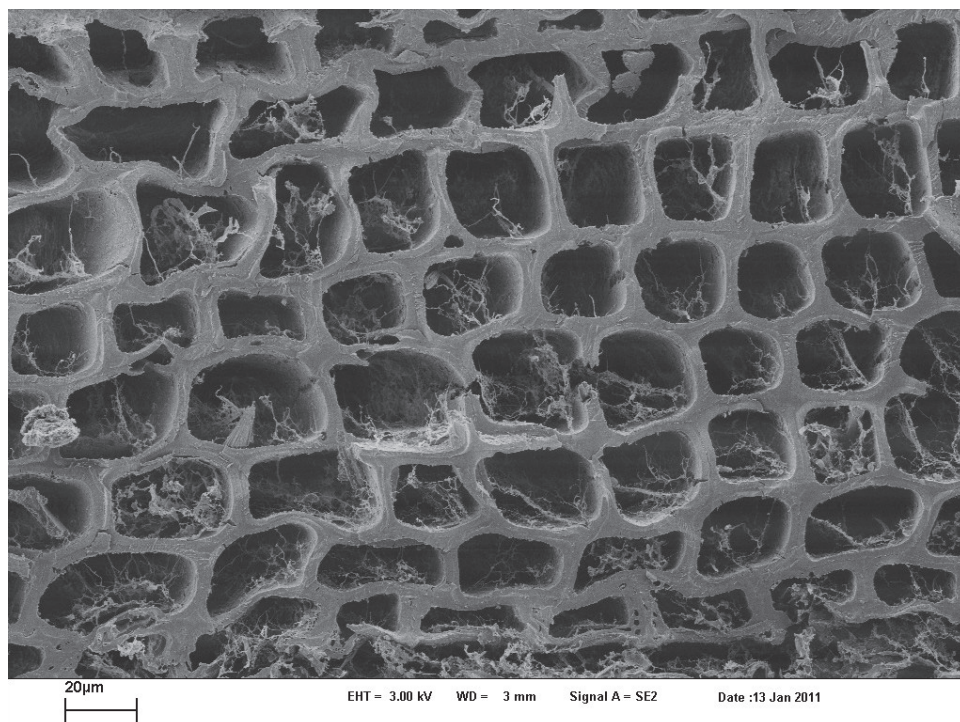
Figure 7.22: SEM image of a freeze-dried piece of archaeological wood (either sample 'Box 7' or 'Stokk 9 sjakt 3' treated with Ca(OH)$_2$.

7.4.1 Impregnation experiments and imaging

The samples are treated with Ca(OH)$_2$. Upon contact with CO$_2$, this reacts to form CaCO$_3$. For this reason, it is important to seal both the solution and the test pieces during impregnation to prevent the CO$_2$ in the atmosphere from reacting with the solution. With the current debates about CO$_2$ sinks, it might be attractive to label this method as environmentally friendly. One should be aware, however, that the reason the process works is because it is reversible, meaning that when in contact with acid, the CaCO$_3$ releases CO$_2$ along with water and becomes a salt (for example CaCO$_3$ + H$_2$SO$_4$ → CaSO$_4$ + H$_2$O + CO$_2$). This means that CO$_2$ storage is temporary.

Test pieces of wood from the samples 'Box 7' and 'Stokk 9 sjakt 3'were impregnated with a saturated solution of $Ca(OH)_2$. The glasses were sealed with parafilm to prevent CO_2 from reaching the solutions and initiating the reaction. The samples were exposed to air before drying them. The imaging was done on a LEO 1550 FE-SEM equipped with a Gemini detector. An overview of the structure can be seen in Figure 7.22 below.

It is clear that $CaCO_3$ does not grow enough to offer support to the wood. The thin strands left inside the structure are most likely due to ions conglomerating as ice is formed during the freezing process. A close-up of the strands can be seen in Figure 7.23 which clearly shows that they seem to be covered by some kind of minute spherical structures – most likely growing $CaCO_3$ formations.
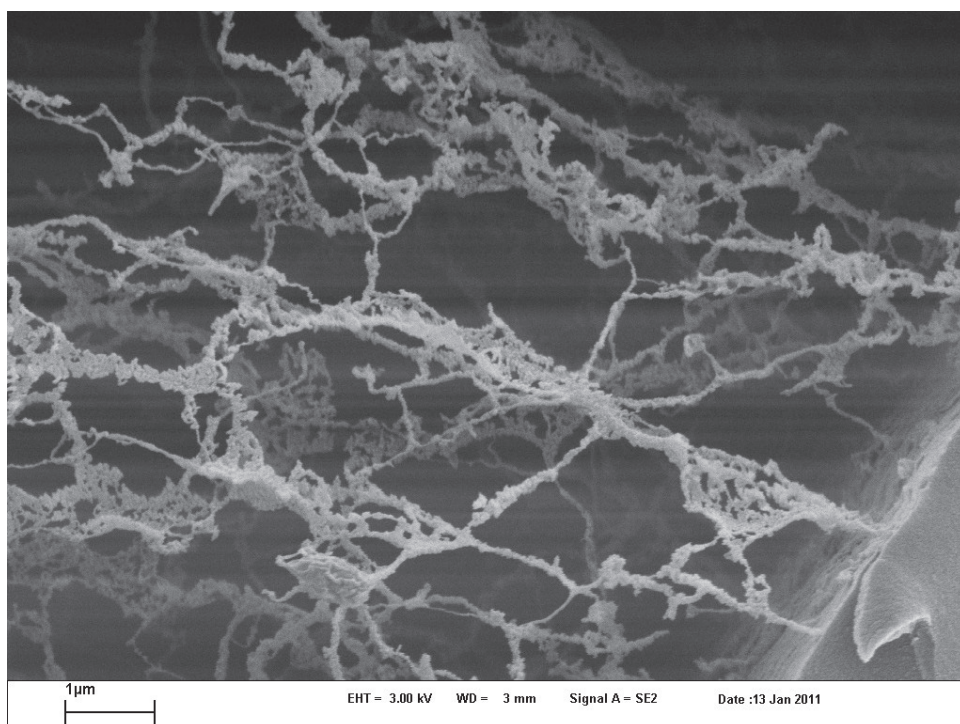

1μm

EHT = 3.00 kV   WD = 3 mm   Signal A = SE2   Date :13 Jan 2011

Figure 7.23: SEM close-up of the structures inside a freeze dried piece of wood treated with $Ca(OH)_2$. Note the uneven structure of the strands which might be due to growth of $CaCO_3$.

7.4.2 Evaluation of calcium carbonate for conservation

These experiments have not been sufficient to fully evaluate the possible applications of $CaCO_3$ for conservation purposes. The imaging indicates that there is some growth inside the wood and thus that penetration is likely efficient. This is expected since the original solution contains ions of limited size rather than large polymer molecules. This means that it should be possible to use similar growth inside the wood to add a reservoir of acid-neutralising agents.

7.5 Hybrid and composite materials

One of the more promising ideas in conservation science might be to mix different materials to achieve certain desired properties. An example is an organic matrix which supports the finds but contains inorganic particles which are able to neutralise acid (these ideas are also expressed in chapter 8.6.1 'Nanoparticles' on page 185 as well as in *Paper 1* in the appendices). Unfortunately, time did not permit thorough testing during this project but a single experiment on mixing PF with cellulose fibres was carried out..

7.5.1 Mixing PF and cellulose whiskers

Since cellulose may reinforce existing polymers, it would be interesting if it could also enhance the properties of the PF if used for treatment of archaeological objects.

The collected but untreated cellulose whiskers (described in chapter 7.2.2.1 'Producing cellulose whiskers' on page 134) were poured into a F:P 1.4 prepolymer mix and HCl added as a catalyst (adjusting pH to just above 0). When mixing, the contests of the beakers became white, unlike the pure PF mix which stays transparent. After standing in the fume hood for an hour, a clear watery phase had formed in the top few mm of the solutions. The solutions were transferred to an airtight container and placed in the oven at 70ºC. The samples were observed over the next several days and although the solid PF material should only take up about 25% of the total volume, the white phase took up about 80% of the volume with the small watery phase on top remaining clear. This ratio did not change visibly over the next week.

After seven days, the lid was taken off the airtight container and the PF was allowed to cure as the water evaporated over the span of a day. What remained was a reddish brown material which resembled the novolac samples described in chapter 6.3.2 'Pure polymer experiments' on page 89 (although of a slightly more brown colouration). If picked up and squeezed slightly, the material fell apart much like a compressed powder.
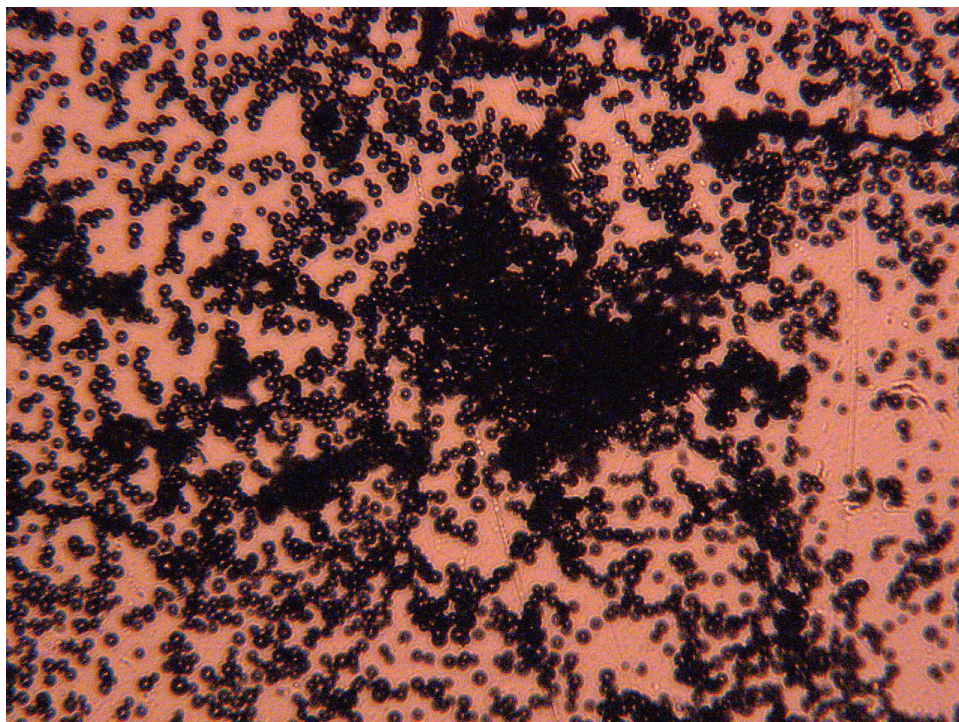

Figure 7.24: Microscope image showing PF spheres formed around cellulose whiskers in suspension. The spheres are 10-20 μm in diameter.

Some of this powder was examined in a Leitz Diaplan microscope using a Phaco 1 160/- lens and with a Imaging Source DFK41AU02 USB colour camera attached in order to determine the shape and size of the individual particles. As seen in Figure 7.24 above, the particles are spheres with diameters about 10-20 μm.

The low pH in the dispersion may cause the cellulose to flocculate rapidly (as seen in chapter 7.2.3.2 'Zeta potential measurements' on page 147). If this is so, the actual size of the flocculated cellulose – and thus of the PF coated spheres – is likely highly random and

the results not reproducible. It is particularly interesting that the PF does not form an organic phase when mixed with the cellulose whiskers but the components seems to form spherical particles. Cellulose might stabilise the PF, possibly forming an emulsion by distributing itself on the surface of formed PF spheres.

While it would be interesting from a pure research perspective to go back and vary concentrations to understand the process better, it may not be relevant for conservation purposes. The spheres produced in this experiment are too big to properly penetrate the pores in archaeological wood and cannot be used as a kind of durable particle 'filler'. On the bright side, the results indicate that PF adheres to the cellulose whiskers in suspension and thus that it may be possible to easily coat cellulose-treated surfaces with PF.

8. Summary and future ideas

The following chapter summarises some of the more important discoveries during this work. Additionally, a number of possible avenues for future research are presented.

Since the aim of this work was to design new consolidants, the theoretical list of requirements for such will be summarised. Of course, the actual results from the tests on various compounds should not be overlooked. Both results on phenol-formaldehyde (PF) as well as more biomimetic materials (specifically cellulose and chitosan) are summarised in the following.

8.1 Chemists in consolidant design

When chemists enter the field of conservation, they have to leave many traditional approaches behind. Working in the museum environment usually means no control over atmosphere or temperature and ventilation is often rather limited. Time frames are often very long in conservation where impregnation can go on for years. This does not mean that the role of chemists in conservation science is limited to performing analyses (although that, too, is important).

The task of finding new consolidants requires a comparison between existing methods as well as an understanding of why some attempts fail. By understanding the molecular structures of consolidants, it is possible to predict roughly how they might behave. It also means that certain chemical groups in a polymer can be exchanged in order to increase flexibility or resistance to acids and oxidation. Modifying surface groups is also a way of controlling solubility or enhancing the interaction between the remaining wooden material and the consolidant. The same approach might substitute a toxic group or solvent with a less harmful one. Similarly, polymerisation reactions or treatments might be broken down into steps so initially toxic monomers are pre-polymerised in order to produce an oligomer which can be used directly in the museum environment (see discussions regarding PF in chapter 8.5.2 'Novolac reinforcement of alum-treated wood' on page 183).

Since cost can be a barrier to implementing a new kind of consolidant, various alternatives should be taken into account. Perhaps the expensive parts of a polymer can be

replaced by cheaper chemicals with similar properties. An alternate synthesis path might reduce production costs significantly. Such considerations are usually not possible for conservation professionals without an extensive chemistry background.

8.2 Designing a new consolidant

Looking back at previously tested consolidants for archaeological wood, it seems like problems with poor penetration or plasticisation are primary concerns. Durability of both the polymer and what remains of the wooden material are also extremely important – as is maintaining the look of the treated wood. Finally, ensuring the safety of conservators who have to handle objects during treatment is also vital. The full list of requirements are most likely so specific that it will not be sufficient to simply use a material designed for a different purpose. Rather, specific research towards new consolidants should be undertaken.

Since reversibility will most likely not be feasible, re-treatability should be an extremely important factor when designing a new consolidant. This is best achieved by leaving an open structure (preferably the structure of the wood itself) to allow for more treatments in the future. Other pressing requirements are ordered in the list in chapter 5.2 'Ideal consolidant requirements list' on page 75.

A single material is unlikely to be able to provide both strength, flexibility, suitable colour and acid-neutralising properties. Thus future consolidants will likely have to be composite systems where each component fulfils a specific purpose. The oft repeated example is a polymer with embedded nanoparticles for acid neutralisation. More concrete ideas are given below in chapter 8.5 'Developing investigated methods' and chapter 8.6 'Future avenues of research'.

8.2.1 PF as a consolidant

Acid-catalysed PFs (novolacs) might be suitable for treating the very acidic alum-treated wood as sulphuric acid (which might be present in several kinds of archaeological wood) does not degrade the cured polymer. Besides, PF is one of the few synthetic polymers which has survived a hundred years worth of real-time ageing in a museum environment.

Looking at the ideal list of requirements (in chapter 5.2 on page 75), PF easily fulfils the first half of the requirements – although nr. 4 (whether it warps the wood) must be verified using larger pieces of wood. Requirements about penetration, shape and durability are fulfilled. It is especially vital that the phase separation which occurs as novolacs polymerise seems to make the organic phase adhere to the remaining wooden structure while water gathers in the lumens and voids of the wood, preserving the wooden structure. Toxicity can be reduced significantly by creating a pre-polymer (for example a pentamer) which is still small enough to penetrate into the wood but does not enter the body as readily as phenol monomers. Colour is not a significant concern for a material which will only be applied to the inner parts of artefacts. Unfortunately, this method cannot be applied to alum-treated wood in its current state as the alum crystals are dissolved by the watery formalin used for polymerisation. Some other treated solvents, like propan-2-ol and acetone, seemed to react with the prepolymer molecules and chance the properties of the cured polymer.

Even though phenol and formaldehyde are toxic materials and the resulting polymer quickly obtains a bright red colour upon contact with air, PF treatment may be a way to treat severely degraded wood and reinforce the centre of powdery fragments. For this reason, it should be remembered as an emergency solution which might be developed and implemented for degraded alum-treated wood.

8.2.2   Cellulose whiskers as consolidants

Cellulose is found in wood already and initial tests showed that such 'cellulose whiskers' (small rods of highly crystalline material which are resistant to acid) adhered to the surface of archaeological wood. During freeze-drying, the whiskers formed into a porous open structure. While cellulose fibres may reinforce other polymers or even help fill voids in archaeological material, the tests showed that it was extremely difficult to keep the whiskers from conglomerating in the presence of metal ions. Even moderate amounts of surfactant did not prevent this flocculation from happening over time. Due to the metal content of archaeological wood, this means that cellulose whiskers will most likely agglomerate before penetrating into the items to be treated. As such, cellulose whiskers fail the second requirement on the list (see chapter 5.2 on page 75) due to lack of penetration. It may also

fail the requirement for interaction with the degraded wood (nr. 5) although this is less clear. For this reason, the method cannot be recommended in its current form.

Cellulose whiskers still fulfil the other requirements in the list. They may still have a role in conservation science as gap fillers which leave an open structure for further impregnation or as reinforcing fibres in another polymer. It is also possible to test a wider range of surfactants in order to determine if the tendency to flocculate can be overcome. It should also be tested how said surfactant affects the treated wood to which it will likely adhere. Ideally, surfactants might be cross-linkable later on to act as a fibre reinforced polymer attaching directly to the surfaces of the degraded wood.

8.2.3   Chitosan as a consolidant

The ability of chitosan to penetrate test samples along with its ability to chelate metal ions and natural anti-fungal and -bacterial abilities makes it a promising candidate when considering new consolidants. Since it can penetrate wood in a 0.1 M acetic acid solution, the resulting pH value of roughly 5 is compatible with the wood (although the acetic acid may certainly react with other metallic items on display). A $2\%^w/_v$ was shown to penetrate into small pieces of archaeological wood and distribute itself evenly after two weeks of impregnation at room temperature. When cutting treated and untreated pieces, it was evident that the chitosan had stabilised the wood, enabling clean cuts with a razor blade rather than the powdery results obtained from untreated freeze-dried samples. This means that chitosan fulfils every point on the list of requirements (in chapter 5.2 on page 75) provided that future test pieces do not warp and costs are comparable to that of PEG because the chitosan baths are easier to recycle. This makes chitosan extremely suited as a potential consolidant.

In the future, it will be imperative to continue these impregnation and stabilisation tests on larger pieces of wood to fully evaluate shrinkage and stability of chitosan-treated archaeological wood before any actual implementation with archaeological material is attempted.

8.3 Methods and approaches

Some of the tools used may have special advantages or disadvantages when applied to the field of conservation. These are discussed in the following.

8.3.1 Imaging

Tomographic imaging is a powerful tool in conservation science. The x-ray synchrotron investigations carried out at the Paul Scherrer Institute offered views of the 3D structure of the degraded wood, allowing us to see how consolidants are distributed inside the degraded wooden matrix (presented in chapter 6.4.1 'Imaging of PF-treated samples' on page 100). Tomographies offer an advantage over more traditional SEM investigations as the 3D reconstruction makes it possible to move along pores and vessels in the wood to see if they are blocked at any point. Blocked vessels would prevent future treatments from penetrating evenly and most likely from reaching significant portions of the wood.

8.3.2 Phase separation

The phase separation witnessed during novolac polymerisation is extremely interesting because it seemed in the x-ray tomographies that polymer material was deposited in the degraded wood, leaving the voids in the wood free of consolidant. This makes such phase separation an extremely desirable quality – no matter that the actual consolidant is – and worth incorporating deliberately into other consilidants by modifying their molecular structure to achieve a suitable balance between hydrophilic solubility and hydrophobic precipitation.

8.3.3 Freeze drying temperature

The freezing of samples was carried out both in liquid nitrogen (-196ºC) and in a normal freezer (about -18ºC). Samples frozen at the lower temperature seemed more prone to cracking during the freezing process and whatever consolidant was applied often extruded out of the ends of the treated wood. Especially the latter problem was significantly less

pronounced when freezing at high temperatures – even if the sample was subsequently cooled using liquid nitrogen.

In SEM images recorded after freeze-drying, it was very hard to see the consolidant in the samples frozen at high temperatures. In the samples frozen in liquid nitrogen, the consolidant formed strands in the lumens of cells. Most likely, slower freezing times means that consolidant material is pushed into the remaining cell wall material as water in the samples freezes, filling the lumen with ice. It is possible that this leads to better stabilisation of the treated items.

As discussed in chapter 4.1.1 'Freeze drying' on page 51, water sorbed in archaeological finds may become supercooled. If so, the resulting water might boil during the drying process. This conflicts with the observation above where a mild freezing seems to equate a better distribution of any consolidants added to the wood. For this reason, it may be ideal to freeze treated objects slowly at first and then lower the temperature below -38°C before the drying process commences. Of course, the effect of the growing ice crystals inside the treated items should also be further investigated, as the slower freezing may result in ice crystals growing large enough to damage the remaining wooden matrix. Keeping a low temperature during the drying process might also result in less damage than drying at room temperature and might improve the quality over the results obtained here.

8.3.4 Dynamic Light Scattering

Using DLS is fairly simple and the method provided a good tool for estimating flocculation over time. This in turn gives reasonable estimates of shelf- or impregnation time limits on consolidant dispersions. Even though the theory is developed for spherical particles, reasonable results were obtained for cellulose rods.

On the other hand, the method should not be used without caution. Single distributions of uneven particles may be interpreted as multiple distributions and the width of bands were sometimes absurd (such as a standard deviation of less than 3 nm in a sample of whiskers of highly variable length). In order to avoid 'over-interpretation' of obtained results, other methods – such as turbidity measurements – should be considered as well.

8.4 Closed avenues of approach

Several ideas were put forth during this project which did not really work as intended. While it is notoriously difficult to publish so-called 'negative results', it is still important for the conservation community to know about methods which should most likely not be pursued.

Carbon nanotubes is one such problematic agent. In theory, the stability of carbon nanotubes would make them ideal in fusing inside wood. Unfortunately, carbon nanotubes are extremely expensive, difficult to disperse evenly, and next to impossible to synthesise in a fully reproducible manner. This means that their actual sizes and shapes will vary widely within a single batch. Even assuming that it would be possible to disperse the tubes in ancient wood (which it may not be), the kinds of chemicals required to modify their surfaces to interact and fuse would most likely destroy the wood (concentrated nitric acid is often employed for this). Finally the carbon nanotubes are utterly black and would colour treated wood, giving it an undesirable appearance while on display.

Another problem is furfuryl-related products. While these seem chemically similar to PF, the resulting polymer reacts even more radically, bringing the water in every test sample/solution to the boil. The resulting polymer was pitch black and thus unsuitable for objects which should go on display. Finally, furfuryl alcohol polymer reacted strongly with lead coupons in the Oddy corrosion test, showing that it would be difficult to keep furfuryl alcohol-treated items near other finds being displayed in a museum. Thus it might be possible to add minute amounts of furfuryl alcohol or furfuran without visible negative effects on treated objects but one would need an exceedingly good reason for doing this.

8.5 Developing investigated methods

While some some useful observations were made from the existing experiments, they were insufficient to fully evaluate the applicability of the tested consolidants. The following avenues of research are a logical extension of the performed experiments.

8.5.1 Tomographic imaging

Given the usefulness of 3D imaging, it would be very interesting to run further samples to compare some of the biomimetic approaches with the PF-treated samples. Unfortunately, this has to be part of possible future investigations.

8.5.2 Novolac reinforcement of alum-treated wood

While it should be stressed that using novolacs might not be the most ideal solution for newly discovered wooden artefacts, it might serve as a "Plan B" for existing fragile items. The precarious state of the Oseberg find means that it is essential to work out potential solutions – even if these do not adhere to every ethical ideal, as it would be far worse to lose the objects forever!

Toxicity can be reduced by pre-polymerising the novolac. Oligomer molecules were easily dissolved in propan-2-ol and penetrated easily into the wood. With less than 1% free formaldehyde in the organic phase, the mix should be safe to work with even in a museum. The challenge is to find a way to further cross-link those oligomers without resorting to watery formaldehyde solutions once they have been deposited inside alum-treated artefacts.

Oxidation seems to be the most likely explanation for the colour change in finished PF polymer. If this is so, it can be avoided by storing the treated artefacts in a pure nitrogen atmosphere. Since this is difficult to implement in museums, it might be more realistic to at least postpone the reaction by adding an anti-oxidant. Since one of the more well known is ascorbic acid, it might be possible to have the anti-oxidant act as a catalyst for the novolac polymerisation as well. As previously stated, colour will not be of significant importance if the polymer is only used to stabilise the inner regions of existing artefacts.

The phase separation which occurs in watery dispersions may not happen in organic solvents but if a suitable solvent could be found, phenol-formaldehyde has been shown to have a suitable affinity for the degraded alum-treated wood from the Oseberg collections to strengthen the objects.

Future studies on alum-treated wood should focus on phenolic prepolymers and how to transport them into the artefacts and then cross-link them once they are in place – all without dissolving the alum. Testing a range of solvents on either the monomer mix or

partially polymerised oligomer molecules is not particularly difficult – although any impregnation tests at room temperature and pressure are likely time-consuming. Still, such experiments could lead to an 'emergency procedure' which could be implemented to strengthen the alum-treated Oseberg material provided biomimetic alternatives cannot be easily developed or implemented.

8.5.3   Epoxy novolacs

This study only focused on pure PF but several novolac epoxies are commercially available. The high aromatic content stabilises the polymers and should also helps stabilise the ether bonds of epoxies, making them less susceptible to oxidation. As PF oligomers can be dissolved in 2-propanol, it might be possible to introduce the oligomers in toluene or a similar solvent which will not dissolve alum. Such a consolidant might be used to grow a new framework inside the highly fragile alum-treated objects on display. Since only the core of these objects will be treated, it makes it possible to use consolidants with a red or brown colour.

8.5.4   Further chitosan developments

Out of the tested materials, chitosan seemed the easiest to implement for future treatment of waterlogged finds. The relative ease of use, however, makes it all the more imperative that the material is thoroughly tested before being applied to finds of actual value.

Since it was difficult to see chitosan in the SEM images of treated samples, it might be useful to develop a procedure to impregnate and freeze-dry samples in such a way that the chitosan is more easily seen (even if this might not be the optimal distribution for preservation – see chapter 8.3.3 'Freeze drying temperature' on page 180).

The fixation rate of chitosan to wood has only previously been performed on fresh wood and as degradation changes the chemistry of wood, these tests should ideally be run again on archaeologically degraded wood.

In order to determine proper penetration times, larger pieces of wood should be impregnated and freeze-dried before the chitosan penetrates all the way through the material. To gain a better understanding of the breadth of application, wood of multiple

genera in varying degrees of degradation should be treated with chitosan with different degrees of depolymerisation. This would provide the best overview of how applicable the method is to actual larger archaeological finds.

The use of acetic acid should be thoroughly considered. Ideally it should be neutralised before freeze-drying as it may corrode metal items if released in a museum environment (ideally, treated objects should not affect metal coupons in an Oddy test – see chapter 6.3.2.4 on page 95 for more information). De-gassing should be measured from treated objects (both with and without neutralisation) to get a better idea of the effectiveness of such treatment.

That chitosan is soluble in acids could potentially be a problem since the consolidant might dissolve or form a swelling gel inside the treated wood. Tests with varying levels of pH and RH should be performed in order to determine if or to what extent this actually happens.

The stability of chitosan has not been tested. This means that chitosan could potentially fail as quickly as existing unsuitable plastic products. Hopefully, the ring structure will make it more chemically stable than many of these linear molecules but accelerated ageing tests (preferably in various atmospheres) should be carried in order to evaluate whether chitosan will last long enough in a museum environment to be implemented as a consolidant.

8.6   Future avenues of research

Unfortunately, this work has merely managed to skim the surface of a vast ocean of possibilities, and many interesting experiments could not be performed at all during this project. The following areas show promise in the treatment of archaeological wood and should be the base for further investigations.

8.6.1   Nanoparticles

In order to neutralise acid generated inside wooden artefacts, deposits of a slightly alkaline materials are desirable. Nanoparticles have already been applied to serve this function (see chapter 4.1.10 'Nanoparticle treatments' on page 68), and should certainly be

integrated into treatments of archaeological wood in the future. As shown, $CaCO_3$ might grow inside wooden artefacts as the object is exposed to CO_2 in the air and solutions for this purpose may be easily made. The problem with the tested method is that the initial $Ca(OH)_2$ solution is highly basic and may damage the wood if left for long. Thus short impregnation times are a requirement. An alternative solution would be to look at chemically similar nanoparticles in order to test whether a less basic alternative can be found.

It should be tested whether it is possible to freeze-dry the samples immediately after the impregnation and then expose them to air to initiate the reaction. Since a moist environment should speed up reaction time, the samples could also be left in solution. How and if such changes affect the structure and growth of $CaCO_3$ (or similar acid-neutralising deposits) could be important for treated artefacts.

Beyond acid neutralisation, nanoparticles might also be integrated into other consolidants in order to improve mechanical properties. Silicate particles might be especially suited for this task due to their durability.

8.6.2 Silicate compounds

As mentioned in chapter 4.1.8 'Silicon oil treatment' on page 66, various silicon oils have already been tested on archaeological wood. The fact that a consistent conclusion has not been reached means that the method has some potential but possibly that common commercially available products do not possess ideal qualities. The high pH values associated with many silicate compounds make them undesirable for treatment of wood. While this does not mean useful molecules cannot be designed, it makes it more difficult to draw upon existing knowlegde. Since it is possible to change the chemical properties of Si polymers simply by introducing new functional groups, it is also possible to control how closely the polymers adhere to the remaining cell walls this way. In theory, this allows the monomer or oligomer molecules to penetrate in a suitable solvent, become sorped to the wooden matrix, and phase separate so the structure of wood may be retained (as was the case for the phenol-formaldehyde, see for example Figure 6.14 on page 108). Thus after freeze-drying the polymers can react with oxygen to cross-link, slowly strengthening the

artefact while leaving the structure open for future consolidants. In fact, the ability to cross-link upon contact with oxygen – rather than degrade – is an extremely desirable quality in consolidants which will most likely be kept in normal atmospheric air.

The anti-swelling effect observed for some silicates mean that they may be valuable in combination with other consolidants which tend to cause slight swelling. Thus a hybrid material which is partially silicate might could potentially be a very good consolidant.

8.6.3   Electrical mobility

While the properties of chitosan as a physical stabiliser could be evaluated partially, it was not possible to determine how efficiently the molecule binds metal ions. Both the Technical University of Denmark and the Norwegian Forestry and Landscape Intsitutehave experimented with moving metal ions in electrical fields. This existing technique might be used to reduce the metal ion content in found or treated wood, reducing the amount of catalyst available for ongoing oxidation processes. In relation to the experiments performed in this study, the method might be used to evaluate the effect chitosan has on the mobility on metal ions inside archaeological wood.

8.6.4   Artificial lignin

Although the PF is a kind of 'optimised lignin structure', it has drawbacks (chief among them toxic components and brittle products). Other kinds of lignin-like polymers could be explored and *in situ* polymerisation could be attempted. This section drawn upon chapter 3.2.4 'Chemical modification and synthesis of lignin', starting on page 24, in order to speculate on how the knowledge might best be applied to wood conservation.

Concerning DHP, the question is whether it would be advantageous in conservation to actually produce such a structurally stringent polymer or whether it would be better to synthesise something closer to actual lignin. A more random structure might allow the polymer to better interact with the existing degraded wood. Provided the polymer bonds to the existing degraded wood, or even adheres closely enough to it, it might offer better support than a chemically better defined but less flexible polymer. Of course, chemical simplicity most likely means that it is easier to predict the degradation behaviour of said polymer.

Since polysaccharides influence the structure of artificial lignin in a way which makes it resemble natural lignin, the *in situ* polymerisation of lignin inside archaeological wood might produce lignin which is more similar to plant lignin than if polymerised on its own. For this reason, it is essential to test all lignin-like materials on actual archaeological wood pieces before drawing any final conclusions about their structure and durability.

It is clearly possible to produce a DHP with very lignin-like properties. Costs, however, are very high. Coniferyl alcohol costs about 2600 NOK/g but might be produced from vanillin in stead. Since 10 kg of vanillin costs about 3000 NOK, the low yield is not a financial problem. It is more of a problem that the synthesis requires several steps and involves other fairly expensive compounds. Both eugenol (about 500 NOK/kg) and vanillin should be considered as possible raw materials for lignin-like polymers. If not, the cost of artificial lignins will make it impossible to implement them on a larger scale by museums.

Another financially sound possibility is to look for leftover lignin from the pulp and paper industry. Such lignin is currently very cheap since it is considered a waste product. It is usually heavily sulphonated. Since sulphonation improves solubility in water, it may be a desirable quality for artificial lignins used for conservation – even though sulphur is generally frowned upon in conservation treatments. The alternative is to use other solvents than water. Such solvents may require better precautions due to toxicity but they might also allow a re-treatment of the alum-containing wood. It will be vital to test such syntheses with non-corroding solvents and in ion rich environments if they are ever to be used on the actual Osebers finds on display. Such a procedure, if it can be implemented, would produce a very attractive solution to the current state of the find.

Using 2,6-dimethylphenol to form a lignin-like structure should also be tested. The reversible treatment is highly desirable but seems to have been carried out under highly alkaline conditions, making it inapplicable to waterlogged artefacts. When it comes to commercial feasibility, 2,6-diphenylphenol is much cheaper than actual monolignols – around 550 NOK per kg.

As can be seen, there are several avenues which might still be applicable to archaeological wood despite the high cost of many compounds. Another attractive solution

is to combine said lignin with other polymers to produce a more desirable product. When using lignin, additional Oddy tests should be run on all products as lignin-containing PF samples seemed to cause corrosion of lead (see chapter 6.3.2.4 on page 95).

8.6.5 Composite and hybrid materials

Since wood is itself a composite, it makes sense to mimic similar structures. There are countless ways of going about this and most of them would be a combination of approaches already mentioned. It might be possible to mix cellulose fibres or nanoparticles into another consolidant to improve its resistance to acid or mechanical performance.

Chitosan and cellulose whiskers adhere to one another, and films can be made from alternating layers of these polymers (see chapter 7.3.1.2 'Chitosan-cellulose film' on page 159). This means that the same approach might be used inside archaeological wood. A highly deacetylated chitosan will have a positive charge and adhere to the existing wooden matrix. An artefact immersed in chitosan might thus be impregnated and then rinsed to remove excess chitosan. Following this, the chitosan-coated wood could be immersed in a bath of cellulose whiskers with enough surfactant to keep them from flocculating. Provided the surfactant does not prohibit the cellulose from attaching to the chitosan, films could be formed. Given enough consecutive treatments, the chitosan/cellulose film might be strong enough to support the wood. If not, another polymer could be grafted onto either layer to reinforce it – as shown when PF adhered to cellulose whiskers and formed microspheres in stead of conglomerating at the bottom of the beaker.

Tests carried out during this study showed that it was possible to incorporate lignin into novolac structures even at room temperature but whether the two polymers bonded chemically was not tested.

8.7 Closing remarks

This thesis has attempted to sum up the major points of a very cross-disciplinary collaboration. The extensive background section should be helpful for new people joining the project – no matter what their background. In addition, the background material, along

with discussions with the other collaborators, has been the foundation for the list of requirements for future consolidants.

As for the experiments themselves, they have helped show promising properties of new consolidants (such as the phase separation during novolac polymerisation) and even revealed that chitosan shows a lot of promise as a consolidant for archaeological wood. It has attempted to mix the earliest industrial polymer chemistry (phenol-formaldehyde) with the materials of the present and future (biomimetics).

The most exciting part of the work, however, may well lie in where it leads. Numerous roads towards new consolidants have been discovered. Especially composite materials may solve many of the problems with poor flexibility, durability, or acid-resistance found in consolidants today. New approaches should hopefully lead to better treatments, allowing us to preserve our past for future generations to enjoy – and learn from.

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10. Appendices and papers

Paper 1:

Mikkel Christensen, Hartmut Kutzke, Finn Knut Hansen
New materials used for the consolidation of archaeological wood – past attempts, present struggles, and future requirements
Journal of Cultural Heritage **13**(3), p. S183-S190, 2012.

The paper describes most of the material presented in chapter 5 'Future consolidants' and gives some of the initial tests for cellulose whiskers found in chapters 7.2.3 and 7.2.3.1.

Paper 2:

Mikkel Christensen, Finn Knut Hansen, Hartmut Kutzke
Phenol formaldehyde revisited – novolac resins for the treatment of degraded archaeological wood
Archaeometry, submitted with revisions

The paper deals with the applications of novolacs in conservation science and sums up most of chapter 6. It deals specifically with the kinetics experiments summed up in chapter 6.3.2.5.

Paper 3:

Mikkel Christensen, Erik Larnøy, Hartmut Kutzke, Finn Knut Hansen
Enhanced stability of archaeological wood by treatment with chitosan and modified chitosan solutions
Journal of the American Institute for Conservation, submitted

The paper describes the impregnation experiments carried out on chitosan (especially chapter 7.3.2.3).

Appendix A:

Mikkel Christensen
Researcher grand prix – when ph.d. students do edutainment

Background information, thoughts and actual presentations by M. Christensen (with some Norwegian language input and musical assistance from Christina Kobb).

I

II

III

Appendix A:

Researcher grand prix
when Ph.D. students do edutainment

Table of Contents

If there was one thing I never thought I would be doing as part of my Ph.D. it would be singing in front of (and aided by) 400 people outside of my own field then turn to three judges who would score the performance. Still, this is how things turned out after I signed up for, and ended up making it all the way to the national final in, a competition in edutainment. This appendix explains what the competition was, the material I presented, and what I had to consider and learn along the way.

Concept

In 2011, the five major university cities in Norway (Oslo, Stavanger, Bergen, Trondheim, and Tromsø) all sent two hopeful candidates to a national final. The goal was to tell people about your research in an easily understandable way in just four minutes using whatever props or PowerPoint slides you thought would make it interesting. The name of the game was 'Forsker grand prix' – or 'researcher grand prix' for a literal translation (It should be noted that, in Norway, the term 'grand prix' is often associated with the Eurovision Song Contest or 'Melodi grand prix' – rather than car races – which might help explain the format and the time limit).

The number of hopeful candidates varied from town to town but in Oslo there was about 65 applicants from which 20 were selected to actually participate. The fields of study were widely distributed and included literature, law, music, psychology, medical sciences and geology as well as chemistry. We 20 met for a two-day introductory seminar and then proceeded to write, help one another, and be coached before the semi-finals.

Execution

The contest ran for two rounds in Oslo. First were two semi-finals were 10 candidates participated and only half proceeded to the Oslo final. A single candidate only got to one semi-final so these effectively reduced the number of participants to 10 for the Oslo final. The two highest ranking participants from each regional final then went on to the national finals in Bergen where a grand winner was determined.

The first semi-final (which I did not attend) was on the 21st of May in Oslo and the second on the 18th of June. The Oslo finals were on the 24th of Setember, the weekend before the national finals in Bergen on the 2nd of October.

After each presentation the performance was scored. Three judged were present. One with an acting background, one a journalist, and one with an academic position and education. Each would score the presentation from one (lowest) to six (best). In addition, audience members were handed manometers and would also score the presentation. The scores from the judges were averaged and the scores from the judges and the audience each counted for 50% of the total score. While the scores from the judges were publicly known immediately following each presentation, the scores from the audience were not revealed. Rather, the winners of each round were simply declared, maintaining suspense up to the very end.

For the semi-finals, only a four minute presentation was required. After all participants had finished, the scores were tallied and the five who would go on to the finals were announced. Fir the Oslo and national finals, an additional presentation was required. At first, all 10 participants would present four minutes. The best three, based on total scores, were nominated. Then there was a break during which the judges would nominate a 'wildcard' to proceed as well. The selected four participants did a six-minute presentation further elucidating their chosen topic. The final winner(s) were then declared based on total scores for the second round.

Motivation

When I initially wanted to sign up, it was partially because such a cross-disciplinary study as chemistry and Viking Age artefacts more or less begs to be presented in this way. 2011 was the international year of chemistry and I felt that my projects represents an interesting but very untraditional view of what chemistry might be about. Encouraged by my collaborators at the museum, I signed up.

Language

Several nationalities participated and while most spoke or understood Norwegian, several presentations were given in English. Due to these being the only officially allowed languages, I asked if I should present in English but was told by the local organisers that Danish was my only acceptable choice. While speaking your native language is usually not a hindrance, it did mean that I was speaking a 'dialect of Norwegian' which might not be as easily understood as the regional accents of the other competitors. I decided that I would speak slowly and extremely clearly (but try not to offend the intelligence of the audience by

replacing too many Danish words with Norwegian ones). After the first rehearsal, I was told that it was difficult to understand me initially (the audience had to chance to 'adjust' to my way of speaking and speaking through a microphone probably only made things worse). Based on this, I really forced myself to speak clearly despite being nervous and completely abandoned the idea of doing something akin to a typical modern stand-up routine where sentences are delivered very quickly (incidentally, the winner of the national finals had exactly this kind of presentation style). I must have succeeded in keeping my speed down as I finished all presentations the way I rehearsed them – only a few seconds before my time was up.

Coaching and planning

While the bulk of the work was solely up to the individual participants, we were coached both initially and once before each show in Oslo. While it is not possible to note everything interesting which went on, I will mention a few points I felt were particularly helpful in the hope that they might also be useful to other researchers speaking to audiences other than colleagues within their established field.

During the initial meeting we saw several presentations to improve our performance on stage. What particularly struck me was the following two points (made by

1) Nowadays, nobody truly respect academics simply because they are more learned than everyone else. If you want to get the attention of the audience, enthusiasm is really the only way to do it.
2) The classical saying 'just be yourself' is actually not what most people want. They want to be entertained. If you can project the personality of a brilliant stage performer, this bit of acting might be far better than what you as a person would naturally act like on stage.

Another presenter started out by telling seemingly randomly about the male Grévy's zebra which will guard watering holes, preventing female zebras from drinking from them unless they mate, then went on to compare this with his own high school life. The point being that while the zebra may have an extremely simple strategy, it is a strategy which nonetheless works! He then told us that while we might forget everything else he said, the behaviour of this particular kind of zebra would stay with us for years and that we, too, should strive to do something which worked for us – and would be remembered by the audience. At the time, I doubt many of us understood how important this advice actually is.

I was coached by Niels Peter from 'Det Andre Theateret' in Oslo. He was also present to help us with team-building exercises and a few other pointers during the initial meeting. For my first personal session, he listened to my presentation and made three excellent observations:

1) Usually it is true that you cannot underestimate your audience. While this sounds cruel, it is often difficult for people from other fields to understand your speciality which you have studied for years. If anyone brings their children it would be nice if they also understand most of what is going on.

Illustration 1: The presenter holding up the replica of the animal head post from the Oseberg find (photo by Bjarte Aarseth).

2) While entering and doing a presentation is fine for a conference, it does not win a competition like the Researcher grand prix. In order for the audience to vote for you, you need a suitable introduction which makes them personally involved as well as make them relate to you as a person as well as a researcher. Starting with a mystery (such as an incomprehensible slide) might also get people interested.

3) While four minutes seem like no time at all, the audience can only think about things when you stop talking. Pauses are important.

4) Voice is important. While it is easy to get caught up in your own presentation and talk about something in a loud, excited voice, it is sometimes more effective to pause and lower your voice. This creates diversity and helps keep focus on you. The audience will not be able to listen well to a presenter who sounds excited all the time.

Since Niels Peter also advised getting props – something physical to hold on to rather than just the images in the presentation behind me, I went to Bjarte Aarseth who is a woodcarver working at the Viking Ship Museum. He kindly lent me a replica of one of the animal head posts from the Oseberg find (which he has carved himself). An image of me with the ritual head post is shown in Illustration 1.

Web page introduction text

All participants were put on the internet. The following short text accompanied my image:

DANISH (English below)
Navn: Mikkel Christensen

Institution: Kjemisk institutt og Kulturhistorisk museum ved Universitetet i Oslo

Tittel: Kemi til kultur – hvordan kan vi bevare vikingeskatte?

Baggrund:
Jeg er født i København og har studeret kemi og matematik ved universitetet dér. Mit speciale var et samarbejde med Nationalmuseets Bevaringsafdeling, hvor jeg forsøgte at forstå, hvordan arkæologisk træ er påvirket kemisk. En dag fik vi besøg en gruppe norske konserveringsstuderende og museets kemiker, Hartmut. Han opfordrede mig til at søge en stipendiatstilling i Oslo. Derfor kom jeg hertil.

Forskningsprojektet:
Fokus for mit projekt er at udvikle nye metoder til at bevare arkæologisk træ, da eksisterende metoder ofte ikke er langtidsholdbare eller tilstrækkelig effektive. Enkelte – så som alunkonserveringen, der er benyttet på mange af de unikke udskårne objekter fra Osebergfundet – er direkte skadelige over tid. Derfor er det nødvendigt at udvikle nye bevaringsmidler, som sikrer, at man kan behandle objekterne igen i fremtiden, hvis de skulle begynde at blive skrøbelige. Strukturen inde i træet må derfor være åben efter behandling. På Kjemisk institutt har jeg set på traditionelle polymerer (som f.eks. Bakelit), men er begyndt at benytte 'biomimetik' (materialer inspireret af naturens design) til at forsøge at "forstærke gammelt træ med nyt træ". I øjeblikket fokuserer jeg på højkrystallinske resistente cellulosefibre til at forstærke objekterne – alene eller i kombination med andre stoffer.

Fremtidsdrømme:
I fremtiden håber jeg på at blive del af et større skandinavisk projekt – gerne med samarbejde med biomimetriske forskningsinstitutioner i resten af verden – der arbejder med at analysere fund og udvikle metoder til at bevare dem. I min fritid håber jeg på at lære nye absurde sange, diskutere alt fra science fiction til mytologi med nye mennesker og fortsætte mine miniaturespil og -maling.

ENGLISH
Name: Mikkel Christensen

Institution: Department of Chemistry and Museum of Cultural Heritage at the University of Oslo

Title: Chemistry for cultural heritage – how can we preserve Viking treasures?

Background:

I am from Copenhagen and studied chemistry and mathematics at the university there. My Master project was a collaboration with the National Museum of Denmark. I tried to look at chemical changes in archaeological wood. One day a group of Norwegian students of conservation were visiting and their accompanying chemist suggested that I apply for a Ph.D. position in Oslo. Thus I ended up here.

The research project:
My primary objective is to develop new ways to treat archaeological wood. Most existing methods are either not stable in the long run or have other detrimental side effects. The latter is true for the alum-treated objects from the Oseberg mound in Norway, which means that the most uniquely carved Viking Age artefacts in the world are threatened. Future materials must have an 'open' structure so it is possible to re-treat objects if the existing consolidants begin to degrade. At the Department of Chemistry I have tested traditional polymers (such as Bakelite) but have begun to work with biomimetic materials. Such materials are inspired by existing designs in nature and I am thus working on 'reinforcing old wood with new wood'. Right now I am focussing on highly crystalline and resistant cellulose fibres which can strengthen the wood – either alone or in combination with other materials.

Hopes for the future:
I hope to continue working with the analysis and preservation of archaeological objects in the future – preferably as part of a Scandinavian research group collaborating with biomimetic institutions from around the world. In my free time I hope to learn new absurd songs, discuss everything from science fiction to mythology with the people I meet, and continue my miniature painting and gaming.

Four-minute presentation

In order to focus on a relatively simple message, I tried to base the first presentation on the fact that the ageing wood needed reinforcement and that I was looking at cellulose fibres in an attempt to 'put fresh wood into the old wood' – even if there might be problems with using cellulose without additional support. My original concept included a slide to introduce the concept of biomimetics but I abandoned it after the coaching session for a longer introduction. Eventually, I ended up with the following presentation for the semi-finals in Oslo:

I entered stage with a metal suitcase handcuffed to my wrist (I ended up abandoning the handcuffs later on as they were tricky to remove quickly and difficult to see from the back of the room). From the suitcase I pulled a 1:1 replica of an animal head post from the Oseberg find – generously lent to me by its creator, Bjarte Aarseth from the Viking Ship Museum. I held this in one hand during the introduction.

The presentation won me the first place at the semi-finals in Oslo and I felt that the audience responded well to it every time it was performed. What follows is each slide as shown with the original Danish text in italics followed by an English translation (note that an accurate translation of the Danish text has been attempted. This means the English might be tweaked and made more eloquent in case the presentation is ever to be given in English). The text is the one used for the semi-finals with one added sentence about my own work beginning (as one of the judges felt that was the only weak point of the show). In

subsequent showings, I left out the warfare references as I thought Norway might want something more peaceful after the bombing and subsequent shooting on the 22nd of July 2011 (a day I returned from Denmark to Oslo to witness an almost tangible desolation in the air). Viewed out of context, however, I feel the chemical warfare references are better left in as they provide a kind of sub-theme within the presentation.

Kemi til kultur –
hvordan kan vi bevare vikingeskatte?

Mikkel Christensen

**Kjemisk institutt &
Kulturhistorisk museum
ved Universitetet i Oslo**

Davs! Her kommer en dansker for at redde Norges nationalarv! Her må kemisk krigsførelse til. Dette er mine våben...

Hullo! Here comes a Dane in order to save Norway's national heritage! This requires chemical warfare. These are my weapons...
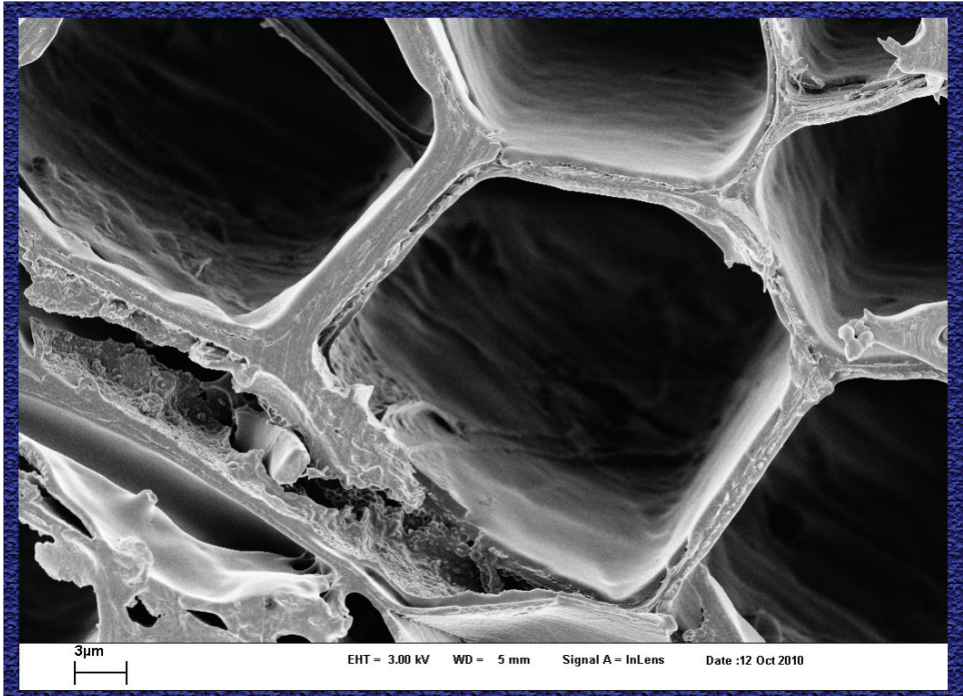
Her er den usynlige fjende – som er inde i ham her.
Er det lysende klart for alle? Nej?!? Hmmm... OK, lad mig forklare...

This is the phantom menace – which resides inside this guy.
Is that obvious to everyone? No?!? Hmmm... OK, let me explain...
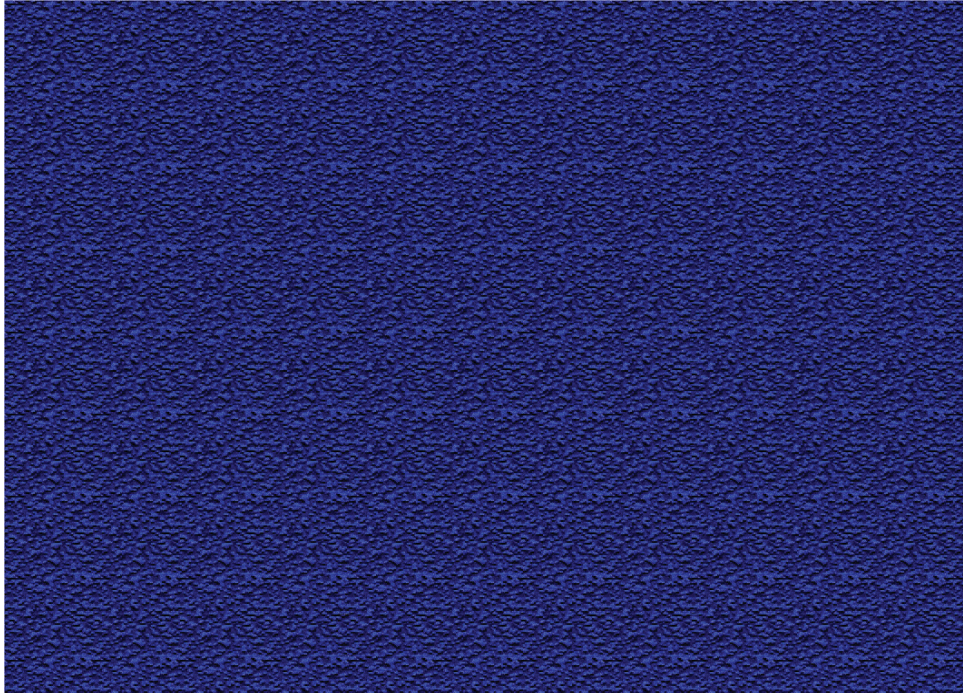
Forestil dig at du kommer ind på museet på Bygdøy. Du maser dig forbi turisterne og ser Osebergskipet. Du beundrer sollyset, som fremhæver udskæringerne. Det er fint. Ingen problemer. Så kommer der en mand med skæg og briller og han tager dig med ud bagved – på lager. Her ser du noget denne dyrehovedstolpe, som skal skræmme onde ånder, ikke virker på:

Imagine that you enter the museum at Bygdøy. You squeeze past the tourists and look at the Oseberg ship. You admire the sunlight which enhances the carvings. It looks nice. No problems. Then this bloke comes along with a beard ans glasses and leads you out back – into the storage. Here you see something which this animal head post, which is supposed to scare evil spirits, does not work on:

Svovlsyre fra den oprindelige behandling. Kemisk krigsførelse som får træet til at sprække og blive til pulver. De vigtigste dele af vikingeskatten forsvinder!

Her kommer vi til mit projekt, som er at opfinde nye metoder til at forstærke det skrøbelige træ.

Sulphuric acid from the original treatment. Chemical warfare causing the wood to crack and turn into powder. The most important parts of the Viking treasure are disappearing!

This brings us to my project which is to invent new methods to reinforce the fragile wood.

Arkæologisk træ

For at forstærke objekterne, må man forstå, hvordan arkæologisk træ ser ud. Set fra enden kan man se store sprækker, men træ har naturligt små huller som kan ses i elektronmikroskop.

In order to strengthen the objects, you must understand what archaeological wood looks like. If you look at the end of this piece you may see large cracks – but wood also has minute holes which we can see in an electron microscope.
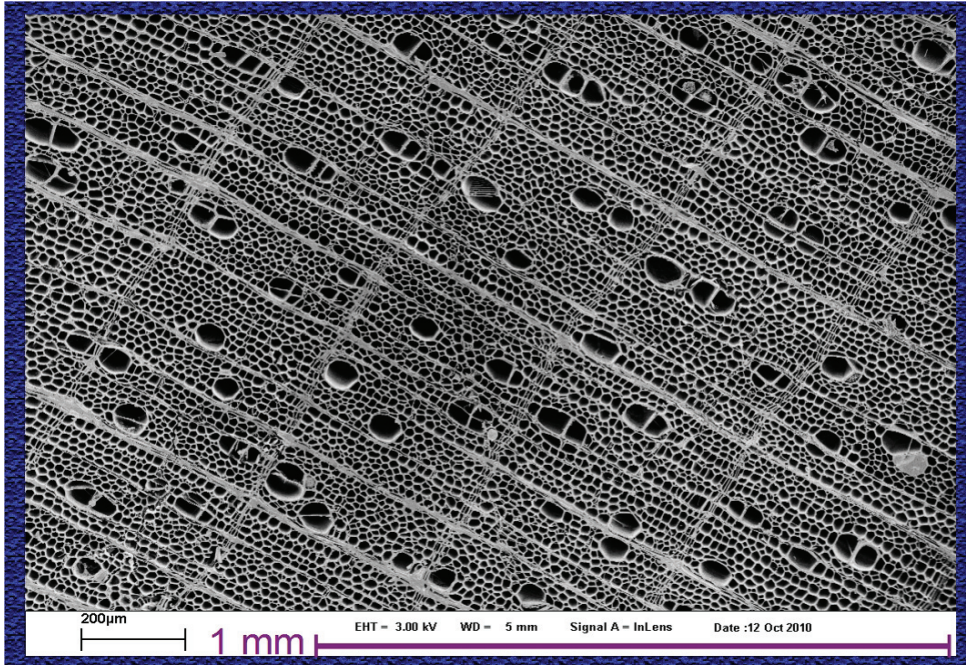
Vi kan forstørre det,

We can enhance it -
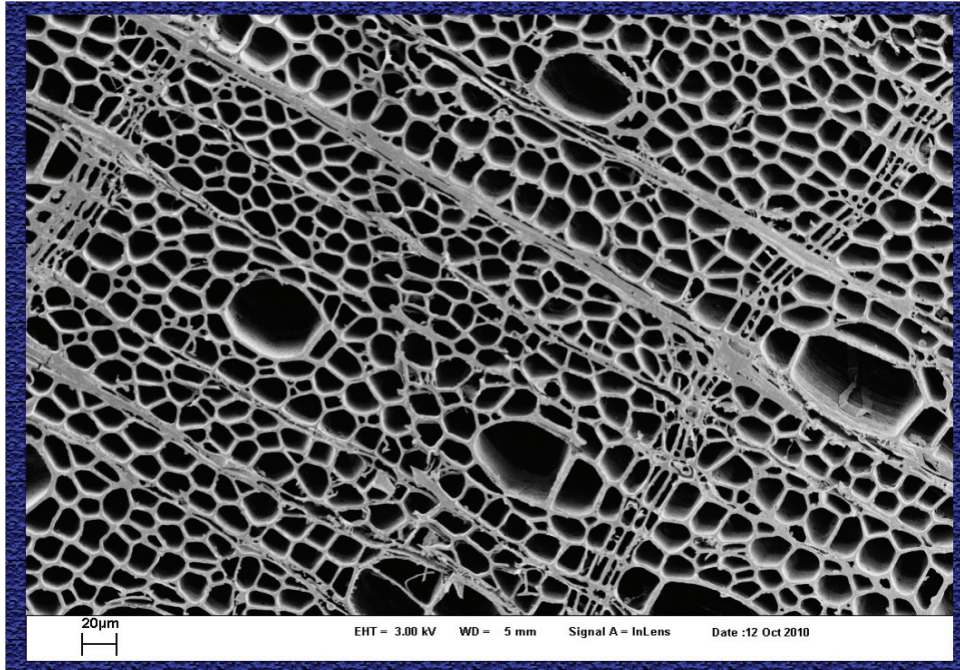
men vi skal længere ind.

but we have to go further in.

20μm EHT = 3.00 kV WD = 5 mm Signal A = InLens Date :12 Oct 2010
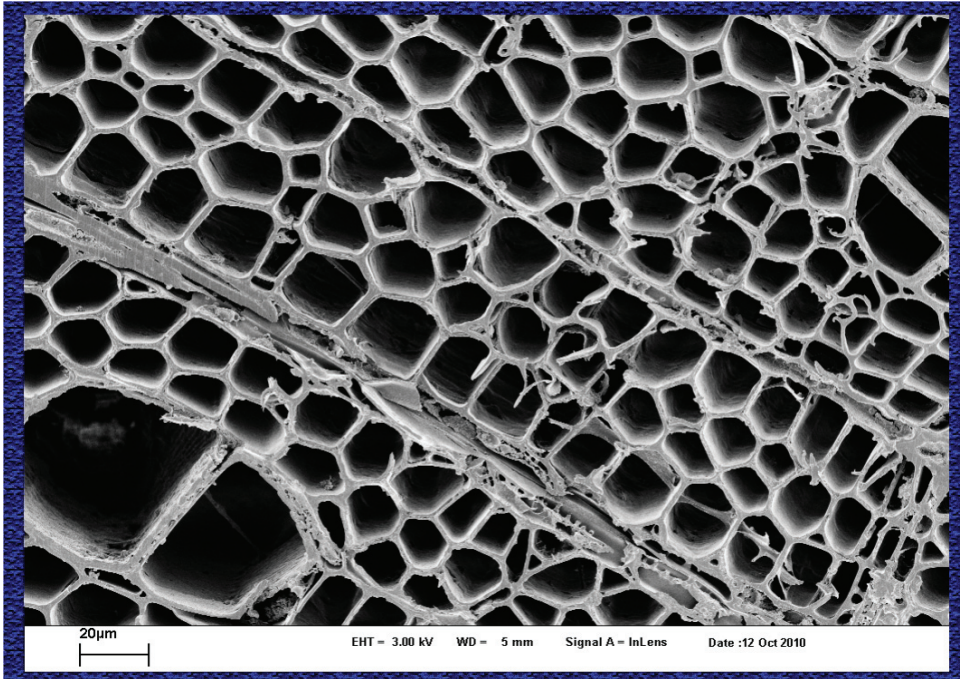
Vi skal helt ind i træet.

We have to all the way into the wood.

3μm   EHT = 3.00 kV   WD = 5 mm   Signal A = InLens   Date :12 Oct 2010
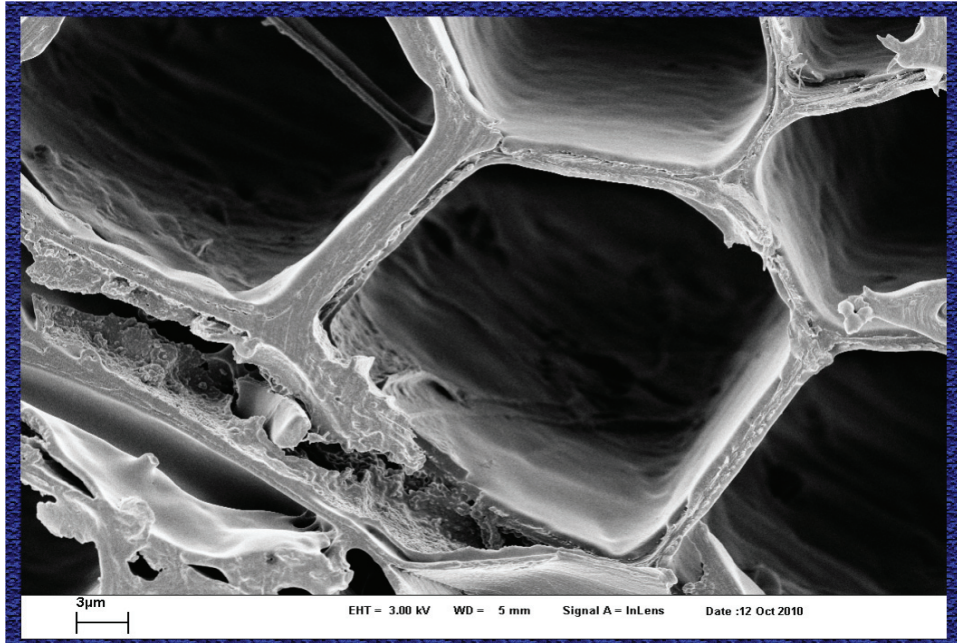
Sådan! Det er her slaget om fortidens fremtid skal stå.

Like this! This is where the battle for the future of the past will be fought.

EHT = 3.00 kV   WD = 5 mm   Signal A = InLens   Date :12 Oct 2010
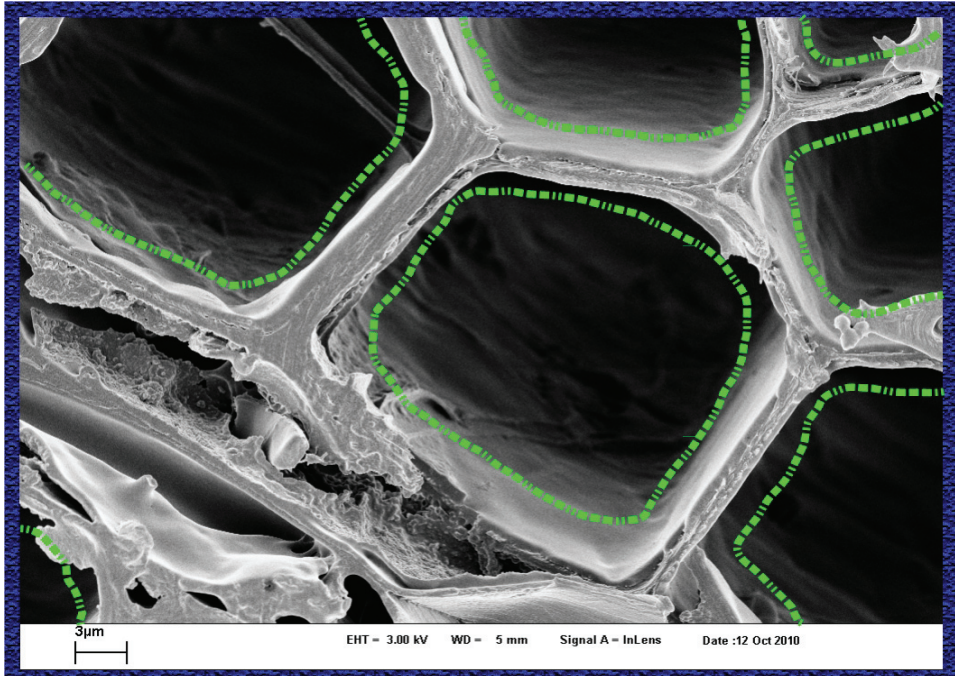
I frisk træ er de hvide cellevægge ofte tykke, men det stof, der hedder celulose bliver brudt ned når træet ligger i jorden – eller står i svovlsyre på museum. Vi er sikkert mange, der har cellulose på, for bomuld består af mere end 90% cellulose.

In fresh wood the white cell walls are often thick but the compond called cellulose is degraded when the wood is in the ground – or is acidic in a museum. Most of us are probably wearing cellulose as cotton consists of more then 90% cellulose.
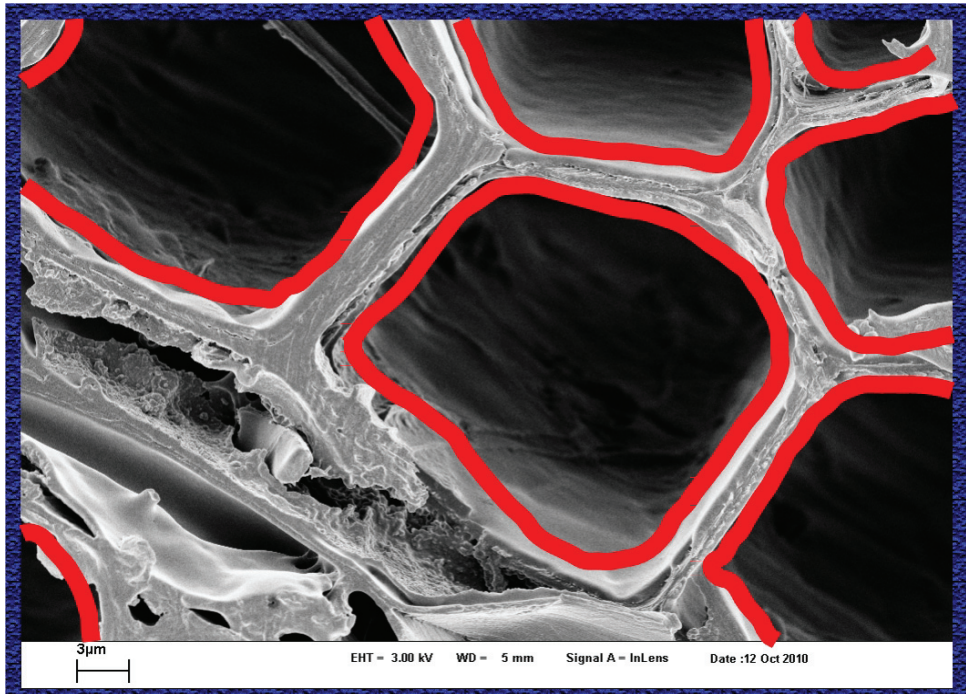
Vi må have et stof ind for at forstærke cellevæggene. Men krigen fortsætter.

We have to get some compound in here to reinforce the cell walls. But the war continues.
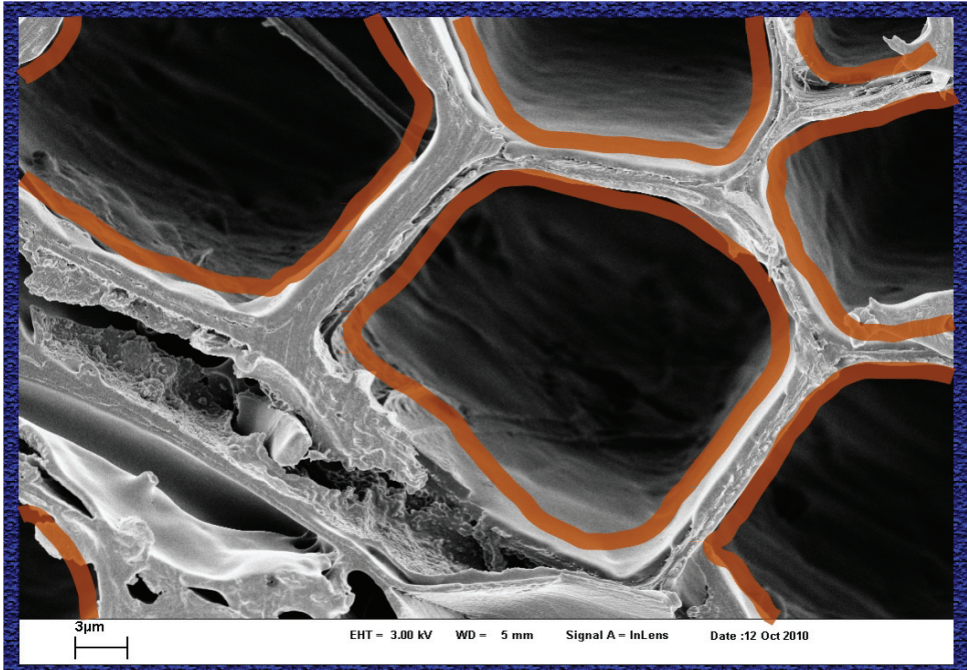
Om 100 år bliver forsvaret nedbrudt.

In a hundred years this defence will also degrade.
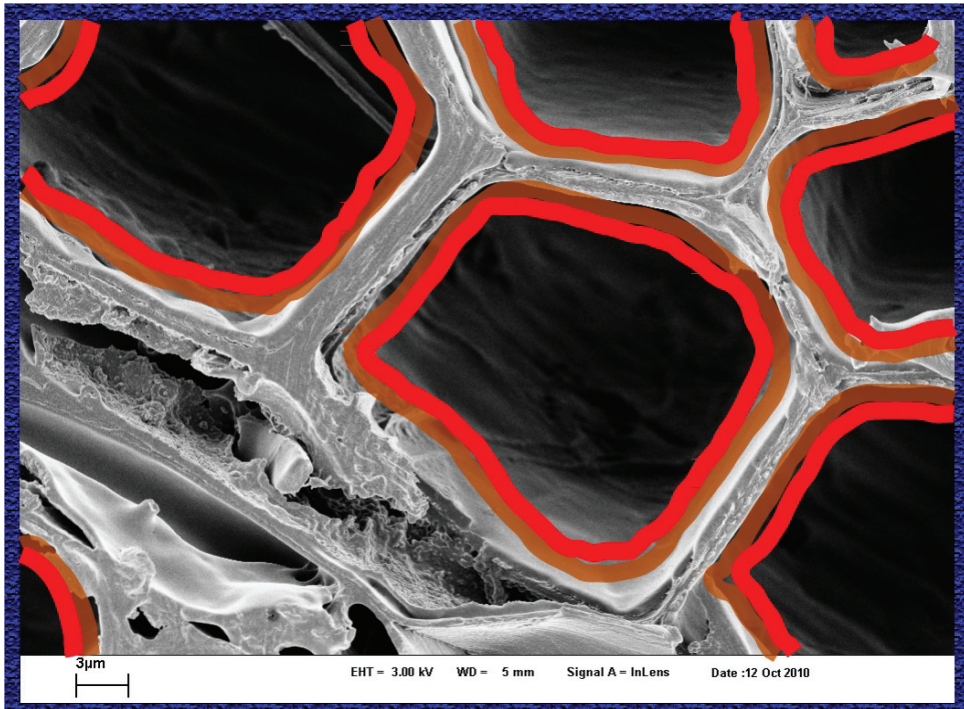
Så behandler man træet med et nyt lag. Derfor er det vigtigt ikke at fylde hullerne.
Men hvad skal man komme ind i træet? Det ville jo være elegant at 'gro nyt træ' inde i det gamle. Derfor har jeg valgt at se på...

We then treat the wood with a new layer. This is why it is important not to fill these holes.
What should we put into the wood? It would be very elegant to 'grow fresh wood inside the old'. This is why I have chosen to look at...

Cellulosekrystaller

Celulose! Undskyld? [ser og peger på en i publikum]Jo, det er helt rigtigt at celulosen nedbrydes i jorden – godt husket.

Cellulose! Pardon? [looks at and points to someone in the audience] Yes, it is true that cellulose is degraded in soil – well remembered.

Cellulosekrystaller

Cellulose + syre =

Derfor må jeg behandle den med svovlsyre, og rense den, så det kun er den mest resistente del, der kommer ind i træet. I vandig dispersion ser den sådan ud.

This is why I have to treat my cellulose with sulphuric acid and rinse it so only the most resistant part of the cellulose gets into the wood. In watery dispersion it looks like this.

Cellulosekrystaller
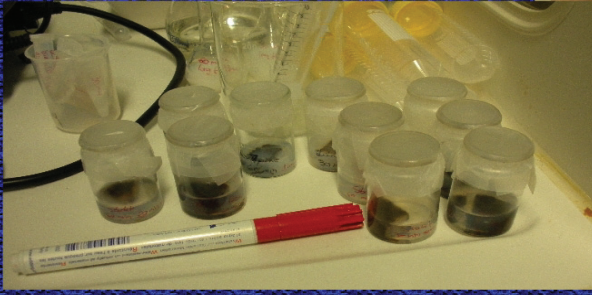
Cellulose + syre =

Her har jeg små stykker arkæologisk træ, som cellulosen trænger ind i.

What we see here are bits of archaeological wood which the cellulose seeps into.
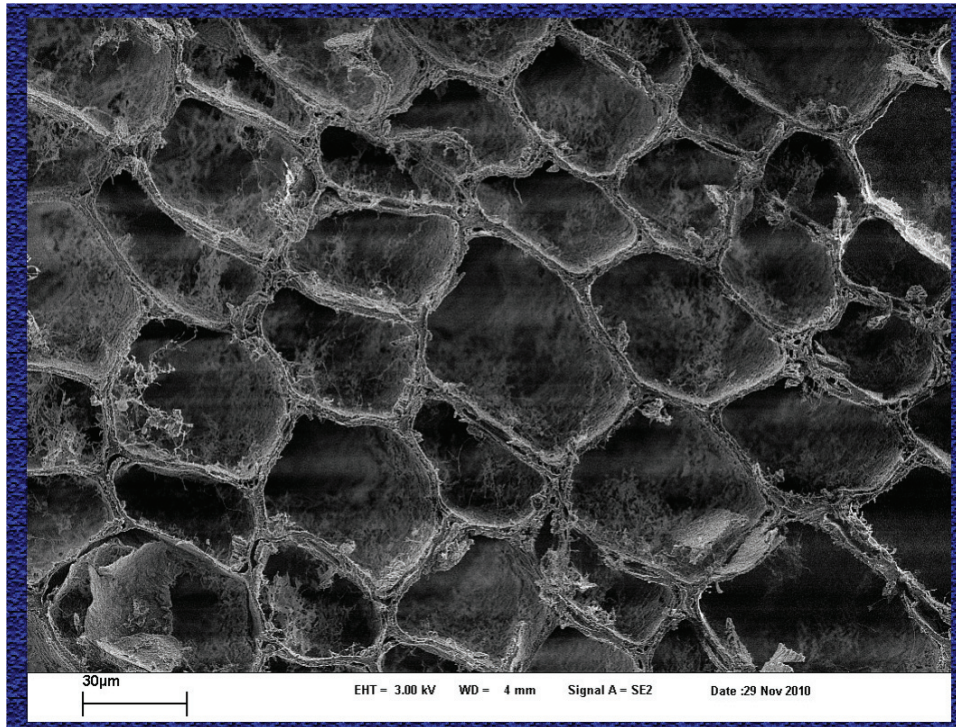
I elektronmikroskop ser man, at cellulosen har lagt sig inde i porerne. I fremtiden fortsætter forskningsprocessen. Jeg må optimere fordeling og styrke så vi kan vinde krigen og bevare de tre typer objekter på museet:

In an electron microscope we see that the cellulose has adhered to the pores. In the future the research continues. I have to optimise distribution and strength so we may win the war and preserve the three kinds of objects which are at the museum:

Dem der nedbrydes af syre fra den oprindelige behandling, dem der aldrig er forstærket og derfor er skrøbelige, og dem der klarer sig forbløffende godt bare med lak. Det var alt fra mig. Genstandende får de sidste ord.

Whose which are being degraded by acid from the original treatment, whose which those which have never been reinforced, and those which do surprisingly well with simple lacquering. That's all I had to say. I leave the final words to the objects.

The sledge says, "Help me, I am sour!", the animal head post "I feel empty inside," and the Oseberg ship thinks "They're complaining... Nah, I think I'll move."

Six-minute presentation

I intended to use my longer presentation to explain the concept of biomimetics and show some of the trials which went before. As I considered how time-consuming it had been to create a four-minute presentation, however, a series of events led me to do something untraditional.

When I originally told Hartmut Kutzke about the contest, he asked if anyone had ever done something completely unexpected – such as singing their project as an opera. While I did not immediately think I would want to do this, the thought stuck in the back of my mind. At the party after the first semi-final, I ended up talking to Christina Kobb who asked me what the notes about 'absurd songs' in my entry on the web page meant. She then offered to play for me if I needed musical assistance. This really got me thinking. Partially because I thought it would be very untraditional and interesting to sing – partially because I realised that with audience participation all the text would have to be on the slides and I would not have to spend time remembering it all. This got me to start writing a song and, remembering that it is nice to involve your audience, I felt I had to write it in Norwegian (as, again, Danish sometimes has different stresses, word order, or even number of syllables). Once again, Christina was kind enough to step in and help me get the text more intelligible before the performance. Susan Braovac suggested the well known tune "Musevisa" which it was a tradition to sing at the museum.

During my second coaching session, we once again talked about introductions and I mentioned that I believed the tune was originally Danish. I was encouraged to use this angle and thus discovered (in http://dansedatabase.dk/nyt_fra_rodder/rod08.htm) that the song was not only Danish but had been written at the time the Oseberg mound was excavated. This fortuitous coincidence made into the presentation.

I got to test this song the night before the Oslo finals at the Techincal museum of Oslo. There were only relatively few people present (perhaps around 20) but I was much relieved that they sang along and seemed to have a good time. I was still surprised by the wholehearted participation from the larger audience next night. The audience sang so loudly that I could barely hear myself in spite of the loudspeakers and the feeling of being 'carried' through your presentation by so many people helping you is incredible. Despite the less enthusiastic score of the science judge, the audience sent me to the national finals. Although I did not proceed to the second round in Bergen, I still felt that the song had served its purpose – and am glad that I got to try something a bit untraditional.

The presentation is given below with the original Norwegian/Danish text and an English translation. The lyrics are translated for content rather than in any artistic way.

Hei.

Jeg har allerede snakket om, hvor mit projekt er nu – altså om at få cellulose ind i træet – men ikke processen bag forskningen.

Efter et par måneder i Oslo var jeg til julebord på museet. Tænk, der synger vi pludselig en gammel dansk melodi. Jeg kendte den som "Moar, jeg skal tisse", heroppe hedder den "Musevisa". Det oprindelige navn er "Svensk Scottish" og den er i øvrigt skrevet samme år som Oseberg blev udgravet. Det morsomme er, at nordmændene har givet melodien nyt indhold så den kan overleve længere. Det er faktisk det samme som jeg gør med det norske vikingetræ.

Hi.

I've already talked about where my project is now – about getting cellulose into the wood that is – but not about the process behind the research.

After a couple of months in Oslo I joined the Christmas party at the museum. Well, suddenly we are singing an old Danish tune. I knew it as "Mummy, I have to pee", up here is is called "Musevisa" [mouse ballad]. The original name is "Swedish Scottish" and it is, by the way, written in the same year as Oseberg was excavated. The funny thing is that the Norwegians have given this tune new contents in order to make it last longer. This is actually the same thing I am doing to the Norwegian Viking wood.

Fellessang:

Processen at udvikle nye metoder
til at bevare gammelt træ

Melodi: Musevisa

Så synger vi allesammen – på 'Musevisa' (eller var det musévisa?)

Then we'll all sing – on "Musevisa" [mouse ballad] (or was it 'Museum ballad?)

I nittenhundrefire ble Oseberg gravd opp
så treet måtte sikres men da ble det pluts'lig stopp.
For det sto lakk og olje for konservering klart
men det gjør treet mørkt og tungt og synes rart.
Alun! Alun! Smelt det i et bad
for da blir treet lyst og lett og vi kan være glad.
Sett det sammen - det må sitte godt
med spiker og med kitt da blir det helt utrolig flott!

Vent, stop...

In nineteen hundred and four Oseberg was excavated
and the wood had to be protected but then things came to a stop.
Lacquer and oil were standing ready for the conservation
but these make the wood dark and heavy and seem strange.
Alum! Alum! Melt it in a bath
when the wood will be bright and light and we can be pleased.
Fit it together – it has to sit well
with nails and with plaster it will look incredibly well!

Wait, stop...

I nittenhundrefire ble Oseberg gravd opp
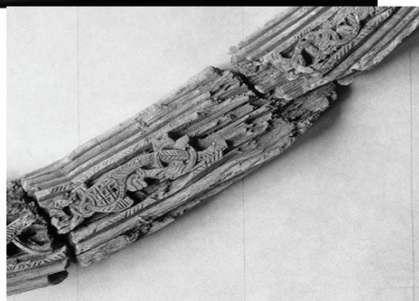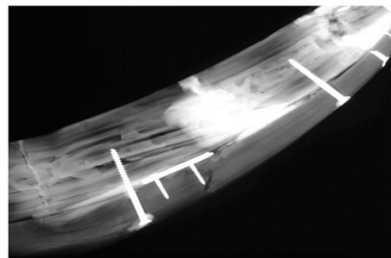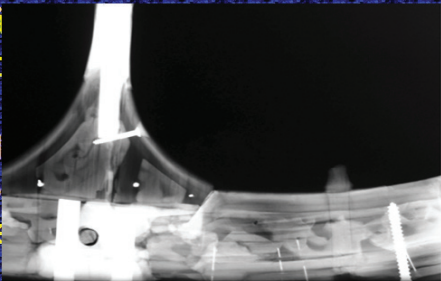
Se på Röntgenbilledet hvorden de oprindelige dele af slæden i virkeligheden er sat sammen. Det gør ikke konserveringen lettere...

Look at the x-ray image how the original parts of the sledge are actually put together. This doesn't make conservation any easier...

Hva ingen kunne spå om, at på etthundre år
fikk svovelsyre langsomt etset vikingskatten vår.
Men nå finnes det plastikk og mat'rialkjemi
med disse blir vi vel våre problemer fri?
Museet må - ansvaret er tungt -
på tross av syre/sprekker holde treet evig ungt.
Hent han dansken – han får tenke nå
en helt ny tilgang til problemet han må finne på.

Støttemaker Ragnar Løchen

What no one could predict was that in a hundred years
sulphuric acid slowly corroded our Viking treasure away.
But now we have plastics and materials chemistry
with these we are quite sure to get rid of our problems?
The museum must – the responsibility weights heavily -
in spite of acid/cracks keep the wood forever young.
Bring that Dane – he has to think now
*an entirely new approach to the problem is his to find.*

Se, verdens eldste plastikk den heter Bakelitt
(ble patentert i nitten-sju) på den vi tar en titt.
Den etses ei av syre, nei den er like hel
og kjemisk ligner den på treets styrke-del.
Bakelitt er fenol-formaldehyd
(kan begge være giftige og det er ingen fryd).
Kan vi få det inn i tre med flid?
Og vil det støtte og bevare treet over tid?

Fenol + formaldehyd

Bakelitt-struktur
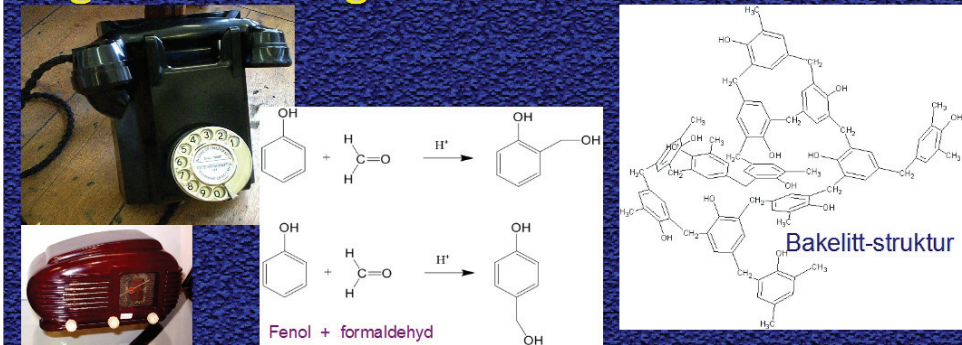
See, the world's oldent plastic is called Bakelite
(was patented in nineteen seven) at this we'll have a look.
It is not corroded by acid, no it is just as whole
and chemically it looks like the strength-part of the wood.
Bakelite is phenol-formaldehyde
(can both be poisonous which is no joy).
Can we get it into wood with perseverance?
And will it support and protect the wood over time?

Se, verdens eldste plastikk den heter Bakelitt
(ble patentert i nitten-sju) på den vi tar en titt.
Den etses...
og kjemis...
Bakelitt e...
(kan begg...
Kan vi få...
Og vil det...
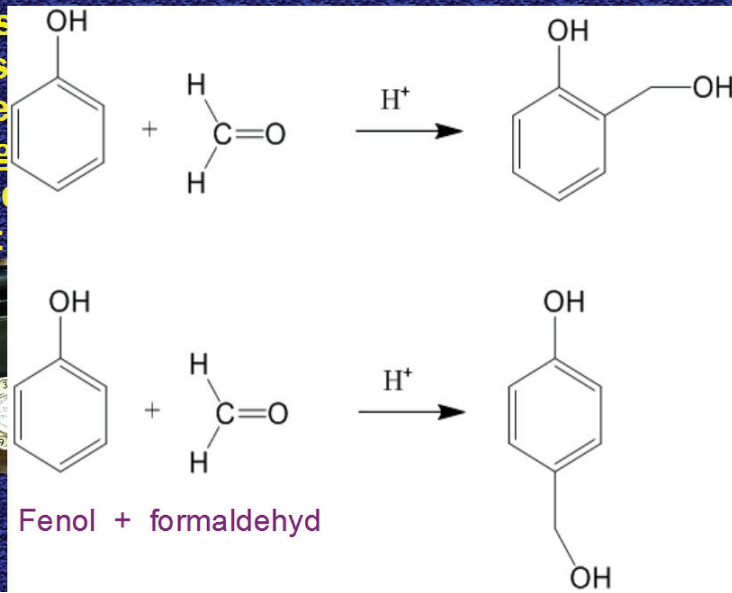
Fenol + formaldehyd

Stop. Kemikeren vil gerne tilføje et par ord. Her er fenol og formaldehyd og de er giftige, men de kommer langt ind i træet og reagerer først til små molekyler og så...

Stop. The chemist would like to add a few words. This is phenol and formaldehyde and they are poisonous – but they get far into the wood and react, at first to small molecules and then...
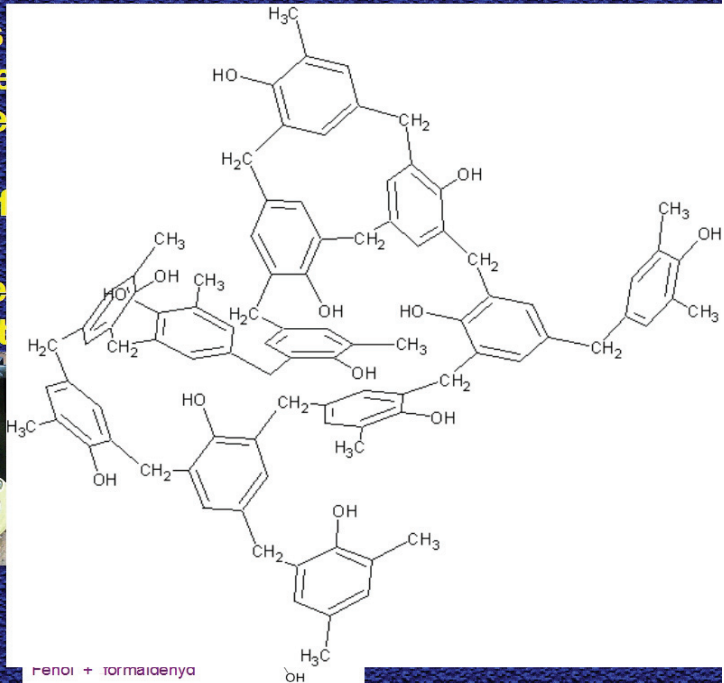
...enormt store molekyler, der ikke længere kan optages i kroppen, og så er de ikke giftige mere. Men virker det på træet? Næste vers...

...enormously large molecules which can no longer be adsorbed by the body – meaning that they are no longer poisonous. But do they work on the wood? Next verse...

Med Bakelitt ble vikingtre nennsomt impregnert
og studietur for 3 til Sveits ble hastig arrangert.
Der skannet vi nå prøver (med ny tomografi)
som Røntgenbilder lot oss se strukturen i.

Mindre prøver

Store maskiner
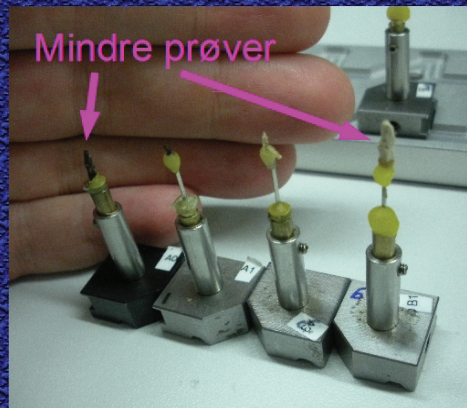
With Bakelite Viking wood was carefully impregnated
and a study trip for three to Switzerland was hastily arranged.
There we scanned samples (using new tomography)
which x-ray images let us see the structure of.

Image text: "Big machines" (left) "Smaller samples!" (right).

Første prøven den ble veldig flott
for stoffet har fordelt seg og det støtter treet godt.
Andre prøven den ble ikke bra
da alunet ble oppløst ble den faktisk mislykka!
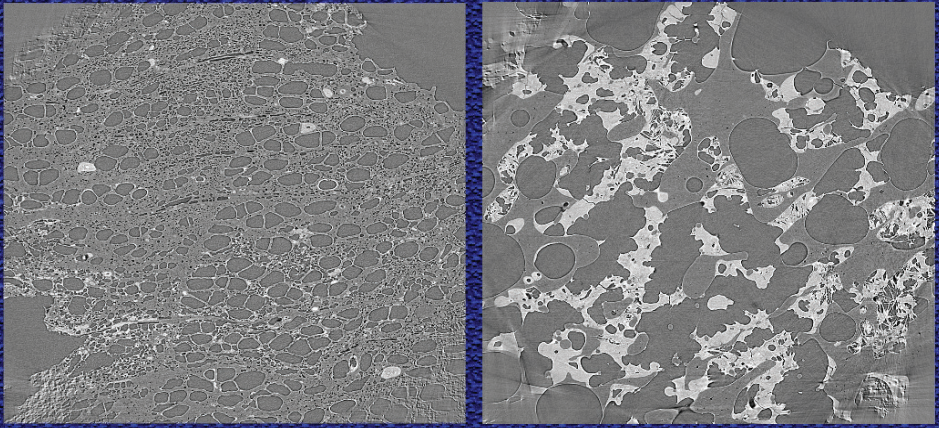
The first sample it was very good looking
because the compound was distributed and supports the wood well.
The other sample it was not good
as the alum was dissolved it actually failed!
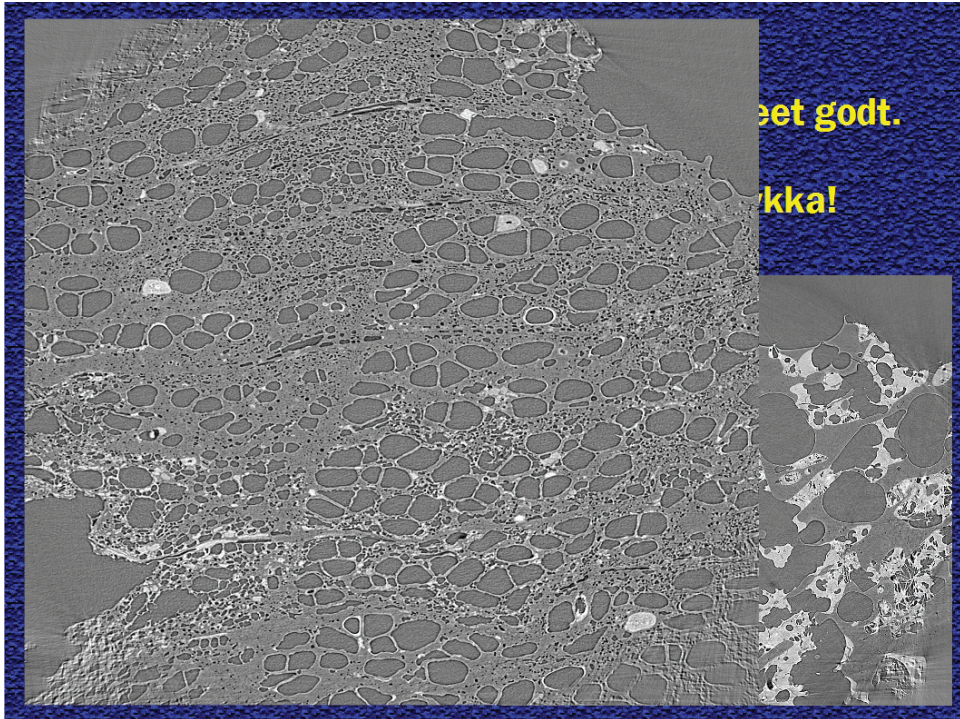
Undskyld, jeg afbryder igen men detteher er virkelig spændende. På første billede kan man se at strukturen af træ er bevaret. Bakelitten har bare lagt et tyndt lag ud over den. Det er hvad vi ønsker. De hvide områder er alun, som er smeltet inde i træet.

I'm sorry to interrupt once again but this is really interesting. In the first image you see that the structure of the wood has been preserved. The Bakelite has just distributed itself as a thin layer across it. This is what we want. The white areas are alum which has melted inside the wood.
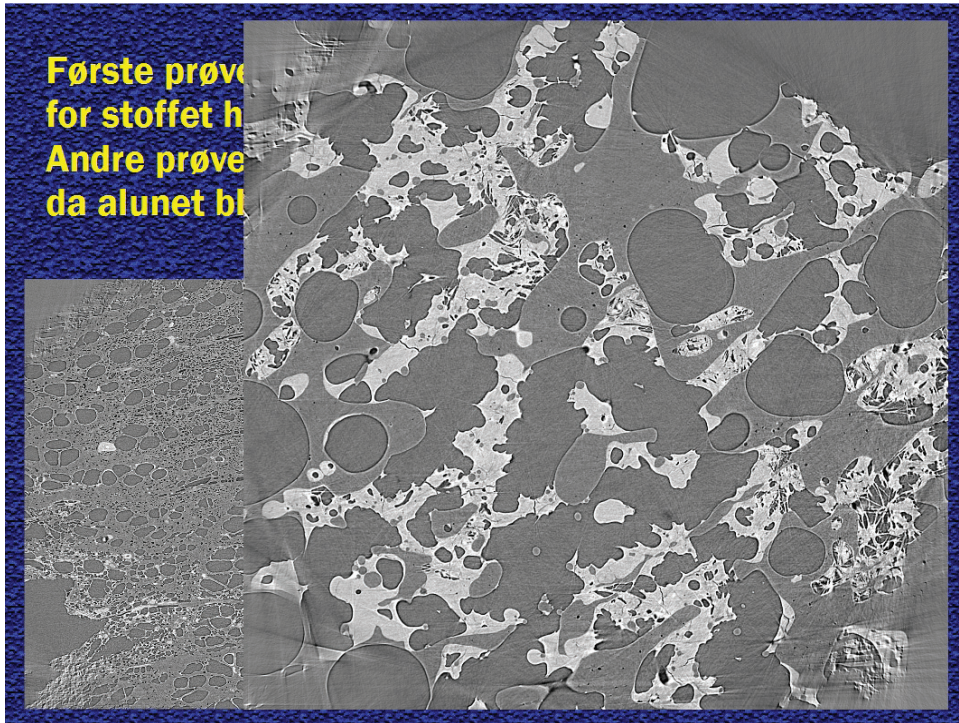
Problemet ser man her, på den anden prøve. Træet har været så ødelagt, at kun alunkrystallerne holdt det sammen. Når vi kommer vand på smelter træet, og der er ingen struktur. Hvad gør man så? Synger næste vers.

Here, in the second sample, you see the problem. The wood has been so degraded that only the alum crystals kept it together. As we put water in the wood, it melts and there is no structure left. What does one do then? Sings the next verse.

Så derfor vi får tenke en helt ny strategi:
Et stoff med styrke og struktur men uten gifter i.
Kanskje får vi lure på „biomimetikk"
Hvor man blir inspirert av all naturens mekanikk.
Hund i skogen renset pelsen sin
derfor dens eier tenkte „borrelås-ideen er min!"
Båter får delfiners dynamikk.
Fra katteøyets skinn en vanlig lys-refleks vi fikk.

Kunstig Velcro

Naturlig borre

Det er biomiketik.

So we then have to think of an entirely new strategy:
A compound with strength and structure but without poison in it.
We could possibly wonder about "biomimetics"
where you become inspired by all the machanics of nature.
Dog in forest rinsed his fur
thus its owner thought, "the Velcro idea is mine!"
Boats get the dynamics of dolphins.
From the shine of the cat's eye a normal reflex we got.

Image text: "Natural burr" (far left) "Artificial Velcro" (middle left).

This is biomimetics.

Hvilket stoff kan velges, som kompatibelt er?
Faktisk cellulose (det finns allerede der).
Ellers kitosan som er „optimert" kitin
med skall fra krabber/reker blir vel skatten fin?
Heisann og hoppsann og fallerallera
en håndsrekning fra mor natur må vikingtreet ha!
Heisann og hoppsann og fallerallera
dytt nytt tre inn i gammelt tre da blir det kanskje bra!

Tak til 'koret', tusind tak til musikken – tak fra mig!

What compound can be chosen which is compatible?
Actually cellulose (it is already there).
Or chitosan which is 'optimised' chitin
using the shell of crabs/shrimp will likely turn the treature pretty?
Heisann and hopsann and fallerrallera
lend a hand from mother nature the Viking wood must!
Heisann and hopsann and fallerallera
push new wood into old wood then all might end well!

Thank you to the 'chorus', thanks a lot to the music – that's all from me!

Gained experience and closing remarks

One of the nicest thing about the competition was, ironically enough, that it did not really feel like a competition. All of the participants from Oslo were friendly and we helped one another during the rehearsals. Suggestions and comments like "Don't stand there – you will block the presentation", "Why did you remove that comment from last time? Put it back in!", or "Wait, let me run to the back and tell you if I can see that clearly" were common. It eventually felt more like we were a group of performers putting on one big common show than a group of rivals who would soon be competing. As mentioned above, Christina even went so far as to play for me during the six-minute presentation and Marianne helped me transport my props to and from the national final. While the show might have been a good learning experience no matter what the interaction between us, I feel that it would have been much less enjoyable without this mentality pervading the set.

I think most of were surprised how little the judges understood or remembered from our presentations. It was often plain that they were criticising things we had tried to explain or asked for more detail about something we already covered. While it is easy to dismiss the judges as incompetent, you really have to ask yourself whether you are the one who could have explained things better. This again makes you wonder what good all the fancy research is if it is to hard to comprehend as to be inaccessible for anyone outside of your own field. Is it better to keep research 'correct' and 'pure' or is it more valuable to take a few understandable points and use these to make others interested in your field?

The untraditional approach of writing a song seemed to go down fairly well. Not only did it engage the audience but it also made my presentation stand out. In a competitive environment it is important to be noticed – and untraditional approaches might not only benefit your score but hopefully also affect how much of the idea behind the show the audience remembers later on. I think it is safe to say that all of the participants will have a different view of when something is science and when it is merely entertainment.

Of course, all participants had to conquer their fears. This, perhaps is one of the greatest boons reaped. Conferences will not seem scary when you have had to perform and be judged publicly in a competition. All in all, participating gave me some nice experiences and hopefully some insights which will be useful in the future.