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PHENOL FORMALDEHYDE REVISITED—NOVOLAC RESINS FOR THE TREATMENT OF DEGRADED ARCHAEOLOGICAL WOOD*

M. CHRISTENSEN,[1,2] F. K. HANSEN[1]† and H. KUTZKE[2]

[1]*Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo, Norway*
[2]*Museum for Cultural History, Department of Conservation, University of Oslo, Frederiks gate 3, P.O. Box 6762 St. Olavs plass, Oslo, Norway*

Archaeological wood is usually severely degraded. The Norwegian Viking Age Oseberg find exemplifies problems arising due to past conservation treatments and the need for new types of preservatives. Phenol formaldehyde (PF) has been investigated as a consolidant for alum-treated wood. X-ray tomography has revealed that it is possible to obtain a porous structure inside the wood, ensuring ethical acceptability by allowing re-treatment. In order to understand the curing mechanics, the kinetics of the initial condensation reaction were elucidated at room temperature. It was found that a second-order reaction using both phenol and formaldehyde concentrations is the most probable mechanism.

KEYWORDS: RESINS, REINFORCEMENT, CONSERVATION, WATERLOGGED WOOD, VIKING AGE

INTRODUCTION

Archaeological wood is normally found in a severely degraded state, in which most of the cell walls have been degraded and whatever remains collapses if dried at ambient conditions due to capillary forces. This makes treatment by a consolidant imperative in order to avoid warping and collapse. Conservation science aims at using analytical data to optimize treatments and improve storage conditions for archaeological artefacts. When problems and damaging processes caused by past conservation treatments are recognized, possible re-treatment procedures and preservation strategies have to be considered, which weigh the possible drawbacks of a given treatment against irreparable damage to the finds.

This study is focused on alum-treated wood, and the interaction between alum and preservatives and solvents is of particular interest. What is reported is an initial study of phenol formaldehyde in this capacity. The goal of this study is to evaluate how well the polymer penetrates the wood, whether it blocks the pores and how quickly phase separation sets in. The problems surrounding the Oseberg find also serve as examples of problems arising due to past conservation treatments, and while they are briefly described here, a more thorough discussion can be found elsewhere (Brøgger *et al*. 1917; Kutzke *et al*. 2009).

The Oseberg find and the alum treatment

This work is part of a project initiated to investigate and save the alum-conserved wooden objects from the Oseberg find from Tønsberg, Norway. It consists of the contents of a grave mound that

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†Corresponding author: email f.k.hansen@kjemi.uio.no

was excavated in 1904. Two high-status women were buried along with draft animals, precious textiles and a plethora of tools for both common and ritual use. The mound also contained the Oseberg ship, as well as richly carved wooden artefacts such as sledges, animal head posts and other ceremonial objects that are iconic parts of the collection. While the ship itself was merely dried, many of the waterlogged objects required stabilization in order to avoid collapse. Most have been emerged in a hot (80–90°C) concentrated alum ($KAl(SO_4)_2 \cdot 12H_2O$) solution. The solution penetrates the wood and alum recrystallizes upon cooling, supporting the wood structure by bulking it (Rosenqvist 1959; Unger *et al*. 2001). Unfortunately, this treatment has initiated an ongoing deterioration process. A degraded piece of alum-treated wood that has been in storage is shown in Figure 1. The wood exhibits a very high acidity (pH 1–2) due to sulphuric acid being formed as a consequence of the treatment (Braovac and Kutzke 2012). This acid is considered the most important reason for the decayed state of alum-treated wood in the Oseberg collections. The alum did not penetrate evenly throughout the objects, as shown in the neutron radiography images in Figure 2. This led to mechanical tension and cracks forming in the treated artefacts. Additionally, screws and nails used to secure fragmented objects to their frames are a source of metal ions, which are known in polymer processing to act as catalysts for degradation processes and have been shown to interfere with the stability of consolidants for archaeological wood (Glastrup

Figure 1 *A piece of alum-treated wood from the Oseberg find. The cracks show how fragile most of the wood is. Note that the acidity of the piece has even caused the original paper that the piece was stored on to degrade (© Museum for Cultural History, University of Oslo).*

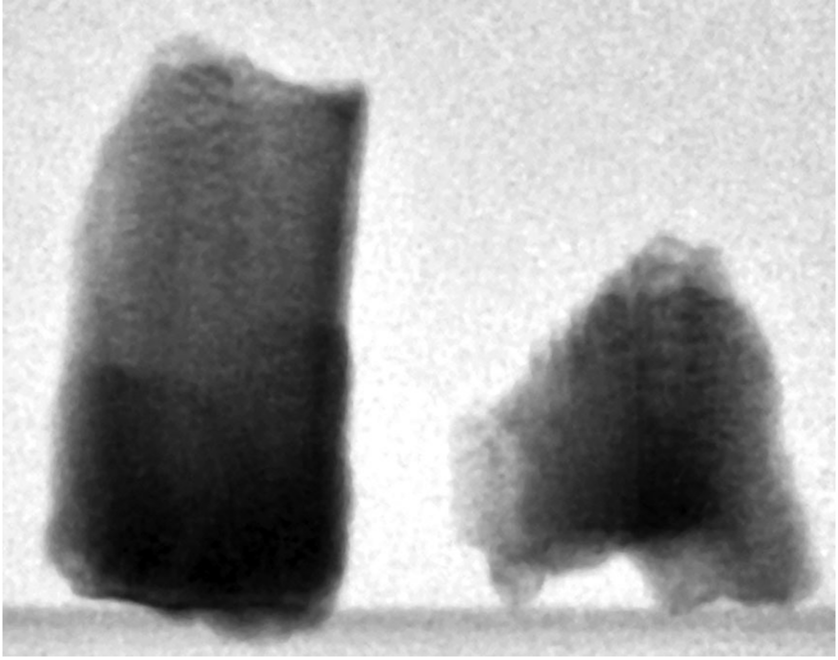

Figure 2 *Neutron radiography images of two samples of alum-treated wood, showing the distribution of material inside the pieces. The light areas are alum-rich, while the dark areas contain little alum. Note the uneven distribution.*

1997). Today, many of the wooden objects cannot support their own weight and the collection is in an alarming condition (Museum for Cultural History at the University of Oslo n.d.). During these studies, watery solvents were found to dissolve the alum crystals, removing the only support inside the treated fragments.

Polymers in conservation science

Many different polymers have been applied to waterlogged wooden cultural heritage but most of these—including poly(vinyl chloride) (PVC) or poly(acryl amide) (PAM)—suffer from problems with either poor penetration into the degraded wood and/or insufficient support of the treated objects (Unger *et al*. 2001). Poly(ethylene glycol) (PEG) deserves special mention, since it has been applied to several finds in Scandinavia, such as the Swedish warship *Vasa* (Glastrup *et al*. 2006). Unfortunately, an acidic environment combined with excess metal ions from spikes in the hull threatens to cleave the PEG chains, softening the consolidant and thus making the wood unable to support itself. This is particularly problematic in the case of the metal-rich Oseberg artefacts. Several resins applied during the 1960s were thought to be reversible, but removal was difficult and often damaged the finds (Baglioni and Giorgi 2006). Poly(ethylene glycol) with an average M_w of 4000 g mol^{-1} will degrade after 1000 h in normal air at 80°C (Han *et al*. 1995). Since PEG is considered acceptable for conservation, it gives an estimate of how long it should take to degrade new materials under similar conditions. Developed in Germany, the Kauramin method, using a melamine formaldehyde copolymer, has been applied (Wittköpper 1998). This polymer is similar to phenol formaldehyde, but the monomers have been reported not to harden below 80°C and water needs to be removed in order for the polymer to cure (Wirpsza *et al*. 1998). This makes the polymer less suitable for *in situ* polymerization of archaeological material.

A general problem is that treatment may lead to blocked vessels and lumens, preventing further treatment of the object. While such treatment might not be needed for a very long time, it is important to consider that even the most durable consolidants will eventually degrade. This means that any treatment of world-class heritage should consider stability on a scale of centuries or millennia, effectively requiring that re-treatment strategies are taken into account. In addition, anything with a diameter significantly larger than 0.55 nm cannot penetrate into the cell wall to replace sorbed water (Unger *et al*. 2001). This means that stabilization at the cell-wall level requires polymerization *in situ*, since pre-polymerized molecules will be much too large. An overview has already been written of how to choose between the more common treatments for archaeological waterlogged wood and their associated strengths and weaknesses (Hoffman 2009).

Requirements for future consolidants

Since it is often difficult in practice to completely neutralize acid and/or remove metal ions from artefacts, a future consolidant should ideally be extremely stable in both acidic and metal ionic environments. As most museum objects are displayed directly in a museum atmosphere, oxygen and a certain amount of water vapour cannot be eliminated. In addition, direct treatment by conservators at the museum is often necessary. This means that a consolidant must be able to cure at ambient temperature and pressure.

One of the most serious threats with consolidating materials, however, is plasticization. When a polymer completely fills every void inside the wood, it becomes impossible to introduce new strengthening materials later. When the polymer eventually degrades, nothing can be done to save the artefact. In order to prevent such a situation, the treatment must be reversible or the object must be re-treatable. Reversibility is theoretically the best option, allowing the old consolidant to be washed out of the treated wood to make room for a new consolidant. While it is theoretically possible to remove a range of consolidants, the fragile state of the treated objects, cross-linking of the consolidant, or practical working environments often make this impossible in practice. Even the choice of solvents might be very limited when treatments are carried out in a museum rather than a laboratory. In order to ensure that objects can be treated later on, without requiring such removal, it is vital to leave a pore system—that is, some kind of open structure—to ensure future accessibility throughout treated museum artefacts.

Especially when considering the alum-treated wood, its advanced state of decay means that reversibility becomes unrealistic. For this reason, any future consolidants developed in order to prevent further decay of the Oseberg and similar finds should leave a porous structure that allows future consolidants to penetrate throughout the artefacts. Some kind of *in situ* polymerization with a well-defined distribution inside the treated objects is a necessity in this case. Phenol formaldehyde is interesting in this regard due to its durability and resistance to acid. While it may not be the ideal solution in and of itself, study of it as a model compound can lead to essential discoveries on how to consolidate alum-treated wood.

About phenol formaldehyde

Phenol formaldehyde (PF), under the name Bakelite, was the first commercially mass-produced synthetic polymer (Crespy *et al*. 2008). Although invented for electrical insulation, it ended up in everything from car dashboards to cameras. Various kinds of fillers—for example sawdust—are often introduced into the polymer mix during curing and these affect the properties and durability of the polymer. Ageing of Bakelite items can often be ascribed to degradation of the filler material (Crespy *et al*. 2008). The polymer itself is produced by reacting phenol with formaldehyde in a condensation reaction using either acid or base as a catalyst (this is further described in the Kinetics section). Catalysts or hardeners can be used but have not been employed in these initial experiments. This means that only the monomer mix has to be distributed evenly inside the wood and avoids a second step in the treatment procedure, making it easier to evaluate the potential suitability of PF as a consolidant.

An acid-catalysed PF is called a 'novolac', while a base-catalysed one is called a 'resol'. Historically, base was cheaper than acid and thus most of the commercial resins described are resols (Baekeland 1909). Note that the term 'novolac' sometimes refers to oligomer molecules, so the PF is not fully cured. In this study, however, we use the term 'novolac' to distinguish our product from the more common base-catalysed resols, even if the said novolac contains enough formaldehyde to cure fully. Both are chemically similar amorphous thermoset polymers, but novolacs are free of ether bonds and should thus be more stable over time and hence better suited to the preservation of cultural heritage. Both types of resin are resistant to most solvents and even concentrated acids or bases once cured, because the condensation reaction is irreversible (Baekeland 1909). This is a huge advantage in wood conservation, where high acidity threatens many objects—such as the alum-treated items from the Oseberg find. Another point is that PF polymers phase separate during polymerization. The phenol is initially dissolved in the formaldehyde solution but as the molecules begin to polymerize, one organic and one watery phase are formed. Novolacs are more hydrophobic than resols and therefore phase separate at a much lower degree of conversion. Novolacs also have a relatively larger watery phase after phase separation. This is important because it can affect the porosity of the finished polymer and the distribution of polymer inside treated wooden objects, since the phases have different degrees of hydrophobicity and thus affinity for the remaining wooden material. This, combined with the fact that they will naturally polymerize inside the very acidic alum-treated wood, is the reason for these studies focused on novolacs. A few experiments with resols were carried out as well, but these are not part of this publication.

PF has been used before in conservation of both wood and bone (Ventikou 1999; Unger *et al*. 2001), but literature describing its use on wood is rare and often not freely available. In the cases mentioned, a commercial novolac pre-polymer seems to have been applied and cured using a hardener at temperatures in the range of 80–150°C. A wooden bucket from Castell-y-Bere in Wales was brought in for conservation in 1951 and treated with 'Bakelite' (Biek *et al*. 1958). At the time, the alum treatment was traditional, but no longer thought of as desirable. Although the PF gave the wood a dark colour and a resin-like texture, it was still better than wax or methyacrylate polymer. However, it was eventually decided to treat the bucket with urea-formaldehyde instead (also produced by the Bakelite company and thus leading to the confusion about items treated with 'Bakelite'). As in this example, the use of PF for casings and larger objects was generally discontinued both in conservation and in general, as cheaper polymers became available during the Second World War (Crespy *et al*. 2008), and yet PF polymers and copolymers are still much used as water-resistant glues, laminate resins, foundry resins and so on.

Toxicity is a concern when working with PF. Both phenol and formaldehyde are toxic and both skin contact and breathing the fumes of these chemicals causes irritation. Phenol is also classified as caustic, while formaldehyde is a possible carcinogen. According to the supplier, the limit values in soil are 1–5 ppm for phenol and 0.3–0.5 ppm for formaldehyde in various European countries. This means that PF should not be used in conservation without due consideration and safety measures. However, since the alum-treated wood differs significantly from untreated archaeological wood, PF offers several advantages. Being resistant to acid, a PF polymer would not be degraded by extremely acidic archaeological wood. The high aromatic content makes it extremely resistant to biological or physical degradation—especially in the case of novolacs, which do not contain ether bonds in methylol groups in the cured state (Looney and Solomon 1995). From a chemical perspective, this should make PF more resistant to degradation through oxidization as a result of being exposed to air. Since the structure of PF is similar to that of lignin—an important component that stabilizes the wood cell walls—it seems likely that the polymer will be compatible with degraded wood and able to react directly into the remains. The small size of phenol and formaldehyde molecules also means that the monomer solution can penetrate quickly into all parts of samples to be treated. The toxicity of the monomers may be reduced by polymerizing an intermediate product, so-called oligomer molecules, which would penetrate slightly more slowly, but be unable to penetrate human skin and thus be safer to handle. Even though the red colour of the cured polymer may ruin the impression of treated wooden items, the polymer can be used to reinforce the core of treated objects, which will not be seen by museum visitors. Stabilization of the powdery fragments is vital for the continued stability of alum-treated finds—specially if said artefacts are fragments mounted on their frames using screws or pins, as is the case with the alum-treated Oseberg objects. Due to its resistance to acid and similarity to lignin, PF was tested as a model system for possible future phenolic archaeological wood consolidants.

In order to obtain an open structure in the object after treatment, the relatively early phase separation of novolacs may be advantageous. In a best case scenario, the relatively hydrophobic organic phase inside the pores will have a high affinity for the remaining wood cellulose/lignin matrix. Thus the polymer may coat the surfaces inside the degraded wood, leaving the rest of the pore structure filled with water, which will then evaporate. This leaves an open structure after curing, enabling future penetration of a similar or different consolidant. Note that it will be vital to experiment with proper amounts of applied polymer before actual implementation, in order to prevent excess material from blocking the pores of the wood.

In order to be applicable in a museum environment, the polymer has to be handled by conservators and applied at room temperature. The PF in question can be pre-mixed (with or without catalyst) and applied directly in the museum. The pre-polymer mix can penetrate easily into an unblocked wood structure, although surface layers of lacquer or wax may require the use of syringes.

Reaction kinetics

A literature search did not reveal any information on room-temperature PF kinetics, although these have been studied at higher temperatures (Lee *et al.* 2003; Lei *et al.* 2006), even in systems containing lignin (Pan *et al.* 2008; Pérez *et al.* 2009). Therefore, kinetic studies have been carried out at 25°C as part of these studies.

Measuring the reaction speed and estimating the kinetics of said reaction gives an indication of how fast the reaction progresses. In this case, it allows us to estimate how quickly formaldehyde is used in the initial reaction and thus how much of it is potentially left to evaporate. This gives vital information on the toxicity of the original mix as well as the applied oligomer product.

In addition, knowing how quickly the reaction progresses will say something about how fast the molecules grow as a result of the next step in the reaction. If this happens very quickly, impregnation has to take place before the reaction is initiated in order to ensure an even distribution of polymer throughout the treated material.

The reaction kinetics of novolacs has been studied before. These studies used differential scanning calorimetry or rheo-kinetic models as well as temperature-dependent equations to characterize the reaction, possibly including hardeners such as hexamethylene tetramine (Markovic *et al*. 2001; Domínguez *et al*. 2010). None of these studies concern reactions at room temperature and various catalysts are often added. This makes it difficult to compare reaction rates between this and previous studies. The kinetics of the phenol formaldehyde reaction is complex, since formaldehyde may react both at the *ortho* (next to the OH group) and the *para* (opposite the OH group) sites (Looney and Solomon 1995). It has been estimated that the *para* site is roughly twice as reactive as the *ortho* site, resulting in a 1:1 reaction (since there are twice as many *ortho* sites) (Plenco n.d.). The initial reaction between the phenol and formaldehyde is one to one, but a further condensation reaction bridges two phenol molecules with a methylene bridge. These steps are illustrated in Figure 3. It is theoretically possible that formaldehyde will react with multiple phenol sites simultaneously. This will result in a second-order reaction with regard to formaldehyde (for more details, see the Kinetics section). This type of reaction is shown in Figure 4.

After this initial reaction, dimers react further with formaldehyde in a manner similar to that shown in Figure 4 and form larger molecules. Due to the various dimer structures, a significant number of possible oligomers may result. Despite such complexity, it is often possible to describe the kinetics in a simplified manner using simple first- or second-order kinetic

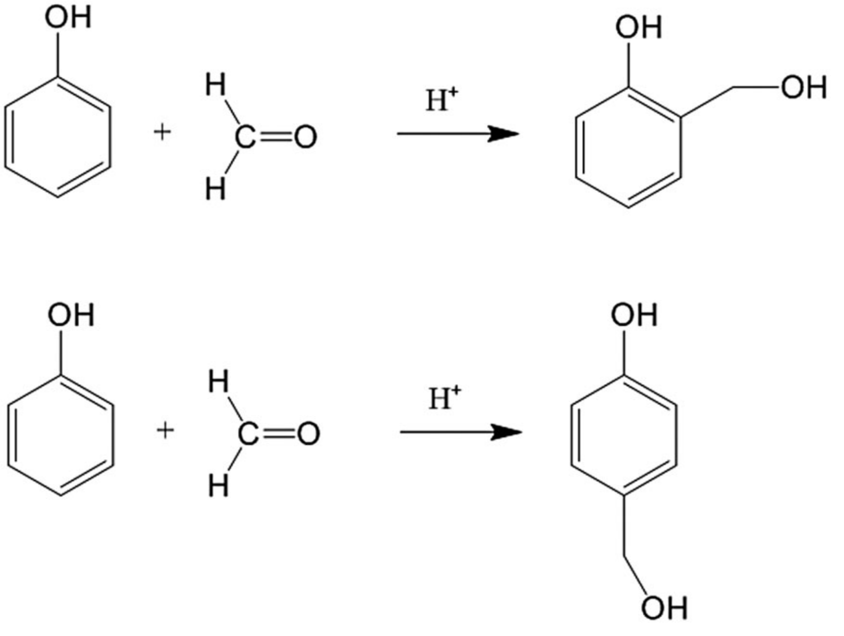

Figure 3 *The initial reaction schematic for novolacs.*

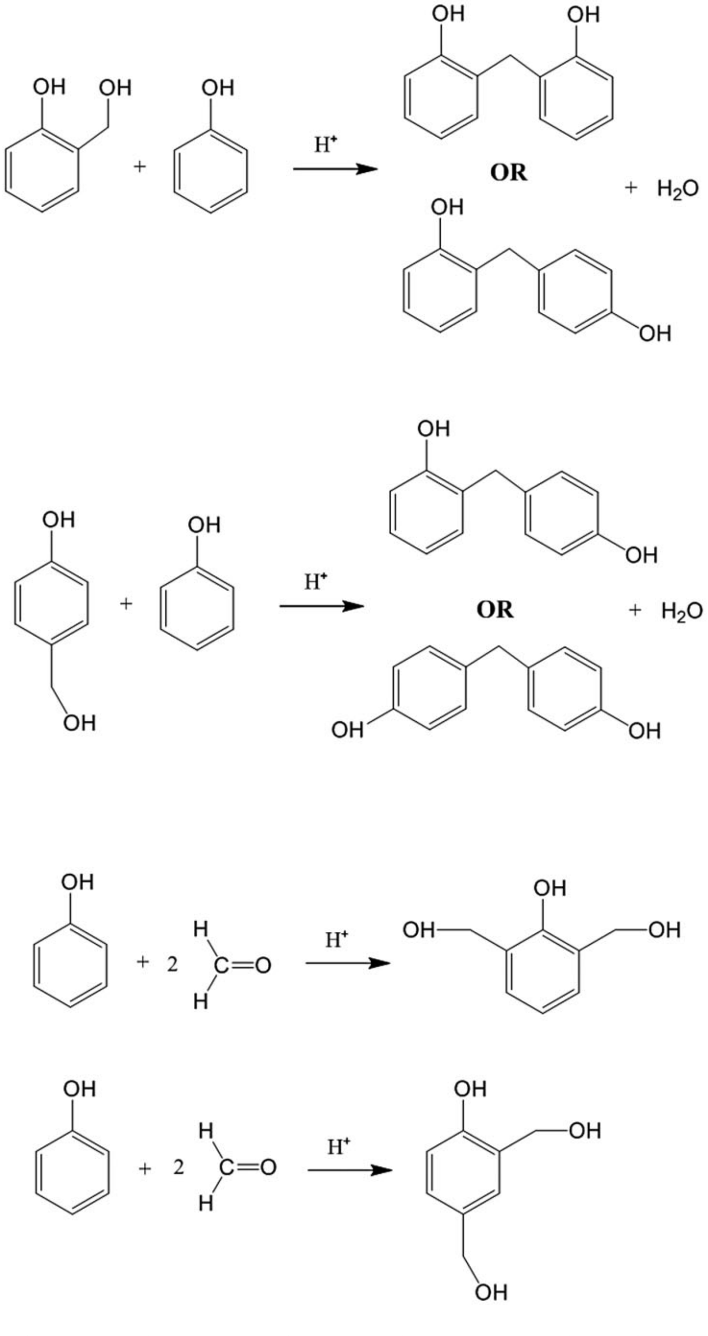

Figure 4 *The reaction schematic required for a second-order reaction with regard to formaldehyde.*

equations, which was also done before advanced computer modelling became commonplace (Debing *et al.* 1958). We have therefore attempted to describe the present results using various simple approaches. Since this reaction is H^+ catalysed, the concentration of acid will also affect the resulting rate constant. The obtained rate constants will therefore implicitly be proportional to the H^+ concentration. This must be taken into account when these results are to be utilized in other systems.

It should be noted that 'novolac' in this case refers to PF oligomers, as is common practice. As the primary goal of these studies is to determine how quickly a polymer will phase separate inside a wooden artefact, the full curing and condensation reactions are not properly described by this method. Since only the initial reaction has been studied, the polymerization was stopped before the material could fully cure. As such, the kinetics do not tell us about the final product but, rather, about speed and toxicity during pre-treatment. The data also give an indication of how quickly the mix phase separates, which can be vital for either separation of toxic phases or distribution inside the wood.

Model I: first-order reaction If the phenol concentration is very large compared to the formaldehyde concentration, it might be conceived that the change in the concentration of phenol does not significantly affect the rate and thus yields a first-order reaction that is only dependent upon the formaldehyde concentration. In general, the rate of the formaldehyde reaction can be expressed as

$$r = -\frac{\mathrm{d}[A]}{\mathrm{d}t}, \tag{1}$$

where $[A]$ is the concentration of the limiting compound, in this case formaldehyde. For a first-order reaction, the rate is

$$r = k_1[A], \tag{2}$$

where k_1 is the first-order rate constant. Integration yields, in the usual way,

$$[A] = [A]_0 \exp(-k_1 t), \tag{3}$$

where t is the time and $[A]_0$ is the initial formaldehyde concentration. This means that plotting $\ln[A]$ against time will yield a straight line from which k_1 may be found. The half-life time of the reaction is as follows:

$$t_{1/2} = \frac{\ln(2)}{k_1}. \tag{4}$$

Model II: second-order reaction with one reactant The assumption that two formaldehyde molecules simultaneously attach to each phenol molecule, and that phenol is not a limiting factor, results in a second-order reaction that depends purely upon formaldehyde. This is illustrated in Figure 4. The rate can then be expressed as follows:

$$r = k_2[A]^2, \tag{5}$$

where k_2 is the second-order rate constant. Combining with equation (1) and rearranging gives

$$\frac{\mathrm{d}[A]}{[A]^2} = -k_2\mathrm{d}t, \tag{6}$$

which upon integration gives

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_2 t. \tag{7}$$

In this case, plotting $1/[A]$ against time yields a straight line.

Models III and IV: second-order reaction with two reactants If one phenol molecule reacts with one formaldehyde molecule, and both influence the rate of reaction, the resulting rate becomes

$$r = k_3[A][B], \tag{8}$$

where $[B]$ is the phenol concentration and k_3 is the second-order rate constant for this reaction. A mass balance gives

$$[B]_0 - [B] = [A]_0 - [A] \quad \text{or} \quad [B] = [B]_0 - [A]_0 + [A]. \tag{9}$$

Combining equations (1), (8) and (9) yields

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k_3[A]([B]_0 - [A]_0 + [A]), \tag{10}$$

or, in rearranged form,

$$\frac{\mathrm{d}[A]}{[A]([B]_0 - [A]_0 + [A])} = -k_3\mathrm{d}t. \tag{11}$$

If $[B]_0 = [A]_0$, this equation reverts to equation (6) and the integral will be given by equation (7). If $[B]_0 \neq [A]_0$, then the denominator can be written as $[A]^2 + [A]([B_0] - [A_0])$, and integration then yields

$$\ln\frac{[A]}{[A]+[B]_0 - [A]_0} = \ln\frac{[A]_0}{[B]_0} - k_3 t([A]_0 - [B]_0). \tag{12}$$

By inserting $[B]$ from equation (9), we obtain

$$\ln\frac{[A]}{[B]} = \ln\frac{[A]_0}{[B]_0} - ([A]_0 - [B]_0)k_3 t. \tag{13}$$

Note that since this reaction type is the only one that depends upon the concentration of phenol, it can be plotted both assuming that formaldehyde reacts with phenol in a 1:1 ratio (III) or in a 1:2 ratio (IV). Both have been attempted.

EXPERIMENTAL

Formaldehyde (37% weight in water), phenol (purity ≥ 99%), hydroxylamine hydrochloride, and 2-propanol were bought from Sigma-Aldrich. In order to prevent the polymer from curing inside glassware and bonding to it, most of the initial trials were carried out in 30 ml polyethylene beakers. Kinetics experiments were carried out using 100 ml glass flasks since these were easier to seal. Note that the polymer did not cure fully during the kinetics experiments and thus the need to remove hardened material from the narrow flasks was not considered.

In order to elucidate the rate of reaction between phenol and formaldehyde, titrations for free formaldehyde were carried out according to the ISO 9397 standard. In this procedure, excess formaldehyde is reacted with hydroxylamine hydrochloride to form hydrochloric acid. The excess of acid is determined through potentiometric titration with NaOH. Pre-polymers with formaldehyde:phenol (F:P) molar ratios of 0.8, 1.0, 1.2 and 1.4 were prepared (see Figures 3 and 4 for the initial reaction). In the following, only the formaldehyde will be mentioned and the ratio of phenol will be assumed to always be equal to 1.0. Note that a ratio less than 1.0 will not be able to produce a curable product and so would not be suitable for treatment without another kind of hardener in the system. However, these ratios might still be interesting for conservation treatments, as part of a multi-step treatment, as the oligomer molecules produced would be significantly less toxic than pure phenol or formaldehyde while still being small enough to penetrate easily into the wood.

For the kinetics experiments, the same amount of phenol (12 g) was used for each sample and five drops of concentrated (35%) HCl (0.15 ± 0.01 g) were added to each sample in order to catalyse the reaction. The resulting pH value was just below zero—which is comparable to the most acidic alum-treated wood. Since the same amount of acid was added to all samples, regardless of total sample volume, the pH value increased slightly with a higher formaldehyde content, since the total volume also increased. The samples were stored at 25 ± 0.1°C using a Julabo MP-6 water bath. A bit of pre-polymer mix was removed using a pipette at different intervals and free formaldehyde was determined. The remainder of the mix was returned to the water bath to continue reacting. The measurements were discontinued when the samples began to phase separate, because the free formaldehyde concentration is unlikely to be homogeneous throughout the sample after this point. Analysis of the pure formaldehyde solution gave a concentration of 39.5% w/w rather than 37% as given by the supplier. This concentration was therefore used for the initial formaldehyde content in the theoretical calculations.

Pure polymer test samples were created by mixing 6 g of phenol with a suitable amount of formaldehyde solution (5 g for a F:P ratio of 1.0) and adding three drops of concentrated (37%) HCl to adjust the pH to just below zero. The reactants were then mixed in a beaker. A similar procedure was used to produce impregnating solutions for actual pieces of archaeological wood. The mixed solution was applied on to alum-treated pieces using a pipette. The mix was immediately absorbed into the degraded wood, which was subsequently sealed in a glass container to prevent evaporation of phenol and formaldehyde. While the pH value is extremely low, it is comparable to the level of acidity measured in the alum-treated wood. This means that the test conditions serve as a kind of ‘worst case scenario’ for degraded material in the Oseberg collections.

Fragments of alum-treated hardwood from the Oseberg find were impregnated with PF. The samples were fragments that had broken off from objects in storage. Both samples were from tools/ornaments made of either birch or alder (the species could not be determined with

Table 1 *Wooden samples used in the synchrotron X-ray tomography investigations*

	Drammen wood	*Oseberg 1*	*Oseberg 2*
Genus	*Pinus*	*Betula or Alnus*	*Betula or Alnus*
Approximate age	*100 years*	*1200 years*	*1200 years*
State	Untreated; very good condition	Alum-treated; light brown; surface is powdery	Alum-treated; dark brown; extremely powdery; cannot be handled without damage
Dimensions	40 × 15 × 10 mm	18 × 15 × 5 mm	10 × 8 × 5 mm
MC_{max}	159%	Unmeasurable	Unmeasurable
PF impregnation result	Only adhered to the surface of the treated piece	Penetrated throughout the piece; left large vessels open	Penetrated throughout the piece; caused it to lose all wood structure

certainty due to the state of deterioration of the wood). As a reference, roughly 100 years old archaeological pine wood from Drammen, Norway, was also investigated. Note that this wood was in much better condition than material from the Viking Age. This meant that it was possible to determine the maximum moisture content (MC_{max}) for the sample from Drammen using the procedure given by Jensen and Gregory (2006). The samples are summarized in Table 1. Wooden samples were impregnated by placing them in a small glass vial. Acidified monomer mix was dripped into the vial. Only a few drops were used in order to avoid forming a plastic block with an embedded piece of wood. The vial was then sealed and left at room temperature for 2 days, giving the mixture time to penetrate into the wood. In order to speed up the polymerization reaction, pure polymer samples and treated wooden pieces were cured by heating them to 70°C for a week. This temperature was chosen because tests for accelerated ageing are often carried out close to this temperature, and because it lies well below the temperature range in which wood typically begins to decompose.

Imaging experiments were also performed in order to study how the polymer is incorporated into the wood structure. Synchrotron-based X-ray tomography was performed at the TOMCAT beam line at the Paul Scherrer Institute in Villigen, Switzerland. One should be aware of that the samples chosen for synchrotron X-ray scanning must be very small. The largest aperture used was 4 × 4 mm, while the smallest was 0.75 × 0.75 mm. Since the alum salts are unevenly distributed inside the wood, and indeed the wood itself is very heterogeneous, we must remember that only small bits and pieces have been investigated. The tomography data shown in this paper are from samples taken near the surface of treated fragments. The samples themselves were carefully mounted on to sample holders using beeswax, which partly penetrated the wood. However, the images presented in this paper were all taken from parts of the samples that were free of beeswax. After being mounted on metal pins, the samples were arranged in trays for automatic processing.

RESULTS AND DISCUSSION

In the following, given that the focus has been on conservation science, the results are described with a particular focus on the advantages and limitations of a potential PF treatment.

Initial trials

The PF samples were both polymerized in beakers and added to wood for *in situ* polymerization. The monomer solution was found to penetrate rapidly into wooden samples, but allowing capillary action alone to suck the solution into relatively well-preserved wood resulted in unsatisfactory distributions, showing uneven penetration of the polymer throughout treated samples (unpublished results). Thus the samples should ideally be immersed in a pre-polymer mix. The pure polymer samples were examined to determine how the colour, hardness and possibly gases escaping during polymerization might affect the finished product.

When using concentrated HCl as a catalyst for polymerization, it was observed that the exothermic condensation reaction can lead to runaway reactions, especially without stirring or temperature control. This is a well-known problem with large-scale production (United States Environmental Protection Agency n.d.). Despite reports that this happens easily at pH 2 or below (Kumpinsky 1995), the process only happened in the test samples below pH 0, and as far as could be determined not at all inside the wooden test pieces. This suggests that runaway reactions are not a threat to alum-treated archaeological wood. Since HCl was used as a catalyst, the extreme acidity of alum-treated wood also means that the monomer mix can be applied directly to the wood without adding any excess acid. In this case, the pH will usually be higher than zero, meaning that there is even less risk of runaway reactions.

It was initially attempted to cure the polymer at room temperature, but as samples took several months to fully cure under these conditions, the procedure was altered to the following. A number of roughly 3 mm thick polymer discs with a diameter of 12 mm, cured at 70°C at the bottom of plastic beakers, were investigated. The colour was observed and if possible the discs were broken using two hands. If the polymer was too hard to break in this way, it was considered fully cured. The results are summarized in Table 2. Simply polymerizing pure PF without fillers showed that at an F:P ratio of less than 1.2, the finished polymer did not fully cure. Insufficiently cured polymers are dark red and deformable due to low molecular weight (oligomer) molecules. With increasing formaldehyde content, the polymers became more opaque and orange in colour. Based on this, it is unlikely that they will offer sufficient support to wooden artefacts. On the other hand, similar samples with an F:P ratio of 1.6 or more often formed cavities during curing at 70°C. When cut or broken, voids up to 10 mm in the longest dimension could be seen inside the hardened polymer mass—most likely a result of escaping formaldehyde and water vapour. It was found that novolacs were typically more opaque than resols, with the latter generally being transparent.

Table 2 *Observed properties of novolac PF samples cured at 70°C*

F:P ratio	*Colour*	*Notes*
0.8	Transparent red	Flowed when moist; powdery when dry; dissolvable in acetone and isopropanol
1.0	Opaque red	Brittle when dry; dissolvable in acetone and isopropanol
1.2	Opaque reddish orange	Cured fully; dissolvable in acetone and isopropanol
1.4	Opaque orange	Cured fully; not dissolvable
1.6	Opaque orange	Cured fully; not dissolvable; pockets of gas formed in several samples
1.8	Opaque yellowish orange	Cured fully; not dissolvable; pockets of gas formed in several samples

It was attempted to dissolve the pre-polymer in a few common solvents. Using a solvent to dilute the polymer may avoid or delay phase separation, and thus ensure that oligomer molecules have higher mobility and can diffuse throughout the wood. In addition, this can prevent the pre-polymer from curing during storage. Acetone (propanone) and isopropanol (propan-2-ol) were tested and both dissolve the pre-polymer and prevent complete curing when the organic phase is diluted. If the F:P ratio is 0.8 or less, the formed oligomer may be dissolved by stirring at room temperature. With an F:P ratio of 1.2, the samples were more cross-linked but can still be dissolved in isopropanol or acetone. It was attempted to re-cure such dissolved pre-polymers. While this was possible, the colour of the polymer changes slightly. Acetone makes the polymer much darker, while isopropanol makes it slightly more transparent and yellow—possibly as a result of the solvents reacting with the partially cured polymer. While wooden samples treated with pure PF become red, the acetone-treated PF turned the wood wine red. Neither treatment was acceptable for the surfaces of objects. The isopropanol-treated samples were transparent and yellow in colour, meaning that isopropanol only changed the appearance of treated wood slightly—even if significant amounts of polymer adhered to the outer surfaces of objects. From a conservation viewpoint, it therefore seems imperative to avoid acetone when thinning PF pre-polymers, whereas isopropanol slightly enhances the look of the treated items by making the resin more transparent and wood-coloured.

As phase separation takes place during polymerization, a clear mainly watery phase forms on top and a mainly organic phase forms at the bottom. The organic phase is initially clear, but later takes on an orange or red hue. Given sufficient time and excess formaldehyde, the organic phase cures and forms a proper PF polymer, still with a completely transparent watery phase on top. At room temperature, the process takes months. This means that the containers have to be sealed to prevent water evaporation while the polymer is still curing, as such evaporation will most likely warp the wood being treated.

Aging tests carried out at 70°C showed that the polymer will visibly darken and become redder or brown as time goes on. In some cases, the polymer may look almost black when viewed at arm's length. A fully cured sample kept at 70°C was observed over the course of more than a year. During this time it did not seem to lose integrity, warp or become noticeably more brittle, as it could not be bent or broken using fingers and it remained unscathed after it was accidentally dropped on the floor. This shows that a PF polymer may be considered for alum-treated objects, as high durability and acid resistance is desired. On the other hand, in unmodified form the polymer is unsuitable for use on any exposed surfaces due to the red colour.

Imaging

As a reference for future tomography, a piece of alum-treated wood from the Oseberg find was investigated. As can be seen in Figure 5, the alum is not evenly distributed in the piece even on a cellular scale. In order to elucidate how the consolidant penetrates, various tests were made with PF. Ideally, the polymer will be evenly distributed throughout the sample before curing and the phase separation will then cause the reinforcing material to be distributed as a layer on the remaining wood matrix, rather than randomly throughout the sample. Although not all of the samples gave the desired result, they are presented here in order to elucidate the optimal application for novolac-based polymers. A piece of the archaeological wood from Drammen, Norway, was treated with a novolac with F:P = 1.4. As can be seen in Figure 6, the polymer did not penetrate evenly and tended to mainly fill the outer layers. Rather than forming a thin layer to support the middle lamellae, the polymer completely bulked several vessels.

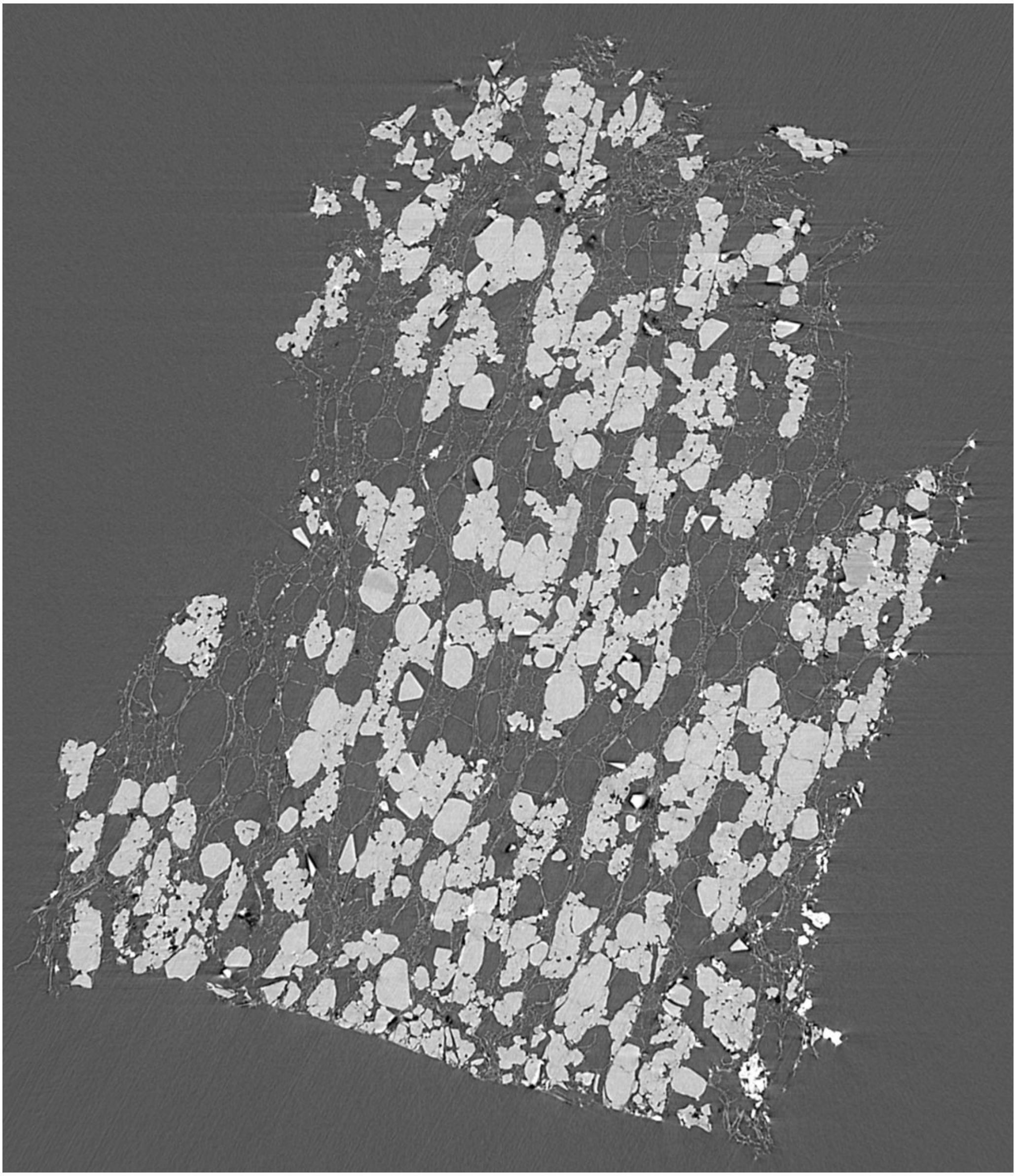

Figure 5 *The X-ray tomography of a piece of alum-treated wood from the Oseberg find. Note the uneven distribution of the alum crystals (solid white areas) in the structure.*

A heavily degraded piece of alum-treated Oseberg wood, roughly 1 × 1 × 0.5 cm (the edges were rounded due to degradation), was also treated with a novolac with F:P = 1.4. The state of degradation is usually linked to the colour of alum-treated wood, so the assumption of degradation was based on the fact that the piece had a very dark brown colour. Additionally, the surface of the piece was clearly powdery due to damage to the wood structure and the fragment had to be handled with care to avoid disintegration. As the piece was impregnated, it deformed within

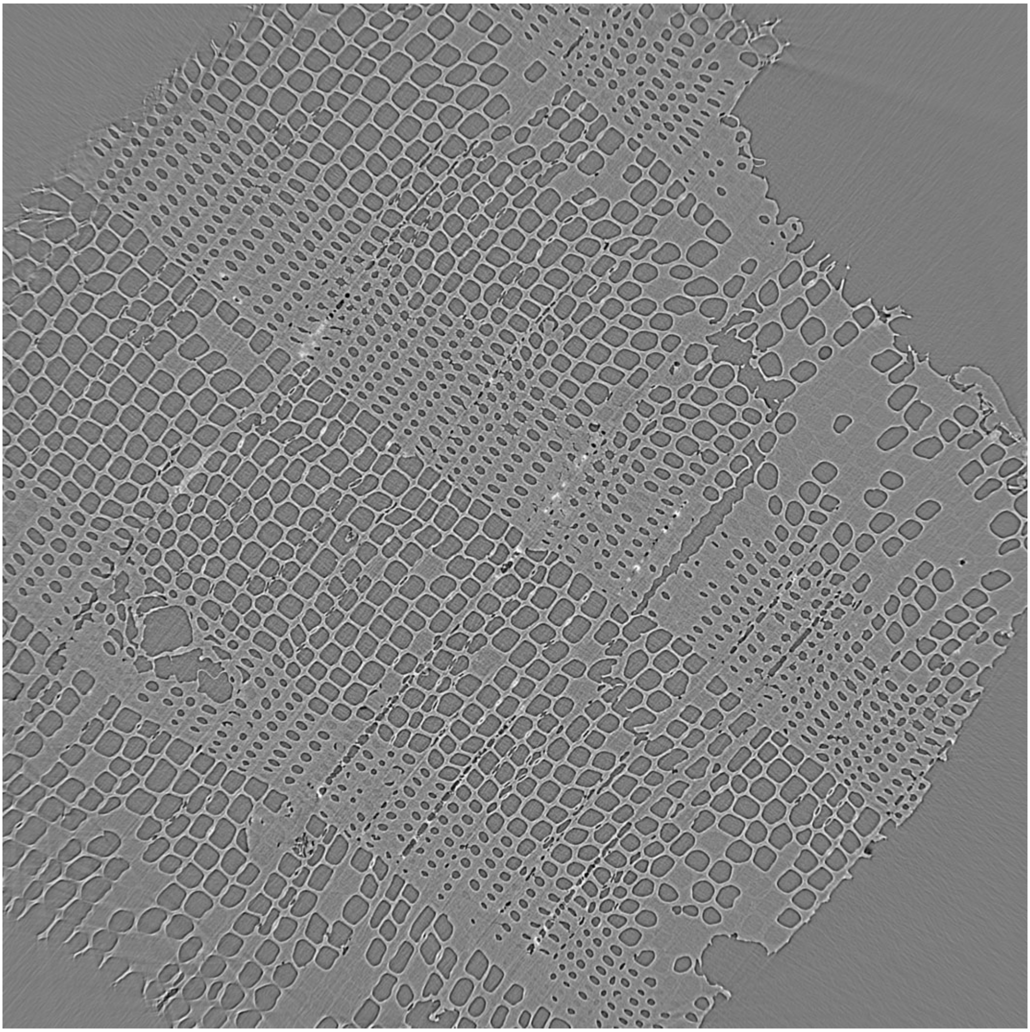

Figure 6 *Archaeological pine wood from Drammen, Norway, treated with an F:P = 1.4 mixture. Penetration is not even and some cells have been completely filled with polymer. The field of view is 1.5 × 1.5 mm.*

half an hour of applying the solution. This meant that the edges became rounded and some flow must have occurred, as the treated piece was bigger at the bottom than at the top. Additionally, small white crystals formed on the surface of the object during the curing process but were not clearly evident immediately after treatment. They could be noticed the morning after and became more noticeable during the 2 days of curing. As seen in Figure 7, the alum was dissolved by the watery solution and no structure is left in the treated piece. While the loss of alum in itself is not bad, the deformation happens before the polymer cures, meaning that the polymer irreversibly fuses the rearranged powder into an amorphous shape. This means that water cannot be used as a solvent when consolidating the severely degraded parts of the Oseberg find without leading to complete loss of the shape of heavily degraded wood. Another piece of alum-treated wood from the Oseberg collections, measuring about 1.2 × 1 × 0.4 cm, was also impregnated with the same

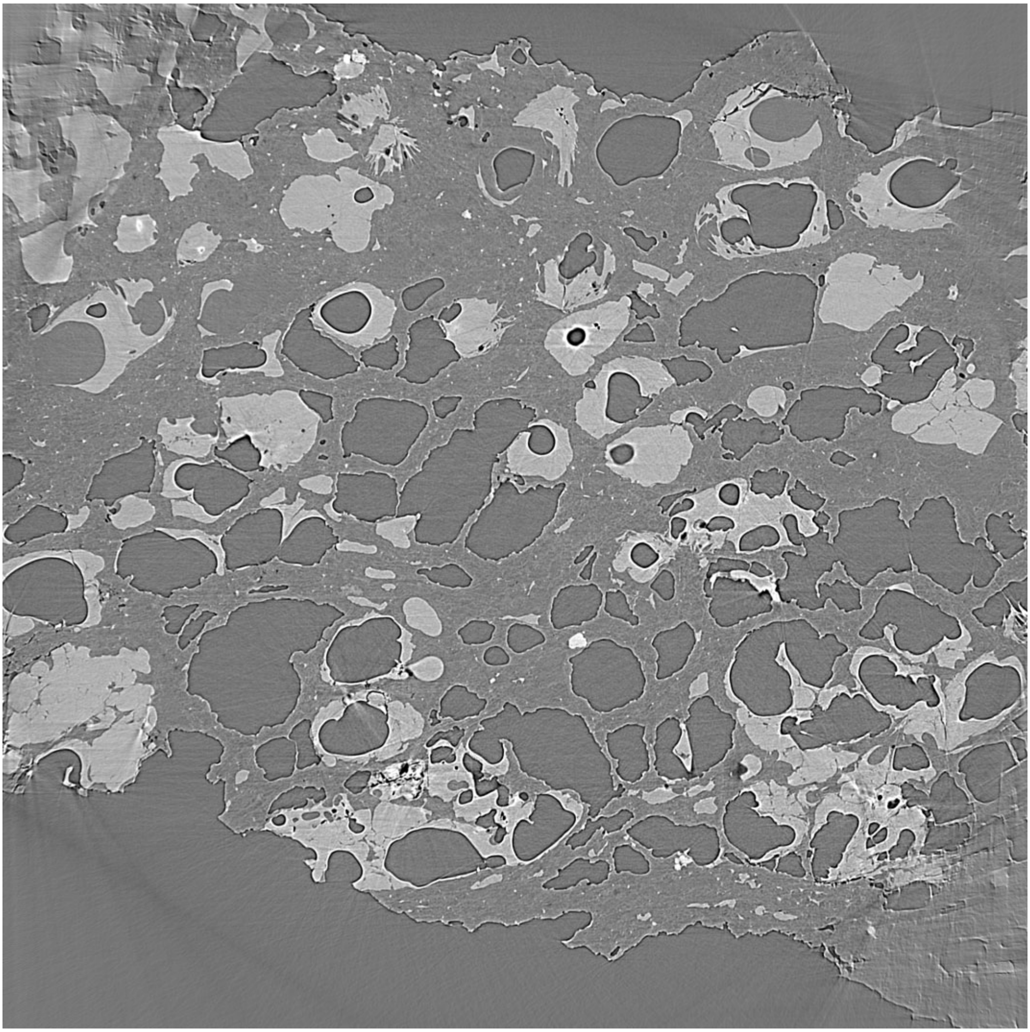

Figure 7 *Very degraded alum-rich Oseberg wood, 'Oseberg 2', treated with F:P = 1.4 pre-polymer. The field of view is 1.5 × 1.5 mm. Note that the alum crystals have recrystallized and no wood structure remains.*

novolac. This piece was assumed to be in better shape and possibly to contain less alum, based on the fact that it was much brighter than the previous piece. The polymer mix seemed to penetrate at roughly the same rate in both treated pieces. The pre-polymer was dripped on to the piece and sealed in a glass tube before curing at 70°C for 2 days. The piece looked unaltered (although slightly more reddish) after PF treatment. Unlike before the treatment, the treated fragment could be handled without cracking or powdering.

As can be seen in the tomography in Figure 8, the structure of the best preserved sample was not completely filled with polymer. Although the alum crystals changed shape, the larger vessels were left open, allowing for a later re-treatment. Although only a single tomography slice is shown, continuous open voids were observed when looking through the tomography slices. This indicates that the PF had coated the wood rather than simply forming closed 'bubbles' inside the

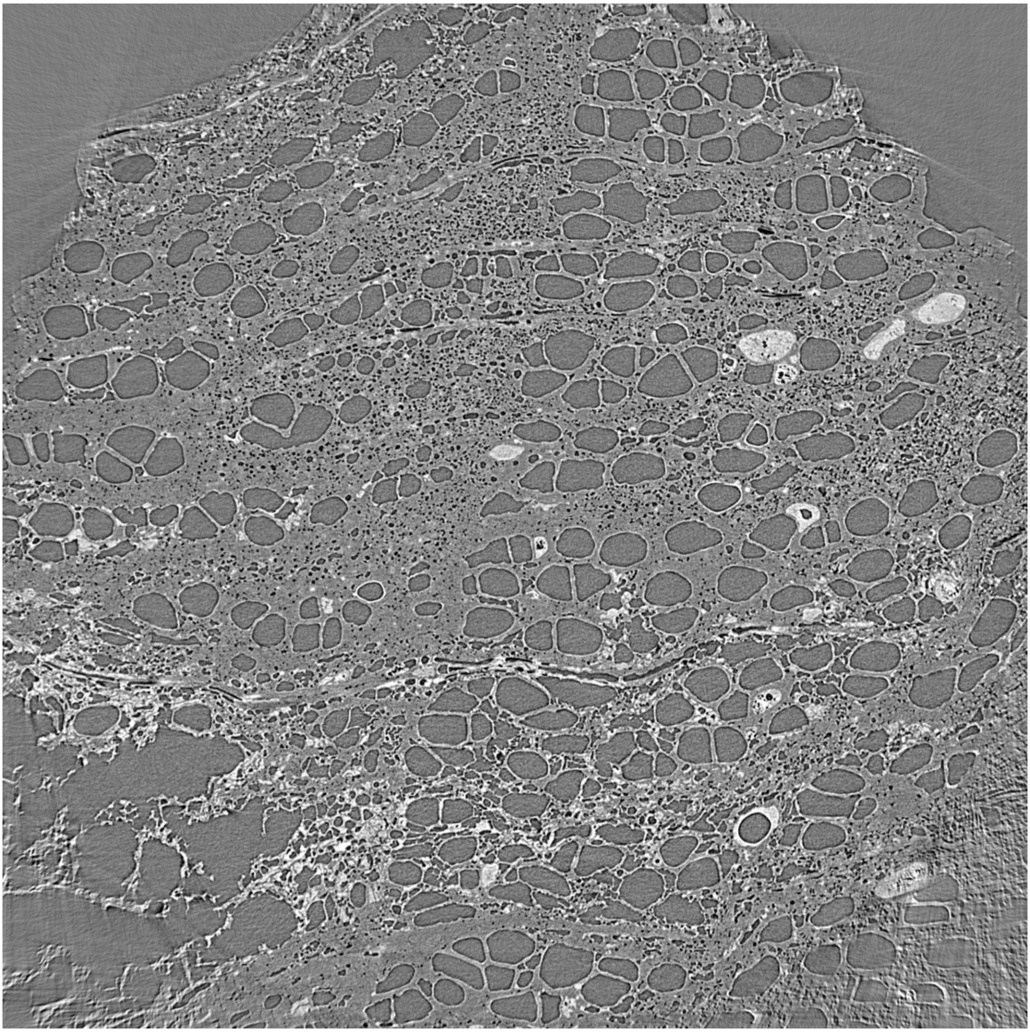

Figure 8 *Alum-treated Oseberg wood in relatively good condition, 'Oseberg 1', treated with F:P = 1.4 pre-polymer. The field of view is 1.5 × 1.5 mm. While it is difficult to distinguish between polymer and remaining wood, the alum crystals (white areas) have recrystallized. Although the fine structure has been filled with polymer, the larger pores remain unblocked.*

treated piece. Since crystals cannot be seen, the alum must have recrystallized and lost its original shape during treatment. Since alum is a bright colour in the tomographies, the white areas are most probably rich in recrystallized alum.

Kinetics

The data obtained from the titration experiments were plotted using the various models outlined in the Kinetics section above. The resulting charts are shown in Figure 9. Comparing the figures, all of the models give roughly linear plots. Upon closer examination, the first-order reaction

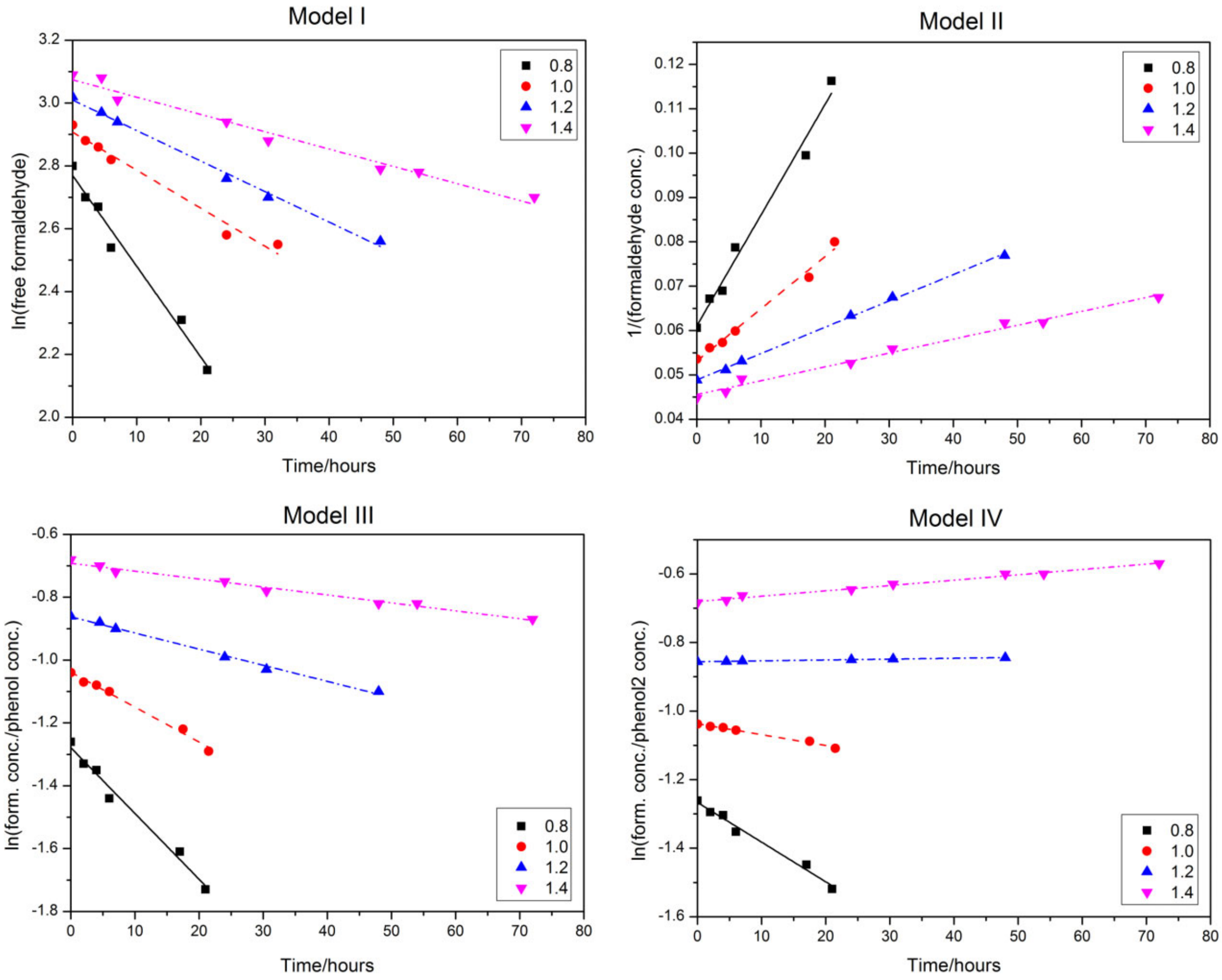

Figure 9 *Measurements of the free formaldehyde content for F:P ratios of 0.8 (■), 1 (●), 1.2 (▲) and 1.4 (▼). The graphs represent the first-order formaldehyde reaction (I), the second-order formaldehyde reaction (II), the first-order reaction regarding both phenol and formaldehyde (III), and as III, but with two phenol molecules reacting with each formaldehyde molecule (IV).*

(model I) gives the worst fit. Both a second-order reaction depending purely upon formaldehyde (model III) and also the second-order reaction depending on both monomers (model IV) give good fits with the observed data. In order to determine if one model is significantly better than the other, a series of residual plots were made and are shown in Figure 10. The first-order model (I) gave the largest and not randomly distributed residuals, with several series starting out and ending with negative values but having positive values in the middle of the series. This lack of fit indicates that a straight line is not a good model here. Both of the second-order models (III) and (IV) are almost identical, but several of the series tend to have several points in a row, either below or above the *x*-axis. The second-order formaldehyde plot (II) seems to be randomly distributed. Since this model also has the advantage that it only depends upon formaldehyde, it is relatively easy to use, as it simply requires a sample of the impregnating solution to be titrated in order to determine how far the reaction has progressed. The result also coincides with a previous study, which showed that a pure sodium hydroxide catalysed system could be described using second-order reactions, although in this case the use of both phenol and formaldehyde concentrations gave the better fit (Debing *et al.* 1958).

Linear fits were made using Origin 8.1 and the resulting data are shown in Table 3. The value plus or minus the standard error is given for slopes and intercepts for the various models. It should be noted that since all the fits are straight lines, the R^2 values should be comparable between models without calculating variances. From the scatter plots and the R^2 values it is seen that the adjusted second-order reaction where one formaldehyde molecule reacts with two phenol molecules gives the best result. However, all of the second-order models give good fits when compared to the obtained data. This means that for rough estimations it is acceptable to use the model that only depends upon the formaldehyde concentration (model II), eliminating the need to calculate the phenol content even though model IV gives the most exact fit. It is important to note, however, that an excess of formaldehyde means that all phenol will react at some point while there is still free formaldehyde left, and that the reaction kinetics must change as the polymer begins to cure. In order to model this reaction accurately to full conversion, it seems necessary to use a computer simulation. This will, however, require the estimation of more reaction rate constants, and we have not seen this as the objective of this work.

From a conservation perspective, the kinetics show that free formaldehyde reacts quickly with phenol. This means that the toxicity of the reaction decreases rapidly with time. The time until phase separation varied from 20 to 74 h (increasing with increasing formalin content). Since the pH level of the solution was similar to that of the most acidic alum-treated wood, it means that the solution could phase separate inside treated objects after as little as a day. Longer curing times are probably because most of the wood is less acidic and also because an F:P ratio of at least 1.2 is desired in order to ensure that the polymer cures. Due to the small size of the monomers, alum-treated fragments from the Oseberg find will most likely be evenly impregnated in this time frame. If the method is ever to be applied to larger wooden finds, however, it becomes imperative to test the distribution of the polymer to ensure that the phase separation does not prevent an even distribution.

CONCLUSIONS

Based on the degraded state of the Oseberg find, there is a desperate need to develop new ways to re-treat alum-treated artefacts. Phenol formaldehyde (PF) polymer was investigated and kinetics modelled for reactions at room temperature to evaluate its suitability as a consolidant for such alum-treated artefacts. What is reported here is the first step in determining the properties

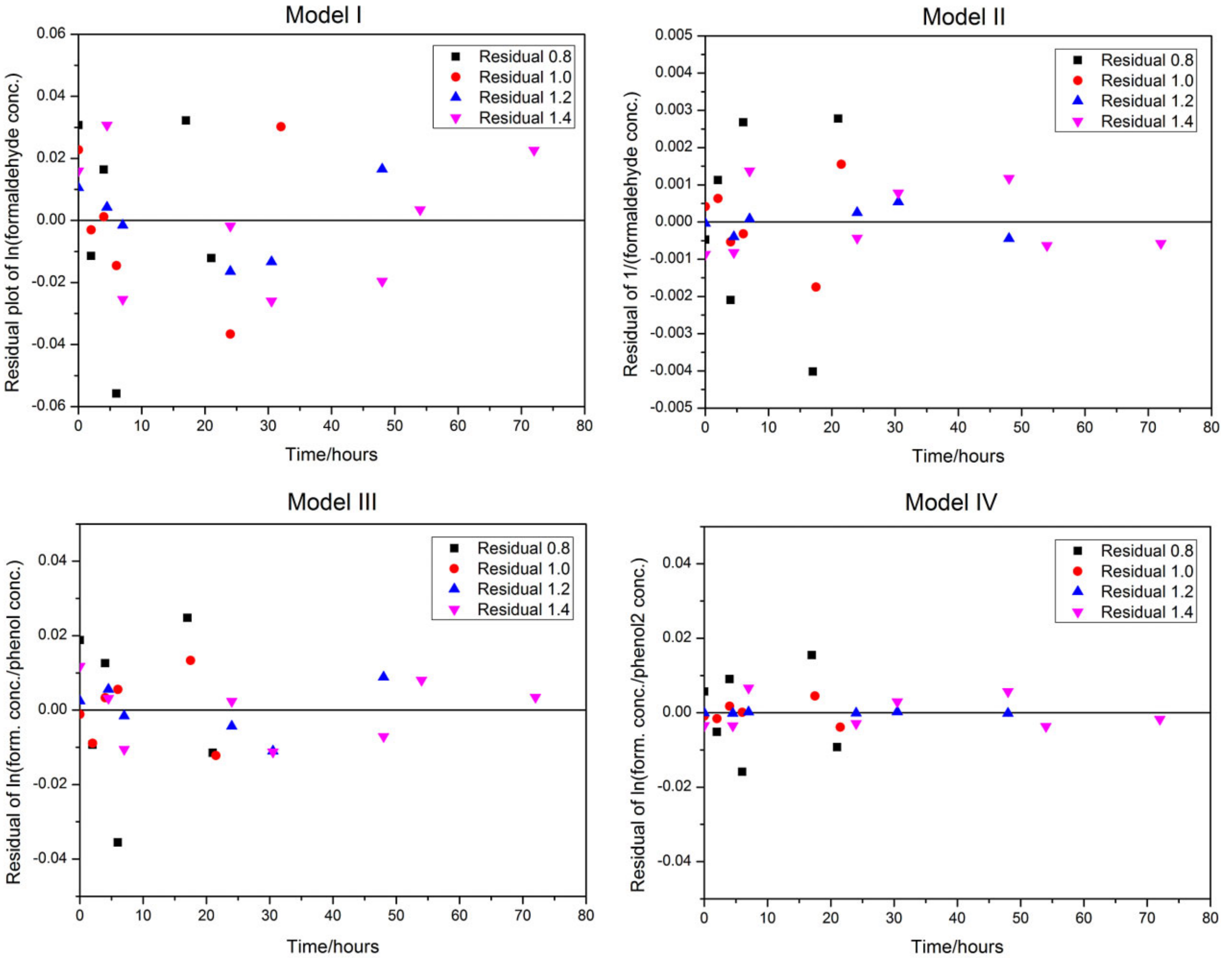

Figure 10 *Residual plots of the above fitted models. The F:P ratios are 0.8 (■), 1 (●), 1.2 (▲) and 1.4 (▼). The graphs represent the first-order formaldehyde reaction (I), the second-order formaldehyde reaction (II), the first-order reaction regarding both phenol and formaldehyde (III), and as III, but with two phenol molecules reacting with each formaldehyde molecule (IV).*

Table 3 *Results for the various models for the investigated F:P ratios: the extrapolated slopes are the observed reaction rates*

Mode	*Value*	*F:P = 0.8*	*F:P = 1.0*	*F:P = 1.2*	*F:P = 1.4*
I	Adjusted R^2	0.97756	0.97178	0.99342	0.973
	Slope	-0.0289 ± 0.0020	$-0.01211 \pm 9.2 \times 10^{-4}$	$-0.00971 \pm 9.2 \times 10^{-4}$	$-0.00551 \pm 3.5 \times 10^{-4}$
	Intercept	2.769 ± 0.022	2.907 ± 0.015	3.00946 ± 0.0090	3.07402 ± 0.0134
II	Adjusted R^2	0.98026	0.98536	0.99851	0.98472
	Slope	0.00250 ± 0.00016	$1.18 \cdot 10^{-3} \pm 7.5 \times 10^{-4}$	$5.94 \times 10^{-4} \pm 1.0 \times 10^{-5}$	$3.12 \times 10^{-4} \pm 1.5 \times 10^{-5}$
	Intercept	0.0611 ± 0.0018	0.05313 ± 0.00075	$0.04887 \pm 2.6 \times 10^{-4}$	$0.04556 \pm 5.7 \times 10^{-4}$
III	Adjusted R^2	0.98019	0.98847	0.99292	0.98043
	Slope	-0.0209 ± 0.0013	$-0.01111 \pm 5.4 \times 10^{-4}$	$-0.00513 \pm 5.4 \times 10^{-4}$	$-0.00252 \pm 1.3 \times 10^{-4}$
	Intercept	-1.279 ± 0.015	-1.0389 ± 0.0063	-0.8625 ± 0.0049	-0.6918 ± 0.0052
IV	Adjusted R^2	0.98217	0.98694	0.99803	0.98671
	Slope	$-0.01157 \pm 7.0 \times 10^{-4}$	$-0.00316 \pm 1.6 \times 10^{-4}$	$2.518 \cdot 10^{-4} \pm 5.0 \times 10^{-6}$	$0.00156 \pm 6.8 \times 10^{-5}$
	Intercept	-1.2667 ± 0.0080	-1.0371 ± 0.0019	$-0.85595 \pm 1.3 \times 10^{-4}$	$-0.68053 \pm 2.6 \times 10^{-4}$

and suitability of PF polymers for this purpose. It should be noted that the toxicity of the monomers used, the brittle nature of the cured product and the red colour of ageing PF make it undesirable for treatment of archaeological wood in general. Future tests on larger pieces of wood must be performed before a full assessment can be given. The cured resins have good resistance to acids and ageing and are chemically similar to the lignin in wood. The phase separation that occurs during the polymerization reaction also makes acid-catalysed novolacs better than the base-catalysed resols for creating a porous structure inside the artefacts. It was shown that in one case, the cured polymer was distributed so that the vessels in the wood are kept open in the surface of a fragment from the Oseberg find. The X-ray synchrotron tomography slices indicate that the organic phase of the PF goes into the remaining wood material. Based on knowledge of the phase separation during polymerization, it may be assumed that the watery phase gets forced into the pores of the wood. This means that the proper amount of polymer in relation to degraded wood should leave an open structure inside the wood and allow objects to be treated again in the future.

The kinetics experiments indicate that the polymerization reaction can be treated as second order depending on both formaldehyde and phenol for the rate equation. This means that free formaldehyde is consumed quickly in the impregnation baths and that sampling of formaldehyde will give a good estimate of how far the reaction has progressed.

Future tests should focus on taking advantage of the phase separation to maintain a porous structure inside treated objects. This principle is especially important because it is applicable to polymers other than PFs and finds other than the alum-treated pieces, potentially paving the road for consolidants that do not fill the wood randomly but maintain its porous structure. Further porosity tests and imaging of samples from the core of treated items should be carried out to confirm that the structure observed in the tomography allows access throughout the treated sample. It is also of vital importance to test more possible solvents, both for larger pre-polymer molecules and for monomers, in order to prevent the dissolution of alum crystals during impregnation.

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