

Original research or treatment paper

# Natural polymers as alternative consolidants for the preservation of waterlogged archaeological wood

Zarah Walsh<sup>1</sup>, Emma-Rose Janeček<sup>1</sup>, Mark Jones<sup>2</sup>, Oren A Scherman<sup>1</sup>

<sup>1</sup>Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge, UK,

<sup>2</sup>The Mary Rose Trust, Portsmouth, UK

In recent years, there has been increased interest in examining alternative polymers for the conservation of archaeological artefacts, particularly waterlogged timbers, providing better, renewable, greener alternatives to poly(ethylene glycol) (PEG). The degradation of PEG consolidants in the timbers of the sixteenth century warship *Mary Rose* has been examined and the rheological and thermal properties of PEG have been compared with its monomethyl and dimethyl ethers and several polysaccharide consolidants (chitosan, guar, and 2-hydroxyethyl cellulose) in order to evaluate their potential as alternative consolidants for the conservation of waterlogged wooden artefacts. Additionally, the effect of the polymers on the archaeological wood was characterised by thermogravimetric analysis and solid-state nuclear magnetic resonance spectroscopy. The results suggest that the future of conservation technologies lies with polysaccharide consolidant materials, which show enhanced compatibility with wooden artefacts with no detectable side effects while also being cheap, with extremely low toxicity, renewable, and sustainably resourced.

**Keywords:** *Mary Rose*, Consolidant, Maritime archaeological wood, Natural polymers, Poly(ethylene) glycol, Treatment systems/materials

## Introduction

The sixteenth-century English warship, *Mary Rose*, was a marvel of her time, the flagship of what is now the Royal Navy and a favourite of King Henry VIII. In 1545, 34 years after commissioning, she sank entering battle with a French fleet in the Solent channel near Portsmouth (UK). She lay underwater largely protected by sand and silt from the currents and fauna of the channel until she was raised from the sea in 1982 (Bell *et al.*, 2009; Millard & Schroeder, 2010). Her excavation from the sea floor marked the beginning of one of the most extensive conservation efforts in modern times.

Based on the state-of-the-art in conservation science at the time, the synthetic polymer poly(ethylene glycol) (PEG) was used to replace water in the ship's timbers (Almkvist & Persson, 2008a, 2008c; Giachi *et al.*, 2010; Christensen *et al.*, 2012). This is a crucial part of the conservation process as uncontrolled drying can lead to the collapse of already fragile wood cells causing further structural damage.

Replacing the water with polymer allows the timbers to be dried without significant shrinkage, protecting the integrity of the ship's structure. In addition to structural instability, biological degradation from marine organisms and water-borne microbes has also become a major conservation issue over time. To combat biological degradation, broad spectrum biocides have generally been added to the polymer solutions during the conservation process (Bjordal *et al.*, 1999; May & Jones, 2008). In the case of the *Mary Rose*, a biocide known as PhaseChem305 was used (Jones, 2013), resulting in timbers that retain their structure after drying and are less prone to biological attack.

In recent years, however, there have been several reports from conservators at the museum housing the seventeenth century warship *Vasa* in Stockholm on disadvantages associated with the use of PEG. In particular, these reports focus on the degradation of PEG to acidic by-products over time, its utility as a solid-state ion transporter (Glastrup *et al.*, 2006a, 2006b; Mortensen *et al.*, 2007; Mortensen, 2009), and the plasticising effect it can have on already fragile archaeological wood (Bardet *et al.*, 2007). Recent work suggests that polysaccharides and

Correspondence to: Oren A. Scherman, Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.  
Email: oas23@cam.ac.uk

oligoamides are the most suitable alternatives to synthetic treatments such as PEG (Cipriani *et al.*, 2010, 2013; Christensen *et al.*, 2012). This is mainly because of their similarity to the wood matrix and/or the lack of acidic by-products on degradation. For the purposes of this work, all natural polymer-based materials irrespective of further synthetic modification will be referred to as natural polymer-based consolidants to distinguish them from fully synthetic materials such as PEG.

As the first stage in a project to develop new conservation technologies for the preservation of archaeological wooden artefacts, specifically the timbers of the *Mary Rose*, it was necessary to understand the specific problems associated with the use of PEG in this artefact so they can be avoided in future conservation strategies. Thus, PEG (molecular weights of 200 and 2000) from previous treatments of the *Mary Rose* was extracted from core samples obtained from the hull and analysed by gel permeation chromatography (GPC) in an effort to understand how the polymer was distributed within the wood, and the types of degradation processes it was undergoing.

Secondly, two PEG derivatives (mono methyl and dimethyl ethers) were studied as potential alternative consolidants and their rheological and thermal behaviours were compared with that of PEG. While the reduction in the number of terminal hydroxyl groups in the PEG derivatives is likely to reduce their propensity to form acidic by-products, reliance on synthetic, non-renewable materials is not the optimum way forward for the development of new consolidants. For this reason, a number of natural polymer-based consolidants were also examined, specifically 2-hydroxyethyl cellulose (2-HEC), chitosan, and guar. In the case of both the synthetic and natural polymer-based consolidants, rheological behaviour, thermal stability of the treated timbers, change in pH after accelerated ageing studies, and the effect of the consolidant on the archaeological wooden matrix studied by solid-state nuclear magnetic resonance (ssNMR) and Fourier transform infrared (FTIR) spectroscopy were all considered in determining suitability. It is important to consider the three most important issues affecting the conservation of the *Mary Rose*, which will determine the applicability of any alternative material. These are structural instability upon drying (Giachi *et al.*, 2010), biological degradation (Bjordal *et al.*, 1999; May & Jones, 2008) and, more recently discovered, the build-up of Fe<sup>3+</sup> from corroded iron bolts that can catalyse the production of acid in the timbers (Sandström *et al.*, 2002; Fors & Sandström, 2006; Almkvist & Persson, 2008b, 2008c). Ultimately, the ability to address these conservation issues will determine the future of any alternative consolidant materials. The results presented in the

following sections show the suitability and potential of natural polymer-based consolidants as excellent alternatives to PEG.

## Experimental

### Materials and reagents

Poly(ethylene glycol), MW 200 and 2000 (PEG200, PEG2000) were purchased from Fisher Scientific. PEG monomethyl ether, MW 350 and 2000 (MPEG350, MPEG2000) were received from INEOS. PEG dimethyl ether, MW 250, 500, and 2000 (DMPEG250, DMPEG500, DMPEG2000), chitosan from shrimp shells, guar gum, and 2-HEC were obtained from Sigma-Aldrich Chemical Company. Acetic acid was purchased from Breckland Scientific. All water used in experiments was ultrapure obtained from a Milli-Q water filtration system. Archaeological wood samples were obtained from an untreated piece of timber from the *Mary Rose* or from core samples of the PEG-treated hull of the ship, which were kept refrigerated before analysis.

### Instrumentation

Extracted PEG samples were analysed using the GPC on a LC-20AD chromatograph from Shimadzu with a refractive index detector from Wyatt Technologies using an Aquagel-OH guard column (8 µm particle size, 50 × 7.5 mm) and Aquagel-OH Mixed-M separating column (8 µm particle size, 300 × 7.5 mm) both from Agilent Technologies GmbH.

Rheological characterisation was performed using an AR-G2-controlled stress rheometer from TA Instruments fitted with a Peltier stage set to 20°C. Strain sweep measurements were performed at a frequency of 10 rad per second, while frequency sweeps were carried out at 1% strain amplitude. All measurements were performed using a 60 mm parallel plate geometry set to a gap height of 0.40 mm and analysed using TA Instruments TA Orchestrator software.

FTIR spectroscopy was carried out on a Perkin Elmer Spectrum One series FTIR spectrometer over a range 400–4000 cm<sup>-1</sup> using a universal ATR sampling accessory.

Thermogravimetric analysis (TGA) was carried out on a Pyris 1 TGA from Perkin Elmer Corporation using a temperature ramp of 293–573 K at a rate of 5 K per minute in disposable aluminium pans.

ssNMR samples were, where required, prepared by ball milling using a Mikro-Dismembrator S (Sartorius) at 3000 rpm until a fine powder was achieved (typically 30 seconds). The powdered sample was then packed into a 4 mm diameter zirconia rotor. High resolution <sup>13</sup>C ssNMR was recorded using magic angle spinning (MAS) and cross polarisation (CP) at ambient temperature using a Bruker Avance

400 WB 3-channel solid-state spectrometer operating at  $\sim 100.5$  MHz with a 4 mm dual resonance probe or a triple resonance probe used as a double. Spinning rate for each experiment was set to 12.5 MHz and chemical shifts measured in ppm ( $\delta$ ) relative to trimethylsilane via glycine as a secondary reference material with the  $\delta C \pm$  signal set to 43.1 ppm. The delay time was set such that the maximum signal intensity was achieved across the spectra.

### *Core sample analysis procedure*

Core samples were removed from the hull or inner decks of the *Mary Rose* using a 5 mm boring tool. The length of the core samples was determined by the depth of the plank from which they were removed, generally in the 10–15 cm region. The core samples were cut to 5 mm lengths and then cut further into  $5 \times 1$  mm segments. Each set of  $5 \times 1$  mm segments were placed in a labelled vial for extraction. Cutting the samples to 1 mm sections increased the amount of PEG which could be extracted from the timber as the diffusion length in the sample is shorter. The vials were filled with 5 ml of ultrapure water, warmed to  $50^\circ\text{C}$  and left to extract for 5 days. After extraction, the water was concentrated to a residue and re-dissolved in 1.8 ml of ultrapure water. For GPC analysis, a 500  $\mu\text{l}$  aliquot was removed from each vial, added to 1 ml of ultrapure water, agitated to ensure complete mixing and filtered into a 1.5 ml GPC vial using a  $0.22 \mu\text{m}$  polyvinylidene fluoride filter to remove any wood particulates which may cause damage to the GPC column. Analysis of the sample was performed in isocratic elution mode with an ultrapure water eluent over 40 minutes at a flow rate of 0.5 ml per minute. The concentration of PEG in the sample was calculated from a standard calibration curve of PEG200 and PEG2000 standards.

## **Results and discussion**

### *Analysis of PEG extracted from the timbers of the Mary Rose*

As described above, PEG was extracted from core samples taken from the hull of the *Mary Rose*, which had been spray treated for 19 years with solutions of PEG200 (12 years) and PEG2000 (7 years) (Jones, 2013). Using a set of PEG calibration standards, the concentration of PEG200 and PEG2000 in each segment of the core samples was calculated. Analysis of the core samples in the final stages of PEG treatment was carried out over the past 2 years, and examples highlighting the PEG distribution in the top and end 15 mm of two different sampling locations are shown in Fig. 1 (sampling locations are shown in Supplementary Data S.1). The relative values of

PEG with respect to timber samples (Fig. 1A), are calculated from the mass of extracted PEG (determined by GPC) divided by the dry weight of the timber after PEG extraction.

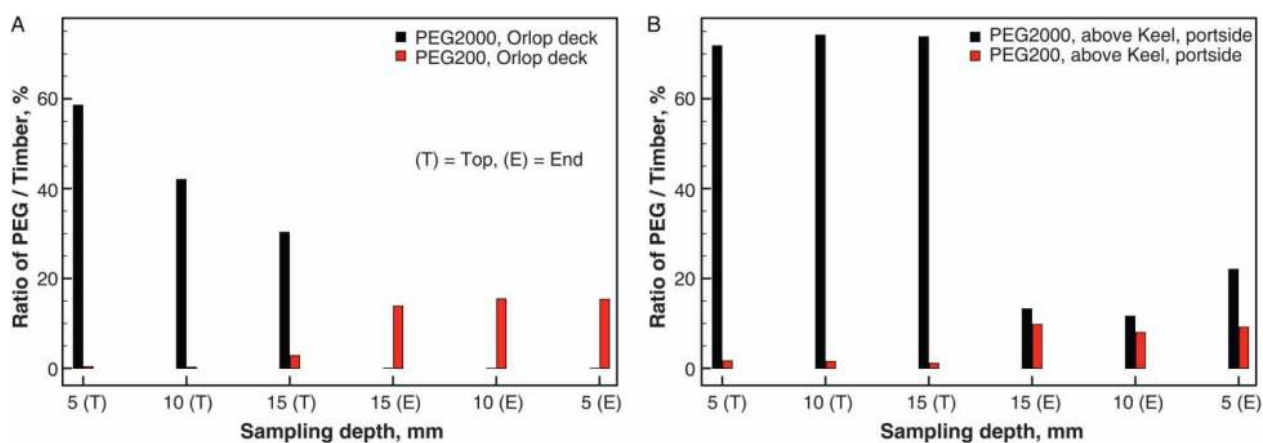
It is clear from Fig. 1 that the distribution of PEG (both 200 and 2000) is uneven throughout all the core samples, indicating that the polymers have difficulty in penetrating the timber effectively, leaving parts of the timber less supported than others. Untreated parts of the timbers are prone to cracking after drying, which can lead to structural damage. Additionally, at several points over the sampling locations there was indication of the presence of smaller PEG chains within the timbers as illustrated (Supplementary Data S.2, Fig. S4). This suggests that partial degradation of the consolidant material was seen during the treatment of the wood over the previous two decades, as these shorter chains are not present in samples taken from the fresh, unapplied consolidants (Supplementary Data S.2, Figs. S2, S3). The apparent degradation of PEG during the treatment process indicated the need for an alternative to this material for the conservation of such culturally important artefacts. With this in mind, the development of new conservation materials for waterlogged wooden artefacts should be of primary concern in the field of archaeological science. This study is, therefore, a useful step in determining the future direction of consolidant development.

### *Accelerated ageing of the potential consolidant materials*

While the short-term behaviour of consolidant materials is an important factor in deciding which are the most appropriate for application, the long-term behaviour and stability are generally more important characteristics, albeit more difficult to determine. Researchers at the Danish Technical University have studied methods to analyse the long-term behaviour of PEG by applying an accelerated ageing procedure. This method allows the estimation of the long-term stability of the consolidant material (Glastrup *et al.*, 2006a, 2006b; Mortensen, 2009).

Following this procedure, samples of each of the natural and synthetic polymers were solubilised in ultrapure water and subjected to accelerated ageing tests. Briefly, this involved preparing solutions of the appropriate concentrations (50 wt% for synthetic polymers and 1–3 wt% for natural polymer-based consolidants in ultrapure water), and heating the solutions to  $70^\circ\text{C}$  for 15 days while continuously bubbling air through the solutions.

Analysis of the accelerated ageing experiments proved to be difficult when comparing natural and synthetic polymers. Ideally, GPC and/or FTIR spectroscopic analysis would enable direct comparison of the



**Figure 1** Data obtained from core sample analysis of *Mary Rose* timbers (A) weight of PEG200 (red) and PEG2000 (black) relative to the weight of timber (%) in the top 15 mm and end 15 mm of a core sample from the orlop deck, (B) weight of PEG200 (red) and PEG2000 (black) relative to the weight of timber (%) in the top 15 mm and end 15 mm of a core sample from the keel (Port Side) (see Supplementary Data for sampling locations).

polymers after the accelerated ageing process with the naturally aged PEG samples from the timbers of the *Mary Rose*. Without the appropriate natural polymer-based consolidant standards for GPC calibration, precise measurement of any change in the molecular weight of the natural polymer-based consolidants treated with harsh conditions could not be made.

Similarly, FTIR spectroscopy proved difficult because of the low concentration of natural polymer-based consolidant in solution compared to the synthetic polymers. For the synthetic PEG samples, an increase in the carboxylic acid band in the IR spectrum would clearly indicate an increase in acidic groups present during the ageing procedure; unfortunately, such a significant chemical change in the natural polymer-based consolidants did not exist.

It was therefore necessary to rely solely on changes in pH to indicate chemical changes in the polymers over the length of the ageing experiment. The results of pH measurements are shown in Table 1, and confirm higher acidity in the case of the synthetic

polymers, while no change in pH is observed in the natural polymer-based consolidant solutions.

The results of the pH testing indicate that the mono and dimethyl ether are not much better at resisting degradation to acidic by-products than the original PEG consolidant. The natural polymer-based alternatives appear to be more chemically stable than the synthetic polymers during ageing tests, indicating that they may indeed be more useful as consolidant materials for waterlogged wooden artefacts in the long term.

#### *Rheological behaviour of the polymer treatment*

Approximation of the long-term behaviour of the polymers has shown that under harsh environmental conditions the natural polymer-based alternatives are more chemically stable than PEG and its mono and dimethyl ethers. While deciding to replace PEG with other synthetic derivatives or natural polymer-based alternatives, it is useful to understand whether the alternatives are also more mechanically stable than the original consolidant material. This is important as the weight of the ship's timbers as a whole is significant and the effect of the weight on the fragile timbers is a major concern in its conservation. The consolidant material must be resistant to strain and yet not be so heavy as to increase the load on the lower timbers in the ship. Increased load on fragile timbers may necessitate mechanical intervention to prevent collapse of the structure as has been described recently by researchers at the Vasa museum (Lechner *et al.*, 2013).

Analysis of the rheological behaviour of PEG and the alternative consolidant materials was an important preliminary study and helped to discard several polymers from consideration for future application. To understand the action of the materials under strain, both the storage ( $G'$ ) and loss ( $G''$ ) moduli of all the polymers were analysed at a constant strain in a controlled stress rheometer. For all experiments, the

**Table 1** pH of PEG, MPEG, DMPEG, chitosan, 2-HEC, and guar before and after accelerated ageing experiments

| Sample  | pH before ageing | pH after ageing |
|---|------------------|-----------------|
| 50 wt% PEG 200 in water                       | 6.5              | 6.5             |
| 50 wt% PEG 2000 in water                      | 7                | 4.5             |
| 50 wt% MPEG 350 in water                      | 6.5              | 6.5             |
| 50 wt% MPEG 2000 in water                     | 7                | 4.5             |
| 50 wt% DMPEG 250 in water                     | 6.5              | 6.5             |
| 50 wt% DMPEG 2000 in water                    | 2.5              | 2.5             |
| 0.5 wt% HEC in water                          | 7.5–8            | 7.5             |
| 1 wt% guar in water                           | 7.5–8            | 7.5             |
| 3 wt% chitosan in 1 vol% acetic acid in water | 6.5              | 7.5             |

concentration of PEG and its derivatives was maintained at 50 wt%, while the natural polymer-based consolidant concentration varied between 0.5 wt% (2-HEC), 1 wt% (guar), and 3 wt% (chitosan). Additionally, complex viscosity of all polymers was recorded over a specific shear rate range to determine any potential impediments to diffusion within the timbers on account of high viscosity.

Fig. 2A and B shows the  $G'$  and  $G''$  vs. angular frequency for the PEG200 and PEG2000 (2A) and the natural polymer-based alternatives (2B). Such measurements are a common method of probing the viscoelastic properties of a complex fluid. Measured over the range 1–100 rad per second, it is clear that the PEG polymers behave as viscous liquids with loss moduli higher than their storage moduli. The phase shift between the two moduli increases slightly for PEG2000 and decreases for PEG200 as the frequency increases, showing a slight divergence and indicating a tendency towards elastic behaviour in PEG200.

Over the same frequency range the three natural polymer-based consolidants have higher overall storage and loss moduli (Fig. 2B), which behave in a similar manner, converging at higher frequencies and showing a tendency towards more viscoelastic behaviour. While there is no major improvement in the  $G'$  and  $G''$  of the natural polymer-based consolidants relative to PEG, it must be noted that the concentration of polymer in the PEG samples is almost 17 times greater than the chitosan solution, 50 times greater than the solution of guar, and 100 times greater than the solution of 2-HEC. This is a significant advantage in the treatment process as support can be achieved with considerably less consolidant material resulting in lighter treated wood, placing less load on lower timbers and increasing the structural stability of the artefact as a whole.

The responses for MPEG350, MPEG2000, DMPEG250, and DMPEG2000 are not shown here as it was not possible to measure the storage modulus of any of these polymers under the same conditions as PEG and the natural polymer-based alternatives. The results suggest that MPEG and DMPEG are viscous materials with no elastic component, a quality not generally suitable for load-bearing materials. The increased elastic behaviour of PEG relative to its monomethyl and dimethyl ether is likely due to the two terminal hydroxyl groups on the PEG chains. These hydroxyl moieties contribute to hydrogen bonding (H-bonding) between chains, resulting in increased elasticity of the polymer solutions. Chitosan and 2-HEC also undergo a significant amount of H-bonding between chains, which contribute to their viscoelastic behaviour.

From the complex viscosity of both PEG200 and PEG2000 and the three natural polymer-based

consolidants (Fig. 2C and D), it is evident that the viscosity of the natural polymer-based consolidants is greater than that of both PEG polymers. While contributing to the increased structural support, the high viscosity of the natural consolidants may also cause problems with diffusion into the wood cells over time.

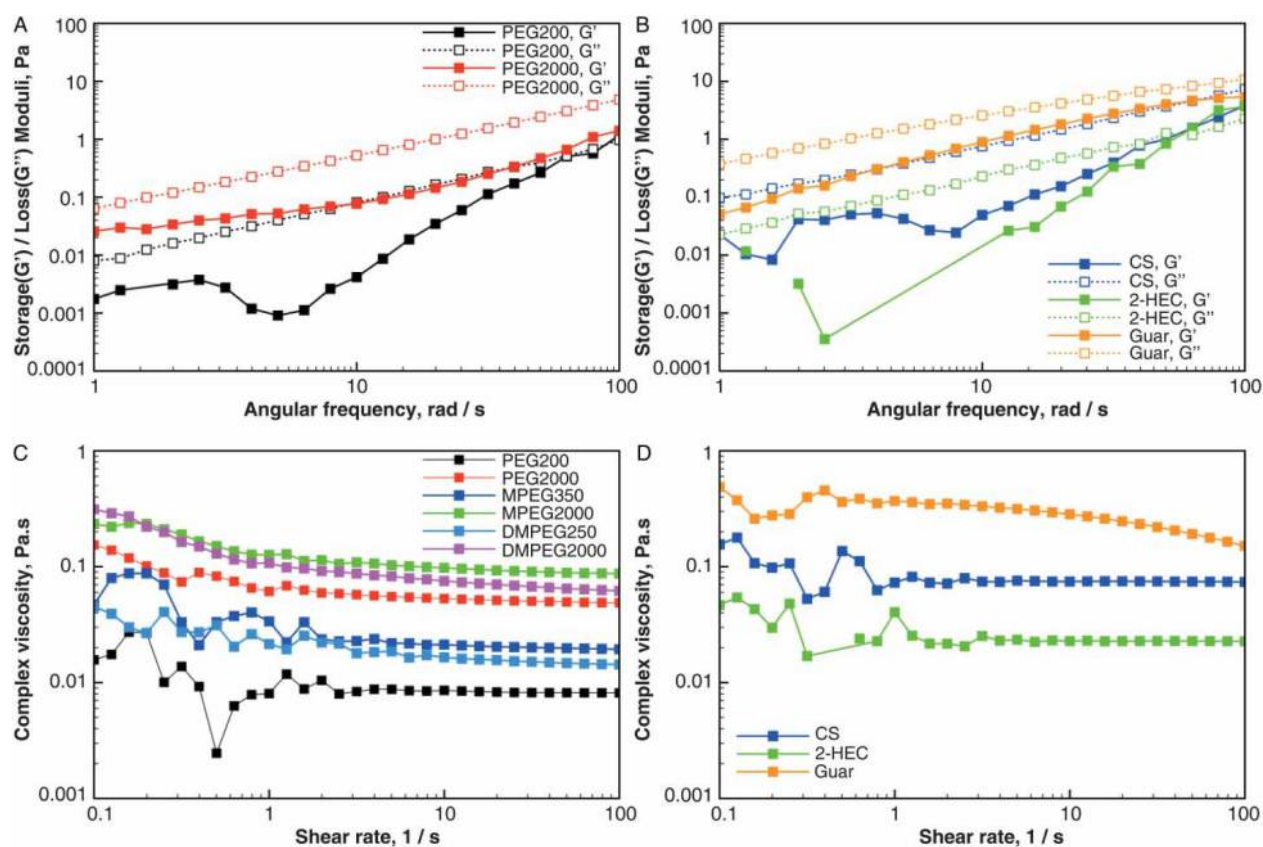
In relation to expected support capabilities, guar appears to outperform all of the polymers examined here, both synthetic and natural, which is not surprising given its common use as a thickening and stabilising agent with good mechanical properties (Parashar *et al.*, 1992). Further investigation, in particular diffusion studies, will be required to determine the effect of the change in viscosity on the diffusion of these alternative consolidants into the timbers of the *Mary Rose*. The rheological results suggest that natural polymer-based consolidants, particularly guar, would provide better structural support than the current conservation strategies.

### TGA of polymer–wood interactions

Compatibility of the consolidant with the timbers under conservation is extremely important; that is, the composition of the consolidant polymer should not negatively affect the integrity of the artefact. Bardet *et al.* (2007) showed through ssNMR that PEG200 exhibits incompatibility with the archaeological wooden matrix into which it was placed, which resulted in plasticisation of the timber leading to potential problems with structural integrity and long-term conservation. Here, both TGA and ssNMR (*vide infra*) are used to determine compatibility of the *Mary Rose* timbers with the polymer consolidants. Fig. 3A and B shows the TGA of PEG200, MPEG350, and DMPEG250 (3A) and chitosan, guar, and 2-HEC (3B)-treated samples against the natural thermal decomposition of the untreated timbers. Untreated timbers begin to burn at roughly 575 K while those treated with both PEG200 and DMPEG250 show a two-phase decomposition, which likely corresponds to loss of PEG/DMPEG around 425–450 K followed by decomposition of the wood at 525 K. This deviation from the natural behaviour of the timbers can likely be associated with a change in the molecular structure of the wood because of the addition of the polymer, resulting in a decrease in the thermal decomposition temperature of the treated wood. MPEG, while not showing a two-phase decomposition, also shifts the degradation temperature of the native wood from 575 K to approximately 525 K, again indicating some effect on the natural behaviour of the timber.

In contrast, samples of timber treated with natural polymer-based consolidants (Fig. 3B) show the same thermal degradation behaviour as the untreated wood. With all three natural consolidants, the





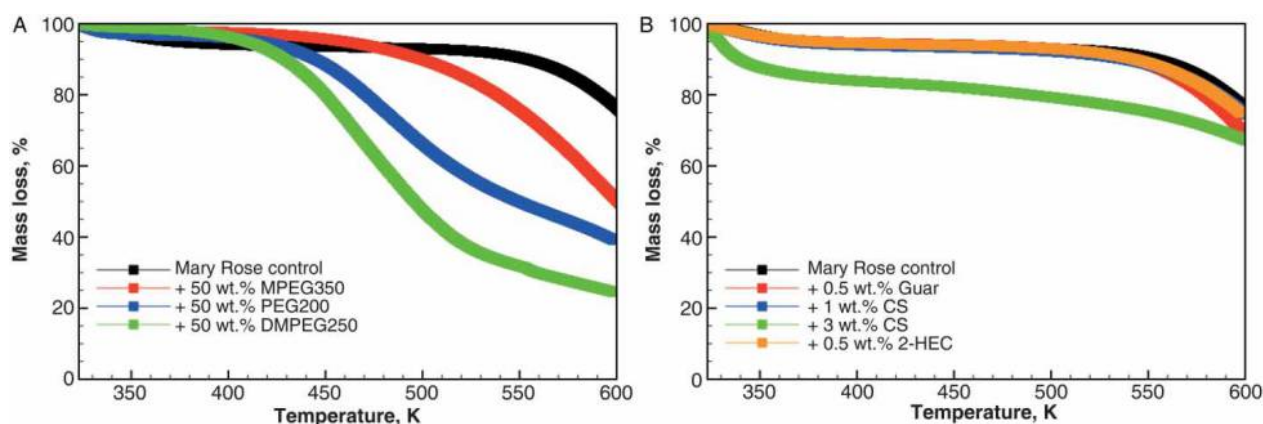
**Figure 2** Analysis of the storage ( $G'$ ) and loss ( $G''$ ) moduli (Pa) and complex viscosity (Pa s) of the synthetic and natural consolidants; angular frequency vs  $G'$  and  $G''$  for PEG200 and PEG2000 (A) and chitosan, guar, and 2-HEC (B) and plots of shear rate vs complex viscosity (per second) for PEG200, PEG2000, MPEG350, MPEG2000, DMPEG250, DMPEG2000 (C), and chitosan, guar, and 2-HEC (D).

decomposition profile of the treated and untreated timbers is identical, regardless of which natural polymer-based consolidant is used. Increasing the concentration of chitosan from 1 to 3 wt% increases the observed mass loss in the TGA profile but has no effect on the decomposition temperature, which remained at 573 K. For comparison, the thermal decomposition curves of the natural polymer-based consolidants (not applied to timber) are shown in the Supplementary Data and display the same thermal degradation as the native *Mary Rose*

timbers. These thermal analyses provide further validation to the argument that natural polymer-based consolidants are far more suitable for the conservation of wooden artefacts than the currently used synthetic polymers or their tested derivatives.

#### *FTIR spectroscopy of the presence of natural polymer-based alternative consolidants within archaeological timbers*

TGA of the treated samples suggests that both the natural and synthetic polymers are penetrating



**Figure 3** Thermogravimetric analysis plots of temperature (K) vs. mass loss (%), for samples of *Mary Rose* timber treated with (A) synthetic and (B) natural polymer-based consolidants.

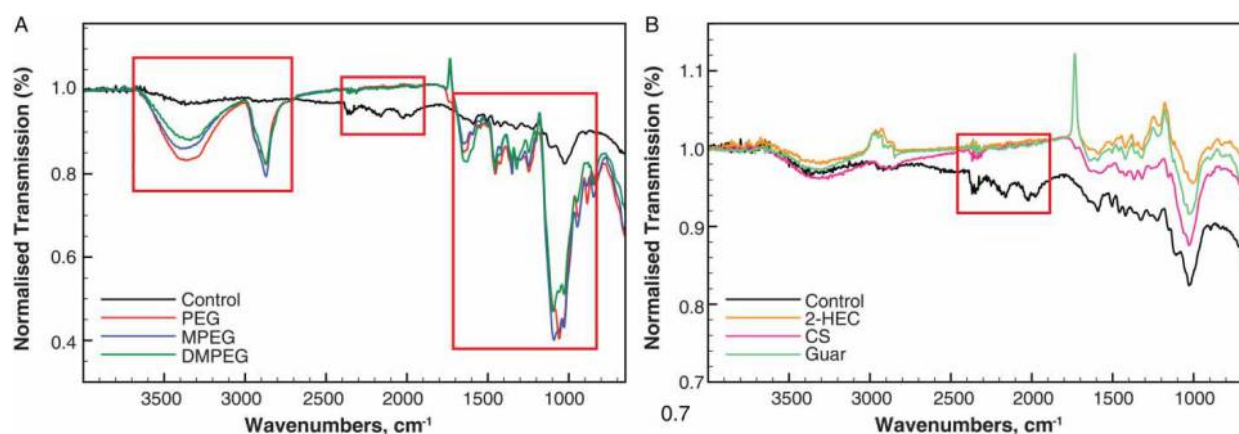
the wood. Further verification of the presence of the natural polymer-based alternatives within the timber was, however, required before analysis of the interaction between the polymers and the timber could be performed. To confirm their presence in the timber, 1 cm × 0.3 cm × 1 cm samples of untreated archaeological wood from the *Mary Rose* were immersed in solutions of 50 wt% PEG, 0.5 wt% 2-HEC, 1 wt% guar, or 3 wt% chitosan for 1 week; they were then sealed in a closed environment for 1 week, and finally subjected to 1 week of freeze drying. On completion of freeze drying, the samples were analysed by Fourier transform IR (FTIR) spectroscopy. The presence of polymer bands alongside the natural wood bands served as a confirmation of the presence of the polymer. The results of the analysis are shown in Fig. 4A and B; the IR of the treated samples are overlaid with the native archaeological wood, and the differences in the spectra are marked.

Fig. 4A clearly indicates that while the spectrum taken is that of PEG- or DMPEG-treated archaeological wood, the majority of the signal in the spectrum is related to the consolidant. Overlaying these spectra with that of the native, untreated wood, shows that there are very few similarities between the control and the treated samples. Looking first at the spectrum of the native untreated wood, all the characteristic bands of wood are clearly present with the exception of the C–H methyl and methylene group (2930–2910 cm<sup>-1</sup>), which is very weak and almost indistinguishable from the baseline (Bodîrlău & Teacă, 2009). This may be an indication of the state of degradation of the wood, that the bands related to the cellulose and hemi-cellulose are weaker than those related to the presence of lignin. After treatment with PEG the band at around 2900 cm<sup>-1</sup> becomes very significant, showing that this band is related to the treatment by PEG or one of its derivatives, as it indicates the C–H stretch of the methyl groups in the polymer backbone. Interestingly, with a reduction in the terminal hydroxy groups (between the PEG derivatives), the O–H band (broad band spanning 3000–3500 cm<sup>-1</sup>, indicating O–H stretches from alcohols, phenols, or carboxylic acids) decreases so it is relatively straightforward to determine which PEG derivative is used by comparing the difference in O–H stretches. As the broad band spanning 3000–3500 cm<sup>-1</sup> could be indicative of the O–H stretches in the PEG consolidants, phenols in the wood, or the O–H stretches of carboxylic acids, further clarification is needed. If the stretches come from the phenols in the wood one would expect the same band in the untreated wood. It is there, albeit rather less pronounced. This indicates a contribution from the wood, or water in the wood cells. It is difficult to provide further clarification of the O–H alcohol

stretch other than it is known that PEG was added to the sample and this band is characteristic in the IR of PEG and its derivatives. Verification of the presence of carboxylic acids is given by the band at around 1700 cm<sup>-1</sup>, indicative of the C=O stretch. Of course, this could indicate the presence of amines or amides, but not having added this to the timber and this band not being present in the untreated wood suggests the source is the C=O of carboxylic acids, or possibly esters present as a result of the consolidation.

Conversely, it is difficult to see the difference between the spectra of the untreated archaeological wood and the natural polymer-based consolidant-treated wood shown in Fig. 4B. The major differences are in the 2000–2500 cm<sup>-1</sup> regions, which are only present in the untreated wood, and the shape of the bands at around 1600 and 1000 cm<sup>-1</sup>. The lack of bands in the 2000–2500 cm<sup>-1</sup> region of the natural polymer-based, consolidant-treated, wood samples may indicate that these bands in the untreated wood sample originate from impurities in the water surrounding the sample, which were solubilised in the treatment solution and, therefore, not freeze dried into the sample. The difference in the band shapes around 1600 and 1000 cm<sup>-1</sup> suggest different origins for these bands. For example, the band at ~1600 cm<sup>-1</sup> in the chitosan-treated sample may be related to a combination of the aromatic C=C bands from the lignin and the primary amine of the chitosan, which both appear in this region. In the guar- and 2-HEC-treated samples, this band is likely to be related only to the lignin band. In all cases, some natural acid formation in the timbers could also lead to the appearance of a C=O stretch in this region. As for the band at ~1000 cm<sup>-1</sup>, the C–O stretching of alcohols, C–N stretching of amines, and again the presence of natural degradation products could each contribute to this band, resulting in certain differences between the treated and the control timber spectra. Of course, due to the similarity between the chemical structure of the natural polymer-based consolidants and the wood itself, it is not as easy to determine their presence; however, the small differences between the bands in the fingerprint region gives a strong suggestion of their presence when combined with the TGA data above.

From the differences in the treated and untreated spectra, it is likely that all of the polymers, PEG and the suggested alternatives, penetrate the timber within the treatment period, which indicates that at least in the short term the natural polymer-based consolidants are viable alternatives for the treatment of archaeological wooden artefacts. The penetration of the natural polymer-based consolidants into the wood is indeed a promising result, as one major concern for the use of natural polymer-based materials



**Figure 4** Comparison of FTIR spectra of samples from the timbers of the *Mary Rose* untreated and treated with PEG200, MPEG350, DMPEG250, chitosan, guar, and 2-HEC.

as consolidants is that their higher molecular weight will retard their ability to effectively penetrate the timbers. The results of both TGA and FTIR analyses reveal that in the short term there is no significant difference in the penetration ability of the natural polymer-based consolidants, likely due to the lower

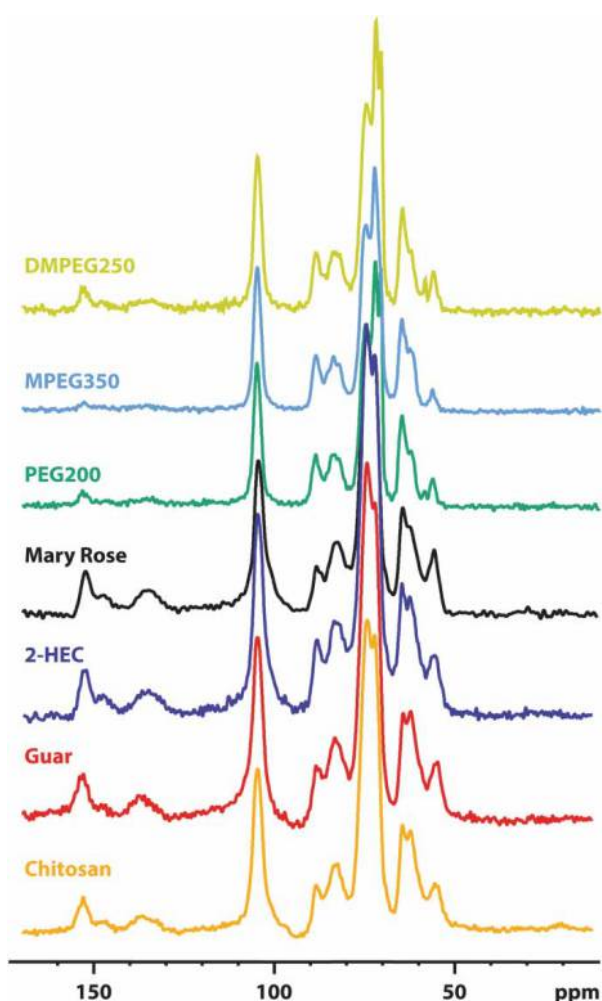
concentration necessary, of these polymers for conservation compared to that of PEG and PEG derivatives.

#### *ssNMR analysis of the interactions between polymer and artefact*

The compatibility of the timbers with the proposed new consolidants was also measured by ssNMR. This study was compared with the extensive work carried out by Bardet *et al.* (2007, 2012). A stack plot of the ssNMR spectra of untreated timber samples and those treated with PEG200, MPEG350, DMPEG250, 2-HEC, chitosan, and guar is presented in Fig. 5.

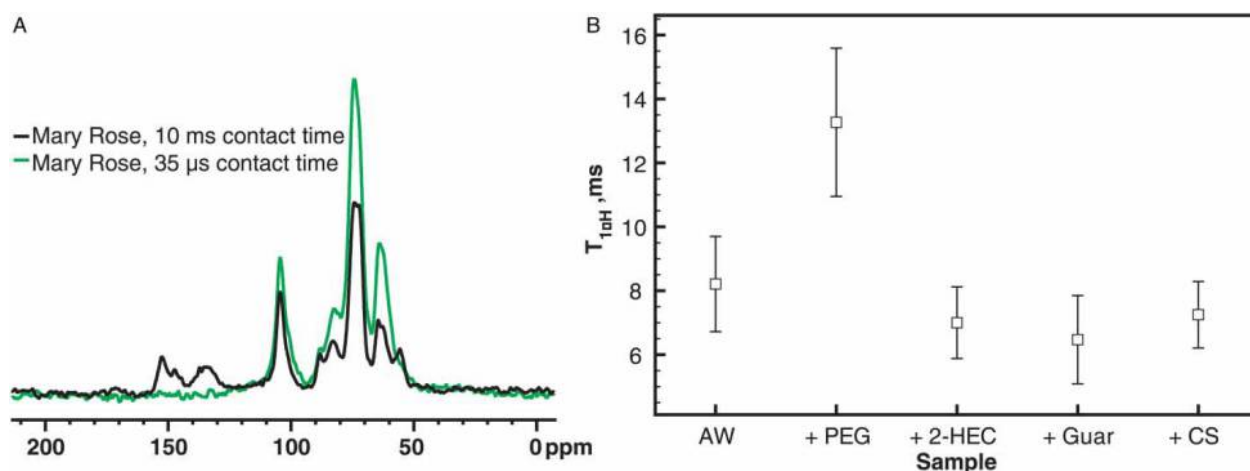
The presence of PEG and its derivatives is observed in the top three spectra by the increased signal intensity at 72 ppm relative to the untreated timbers, the peak at 72 ppm being characteristic of PEG. The presence of natural polymer-based consolidants within the wood is less evident and the identification of the natural polymer signals in the spectra is challenging as much of the chemical structure of the consolidant and the wood is closely related, resulting in overlap of their peaks. Additionally, as comparable solution viscosities can be achieved with natural polymer-based consolidants at a much lower concentration, the wood samples were treated with a substantially lower mass of natural polymer-based consolidant than PEG. While PEG can clearly be seen in the NMR spectra, the chitosan, guar, and 2-HEC, at 17–100 times lower maximum concentrations, are more difficult to detect.

To further explore the system, molecular dynamics were examined through variation in the  $^1\text{H}$ – $^{13}\text{C}$  CP contact time (Bardet *et al.*, 2007). While Bardet *et al.* reported data in relation to the interaction of PEG with the archaeological wooden matrix, the data reported here compares the effect of the natural polymer-based consolidants with that of PEG200 on the archaeological timbers.



**Figure 5** Comparison of ssNMR spectra of samples from the timbers of the *Mary Rose* untreated and treated with PEG200, MPEG350, DMPEG250, chitosan, guar, and 2-HEC.





**Figure 6** Molecular dynamics studies on the interactions of chitosan with the timbers of the *Mary Rose*, (A)  $^{13}\text{C}$  CP-MAS ssNMR of *Mary Rose* timbers at 35  $\mu\text{s}$  and 10 ms contact times, (B) plot of  $T_{1\rho\text{H}}$  calculated from the peak intensities of the 74.6 ppm peak at varying contact time vs. treated and untreated samples. samples include untreated *Mary Rose* archaeological wood (AW) and archaeological wood treated with PEG, 2-HEC, guar, and chitosan (CS).

At this stage in the analysis it was clear, however, that MPEG and DMPEG, while less likely to produce acidic by-products compared to PEG itself, have not shown a significant improvement over the current PEG technology to warrant further investigation. In fact, the rheological data suggests that MPEG and DMPEG are structurally less stable than PEG, making them a poor alternative. For this reason, MPEG and DMPEG polymers were not analysed further due to their poor behaviour in all other analyses. Contact times were set to a series of 10 different durations between 35  $\mu\text{s}$  and 10 ms and the absolute intensity of selected signals resulting from the  $^{13}\text{C}$  CP-MAS NMR experiments were plotted against contact time and then fitted by

$$M = M_0(1 - \exp(-t_{\text{cp}}/T_{\text{CH}}))\exp(-t_{\text{cp}}/T_{1\rho\text{H}})$$

to yield  $T_{1\rho\text{H}}$  and  $T_{\text{CH}}$ , the proton-rotating-frame relaxation time and the cross-relaxation time, respectively (where  $M_0$  is the intensity of the peak at a specific ppm and  $M$  is the total intensity observed when taking into account  $T_{1\rho\text{H}}$  and  $T_{\text{CH}}$ ). Although a two-component fit would likely give a better fit of the data, a single-component fit is enough to give us an indication of any major changes as a result of the consolidant treatment. Each experiment was run for 2048 scans and the absolute intensity data of selected peaks against contact time were fitted using the OriginPro 8.6 software. Due to the challenges of distinguishing the natural polymer-based consolidants from the signals of the timber, it is not possible to directly analyse the behaviour of the natural polymer-based consolidants themselves within the wood. For this reason, the behaviour of signals displaying intensity in both the *Mary Rose* wood and natural polymer-based consolidants were chosen for analysis, as this

allows us to look at the net effect of the molecular dynamics.

The intense signal at 104 ppm, often assigned to the C1 carbon of the saccharide backbone, and the signal at 74 ppm, assigned to lignin and  $\text{C}\alpha$ , were therefore chosen for further analysis (Fig. 6B). These peaks have significant intensity across all contact times investigated, unlike the lignin-specific peaks, which only appear at longer contact times (Fig. 6A).

Fig. 6B illustrates the variation in  $T_{1\rho\text{H}}$  of the 74 ppm peak across the different samples; from this plot it can clearly be seen that the behaviour of the PEG-treated wood differs drastically from that of the untreated wood. Additionally, it is evident that the natural polymer-based consolidant-treated samples behave like the untreated wood and differ from the PEG-treated material, suggesting that the natural relaxation behaviour of the wood has not been affected by the presence of the treatment. The results of the fit show a similarly significant difference in  $T_{\text{CH}}$  (Table 2), indicating that while the PEG-treated wood behaves quite differently from the *Mary Rose* wood, the natural polymer-based consolidant-treated wood does not exhibit modified dynamics.

The increase in  $T_{1\rho\text{H}}$  and decrease in  $T_{\text{CH}}$  of PEG-treated timber relative to the untreated *Mary Rose* timbers indicate less molecular disorder and motion within this material. This result is to be expected as

**Table 2** Variation in  $T_{1\rho\text{H}}$  and  $T_{\text{CH}}$  for the 74 ppm signal of different samples

| Sample                            | AW   | AW-PEG | AW-HEC | AW-Guar | AW-CS |
|-----------------------------------|------|--------|--------|---------|-------|
| $T_{1\rho\text{H}}$ (ms)          | 8.2  | 13.3   | 7      | 6.5     | 7.2   |
| $T_{\text{CH}}$ ( $\mu\text{s}$ ) | 85.3 | 58.9   | 80     | 104.5   | 82.8  |

the crystalline domains, which can be found within the commercial PEG, result in a more ordered arrangement, hence higher  $T_{1\rho\text{H}}$  and lower  $T_{\text{CH}}$ . Crystallinity is not expected within the chitosan, guar, or 2-HEC structures. Comparison of the results presented here with those observed by Bardet *et al.* (2007, 2012) show that, unlike PEG, natural polymer-based consolidants do not appear to affect the natural behaviour of the timbers analysed, indicating a positive outcome for the long-term conservation of wooden artefacts using natural polymer-based consolidants.

## Conclusions

The rheological behaviour, thermal decomposition, and effect on the dynamics of the archaeological wooden matrix probed through ssNMR and FTIR have been examined for a range of consolidants, both natural and synthetic, presented as alternatives to PEG for the treatment of waterlogged archaeological wooden artefacts. While MPEG and DMPEG showed comparable complex viscosity to PEG, the reduction in H-bonding units affected the viscoelasticity of the materials, suggesting they are unsuitable for structural support applications. Additionally, these two polymers are obtained from non-renewable sources and do not have inherent anti-bacterial properties nor native ability to interact with iron saturation in the timbers. The natural polymer-based consolidants tested, in particular guar, showed excellent potential as a structural unit due to the increased load bearing potential shown in the rheological study. The significantly reduced concentrations necessary to prepare these consolidants result in a conserved artefact that is lighter, ultimately reducing stress on the lower portions of the ship. Overall, however, chitosan appears to show the greatest promise. Although its load bearing capabilities were slightly lower at a slightly increased concentration, chitosan adds intrinsic anti-bacterial properties (Tokura *et al.*, 1997), the ability to chelate with iron through the amines in the backbone (Burke *et al.*, 2000), and does not affect the natural relaxation behaviour of the wooden matrix. Future experiments will examine the extent of the anti-bacterial nature of chitosan and its iron chelation ability in the wood of the *Mary Rose*. The results shown here demonstrate that the future of conservation technologies may very well lie with the use, functionalisation, and application of natural polymer-based materials as consolidants. Their increased structural stability at lower concentrations, potential for anti-bacterial and metal chelating properties, reduced cost, renewability due to sourcing from waste products and plants, and their low toxicity make them attractive, greener alternatives to synthetic polymer consolidants based on PEG.

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## List of suppliers

Fisher Scientific (Loughborough, UK), <http://www.fisher.co.uk>

INEOS (Rolle, Switzerland), <http://www.ineos.com>  
Sigma-Aldrich Chemical Company (Dorset, UK), <http://www.sigmaaldrich.com/united-kingdom.html>

Breckland Scientific (Stafford, UK), <http://www.brecklandscientific.co.uk>

Millipore (Billerica, MA, USA), <http://www.merckmillipore.com/GB/en>

Shimadzu (Kyoto, Japan), <http://www.shimadzu.com>

Wyatt Technologies (Santa Barbara, CA, USA), <http://www.wyatt.com>

Agilent Technologies GmbH (Waldbronn, Germany), <http://www.home.agilent.com/agilent/home.jsp?lc=eng &cc=GB>

TA Instruments and TA Orchestrator software (TA Instruments, New Castle, DE, USA), <http://www.tainstruments.com>

Perkin Elmer Corporation (Sunny Vale, CA, USA), <http://www.perkinelmer.com>

Sartorius (Gottingen, Germany), <http://www.sartorius.com>

Bruker BioSpin (Billerica, MA, USA), <http://www.bruker.com/products/mr.html>

OriginPro 8.6 software, <http://www.originlab.com/index.aspx?go=Products/OriginPro>

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