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

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S.1 Sampling locations for PEG analysis in the hull of the \textit{Mary Rose}

A schematic plan of the hull of the \textit{Mary Rose} was obtained from the museum.\textsuperscript{1} On this map was marked the 10 different sampling locations mentioned in the full text of the paper. On the scheme, shown in Figure S5, the \% of PEG (both 200 and 2000) in the outermost 5 mm of the core sample is also recorded.

\textbf{Figure S1:} Schematic of the hull of the \textit{Mary Rose} and the \% of PEG recorded in the outermost 5 mm of the core sample
S.2 Results of PEG analysis

The following figures Figures S2 and S3 show the GPC traces of the PEG standards, which indicates the content of the PEG consolidant before application.

Figure S2: Retention time (min) vs. dynamic refractive index (AU) for PEG200 standards in concentrations from 0.1-1 mg/ml
**Figure S3:** Retention time (min) vs. dynamic refractive index (AU) for PEG2000 standards in concentrations from 0.1-1 mg/ml
Figures S4 shows the GPC trace from an earlier batch of core sample analyses where the total amount of PEG200 and PEG2000 in each sample was analysed and shorter chain PEGs were detected. This clearly illustrates the inhomogeneity in the distribution of PEG in the timbers of the *Mary Rose* and the possible degradation of the PEG within the timbers.

**Figure S4:** Overview of data collected from Core 4 (Hold) analysis: bar chart of % PEG relative to total weight of timber showing the penetration of PEG200 (red), PEG2000 (black) and short chain PEG (blue) per 5 mm section of core sample (labelled by sampling depth)
S.3 Thermogravimetric analysis of natural polymer controls

Figure S5: Thermogravimetric analysis of samples of native untreated timber of the *Mary Rose* and natural polymers chitosan, guar and 2-HEC, compared on a plot of temperature (°C) vs. mass loss (%)
S.4 ssNMR of polymer treated Mary Rose timbers

$^{13}$C CPMAS ssNMR experiments were carried out using a 50-100% $^1$H ramped contact pulse with a contact time of 2500 $\mu$s and a proton power during contact of either 7.5 or 5 dB. Spectra were collected for a total of scans 5 k scans unless the signal to noise of the spectra required more scans. The recycle delay was 2 s and experiments were carried out at ambient temperature. The variable contact time $^{13}$C CPMAS ssNMR experiments were run with dipolar decoupling and contact times varied from 50 $\mu$s to 10 ms. The $^{13}$C cross-polarisation power level was set to 5 dB to provide a $^{13}$C nutation frequency of 70 kHz and the $^1$H field matched with a resulting power level of 6 dB in order to achieve Hartman-Hahn matching conditions. Both $^{13}$C and $^1$H contact-pulses were square pulses. The recycle delay was 4 s. Each spectrum was recorded with 2048 scans. Experiments were carried out at ambient temperature with a spinning rate of 12.5 kHz. Optimisation experiments carried out with a $^{13}$C nutation frequency of 50 kHz suggested reduced signal intensity when compared to 70 kHz. In contrast the optimisation experiments carried out with a $^{13}$C nutation frequency of 80 kHz differed little from the results at 70 kHz. For this reason 70 kHz was deemed to be a high enough frequency to ensure effective $^1$H spin lock during CP.
Figure S6: $^{13}$C CPMAS ssNMR molecular dynamics study on the 104.8 ppm peak of PEG and chitosan treated timbers from the *Mary Rose*. (orange) chitosan and (green) PEG treated *Mary Rose* archaeological wood. $^{13}$C nutation frequency was 70 kHz.
Figure S7: $^{13}$C CPMAS ssNMR spectra of (orange) chitosan and (green) PEG treated *Mary Rose* archaeological wood at 10 ms contact time. Spectra has been normalised relative to the 104.8 ppm signal. Blue boxes: areas of signal intensity in the chitosan treated sample related to lignin residues which are absent or suppressed in the PEG treated sample. Inset: magnified region of the spectra (100-40 ppm) highlighting new signals in the PEG treated sample assigned to PEG itself. The PEG signals are denoted by *. 

References

[1] Jones, M. Personal communication, May 2013.