

**Polymerization of Archaeological Waterlogged Wood Treated With
Polyethylene Glycol**

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One of the most common methods for conserving waterlogged wood is to bulk the deteriorated cellular structure of the wood with polyethylene glycol (PEG). Conservators have developed various methods, some of which combine two or more molecular weights of PEG, to bulk the cell structure of an organically-based artifact; this preserves the diagnostic features of the artifact by preventing severe cellular shrinkage and collapse. The stable life expectancy of PEG appears, however, to be a finite period of time. Artifacts recovered from underwater archaeological sites that have been conserved using PEG treatment strategies show signs of potential instability after 60 to 70 years of treatment. While polyethylene glycol bulking remains the preferred means of conservation strategy for many conservators, we are striving to develop new processes to either reconstitute PEG which may be showing signs of instability or to polymerize in situ PEG to prevent additional damage to the artifact.

The aim of this experiment was threefold. Five sample sections of wood (samples 1-5) were dehydrated using a 2-step cold process of dehydration. Samples 1 and 2 were bulked with PEG 500 with 4% methylhydrocyclosiloxane added by weight. Sample 1 was then polymerized in CT-32 catalyst, while sample 2 was polymerized in CT-30 catalyst. Recent studies at the Conservation Research Laboratory (CRL) have determined that there are substantial differences in the polymerization process when initiated using either stannous (CT-30) or stannic (CT-32) catalysts. The first phase of this experiment would conserve waterlogged wood using each of these catalysts and the wood samples would be evaluated post-treatment to determine the degree of polymerization and any physical differences that may have resulted from the use of these catalysts.

The second phase of this experiment was intended to assist in determining the feasibility of treating large artifacts without the need for chemical immersion. Unlike the first phase of the experiment, in which samples 1 and 2 were bulked with a PEG/methylhydrocyclosiloxane solution and exposed to catalyst fumes, samples 3 and 4 were bulked with PEG and then exposed to concentrated methylhydrocyclosiloxane fumes for three hours, followed by exposure to catalyst fumes for an additional three hours.

Sample 5 was bulked with PEG and treated with a 50:50 solution of dimethyl sulfoxide and methylhydrocyclosiloxane prior to exposure to catalyst fumes. This phase of the experiment would help us determine if larger PEG-treated timbers could be partially polymerized by painting crosslinking agents onto the timbers and exposing them to catalyzing fumes.

Procedures

For the first phase of the experiment, two sections of waterlogged wood (samples 1 & 2) were placed into a metal container containing 500 milligrams of fresh ethanol. These samples were then placed into a freezer-mounted vacuum chamber and a vacuum of 28 Torr was applied for six hours. The ethanol was then replaced with 500 milliliters of fresh acetone and, after placing the samples back into the freezer vacuum chamber assembly, a vacuum of 28 Torr was applied to the samples for an additional six hours. The samples were left in the vacuum chamber assembly and allowed to sit at ambient pressure for twelve hours. In preparation for bulking the dehydrated wood samples with PEG, the surfaces of both samples were lightly patted with dry paper towels to remove as much acetone as possible from the surface of the samples. Both samples were quickly placed into a beaker with 500 milliliters of PEG 500 and placed into a vacuum chamber unit at room temperature. A vacuum of 28 Torr was applied to the samples for three hours and then four percent methylhydrocyclosiloxane (determined by the original weight of the PEG) was mixed into the solution. The samples were then vacuum treated for an additional three hours. After this length of time, no bubbles were noted in the solution and the wood in solution was allowed to slowly return to ambient pressure, where it remained for twelve hours.

After bulking, samples 1 and 2 were removed from the PEG solution and wiped with a paper towel to remove excess PEG from all surfaces of the wood. Sample 1 was then placed into a small containment chamber with 28.4 ml of CT-32 catalyst and sample 2 was placed into a similar chamber with 28.4 ml of CT-30 catalyst. Both containment chambers were then allowed to sit for eighteen hours in a warming oven that had been preheated to 52°C (Figure 1).

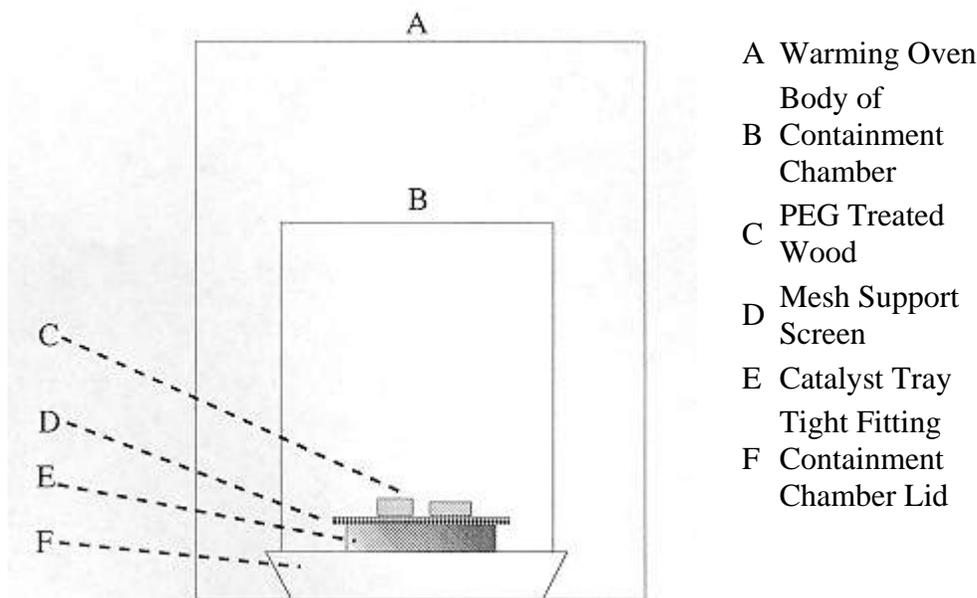


Figure 1 Set-up for CT-30 and CT-32 catalyst applications.

Samples 3, 4 and 5 were dehydrated using the same cold, two stage process of dehydration as described above for samples 1 and 2. In preparation for bulking the dehydrated samples 3 and 4 with PEG, the surfaces of both samples were lightly patted with dry paper towels to remove as much acetone as possible. Both samples were quickly placed into a beaker with 500 milliliters of PEG 500 and placed into a vacuum chamber unit at room temperature. After four hours of applied vacuum (at 28 Torr?), no bubbles were observed emanating from the wood samples; after six full hours of acetone-PEG exchange, the vacuum was discontinued and the samples were allowed to return to ambient pressure where they sat for an additional twelve hours. Both samples were then removed from the PEG solution. After lightly patting the samples with dry paper towel to remove free-flowing PEG, the samples were placed into a small containment chamber and placed into a warming oven that had been preheated to 57°C. The samples were then exposed to the concentrated fumes of methylhydrocyclosiloxane for three hours. Care was taken to ensure that the temperature of the solution did not exceed 30°C, which is just below the flash point for the chemical. A small air pump was used to create a positive pressure within the warming flask, which in turn forced catalyst fumes into the containment chamber (Figure 2). After three hours, the samples were exposed to the concentrated fumes of the CT-32 catalyst using the exact same procedure used for exposing the samples to the methylhydrocyclosiloxane.

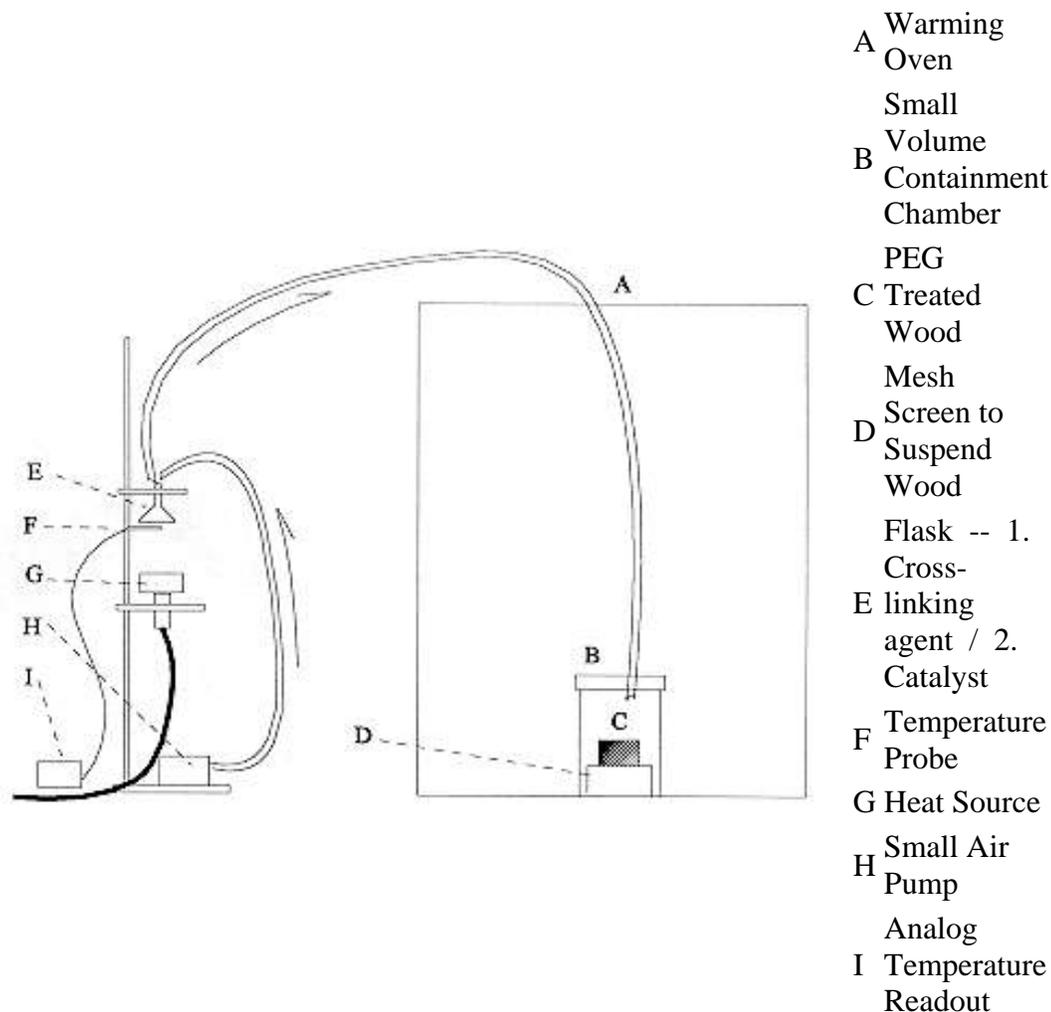


Figure 2 Set-up for Cross-link and Catalyst applications

After dehydration, sample 5 was bulked with PEG 500 using the same procedures as were used for samples 3 and 4. After bulking, however, sample 5 was painted with repeated coats of a 50:50 solution of methylhydrocyclosiloxane and dimethyl sulfoxide. Because these two chemicals have a tendency not to mix at room temperature, the solution was warmed and maintained at a temperature of 55°C while the mixture was applied to the surfaces of the wood with a small brush. After fifteen thin applications, the wood was placed into a containment chamber with a small beaker containing 14.2 ml of CT-32 catalyst. The containment chamber was then placed into the warming oven and exposed to catalyst fumes for six hours at a temperature of 57°C.

After removal from the warming oven, all of the samples were given an initial evaluation as well as continuing evaluations at twelve hour intervals. Pre- and post-treatment weight changes for all of the samples were recorded. Weight fluctuations for each wood sample, however, are difficult to compare; the sizes of the wood samples, degrees of waterlogging and pat-dry state during the weighing process make it difficult to compare across samples. The pre- and post- treatment weights for each samples are listed in Table 1.

Sample	Pre Treatment Weight (g)	Post Treatment Weight (g)	% Weight Change
1	4.42	4.32	+2.2700
2	6.29	6.08	-3.3386
3	4.85	4.75	-2.0619
4	4.64	4.5	-3.0175
5	11.97	12.1	+6.148

Differences in pre- and post-treatment weights for samples 1 and 2 were at first confusing; after reviewing the treatment for each sample, however, it became obvious that large crystalline deposits of PEG had accumulated on the surfaces and in the crevices of sample 1 during treatment. As the crystalline PEG deposits were difficult to remove and tended to remain on the surface of the sample, the mass of sample 1 increased. Crystalline deposits of PEG on the surfaces of sample 2 were considerably smaller and tended to be easier to remove post-treatment without destroying the surfaces of the wood. The weight loss indicated for sample 2 most likely reflects the actual weight loss of the sample.

The reduction of mass in samples 3 and 4 is relatively minimal. Because the samples were crosslinked using concentrated methylhydrocyclosiloxane fumes and polymerized using CT-32 fumes within the warm environment of the containment chamber, the samples should only have accumulated minimal mass due to vapor or liquid intake. This potential weight accumulation would be more than offset by the loss of mass which would be expected within the hot environment of the containment chamber. The weight loss observed in samples 3 and 4, -3.33% and -2.06% respectively, most likely represents water loss from the matrix of the wood as well as a reduction of water within the PEG.

The large increase in the mass of sample 5 can be attributed to the repeated applications of the solution of dimethyl sulfoxide and methylhydrocyclosiloxane. Like samples 3 and 4, sample 5 was placed into the warm environment of a containment chamber, but because dimethyl sulfoxide was used to facilitate the introduction of methylhydrocyclosiloxane into the matrix of the wood, much of the available water that might have been lost due to outgassing had been bound (to what?) during the crosslinking process.

Observations

Nothing unusual was observed during the dehydration phase of treatment for samples 1 and 2. During the methylhydrocyclosiloxane-PEG phase of bulking, however, areas of white material appeared on all the surfaces of the treated wood samples. This suggested that polymerization may have been taking place prior to exposure of samples 1 and 2 to catalyst fumes. When the samples were removed from their PEG solution and their surface wiped prior to exposing them to catalyst fumes, most of this white residue was easily removed from the samples. Inspection of this residue material revealed that the substance ranged in consistency from a thick paste to semi-hard lumps.

After twenty-four hours of exposure to catalyst fumes, the CT-32- treated wood sample (sample 1) felt slightly wet to the touch and crystalline white residue was present on all of its surfaces. No dimensional changes were recorded in the 24 hours following treatment, indicating that no shrinkage had occurred in the sample. The surface grain of both samples 1 and 2 were slightly pronounced, although the wood surface remained very natural in appearance. Like the CT-32- treated sample, the CT-30- treated wood (sample 2) has some crystalline white residue on its surfaces. These deposits are much smaller, however, and the surfaces of the sample 2 felt and looked drier than the surfaces of sample 1.

After 48 hours of curation, samples 3 and 4 appeared to be fully polymerized. The surface of both samples felt dry and both samples had an aesthetically pleasing matte finish. Like samples 1 and 2, the surface grain of samples 3 and 4 was slightly pronounced but no dimensional changes were recorded. Samples 3 and 4 were taken from one small section of wood that was broken in half for this experiment. After conservation as separate samples, both sections of wood fit easily back together, indicating that both sections remained structurally compatible.

Sample 5 remained slightly wet to the touch after 48 hours of curation. Like all of the other samples, the surface grain of this sample was slightly pronounced but the wood retained all of its diagnostic features and remained dimensionally stable. As a means of treating this wood sample to the point that its surfaces felt dry to the touch, the sample was placed into a containment chamber at room temperature with a folded cloth containing 14.2 ml of CT-30 catalyst. After six hours of curation, the sample appeared to be dry.

This experiment was exploratory in nature, with the goal of trying to determine if PEG treated wood samples could be further crosslinked using Conservation Research Laboratory technologies. The aesthetically unpleasing crystalline formations that were noted on samples 1 and 2 were an initial source of concern. These same deposits, however, did indicate that the PEG- bulked wood had been polymerized. Determining the degree of polymerization that may have occurred in samples 3,4 and 5 was considerably more difficult, as no crystalline deposits were observed on any of the samples. In the case of these samples, we will be able to determine the degree of polymerization that has occurred by sectioning them for additional analysis after the samples have been allowed to sit in fresh air for a few days. The effect of fresh air curation as part of the conservation process has not yet been evaluated. The process of outgassing from the

samples may, however, additionally act to cure the samples. Based upon overall appearance, samples 3,4 and 5 appear to have retained more of a natural appearance than samples 1 and 2, in which the wood grain had become more pronounced. After several days of curation, sample 1, which was polymerized using CT-32 catalyst, had lost some its dimensional stability and has warped slightly. In contrast, sample 2, which was polymerized with CT-30 catalyst, has retained its shape and surface texture.

Based upon the data taken from single waterlogged wood samples, it is difficult to determine a single definitive process from among these various techniques. The degree of warpage that has occurred in sample 1 may be attributable to internal factors such as wood grain and degree of dehydration. Repeated trials of wood bulking using materials and processes similar to the process used for sample 1 have yielded good results, and the slight degree of dimensional change is minimal by accepted conservation practices. This single experiment demonstrates that additional research should be directed towards the conservation of waterlogged wood using crosslinking/catalyzing and dimethyl sulfoxide/crosslinking, gas-catalyzing processes. Experimentation using dimethyl sulfoxide-facilitated methylhydrocyclosiloxane crosslinking to penetrate the bulking agent appears to be promising. Previous experimentation at the Conservation Research Lab has proven that dimethyl sulfoxide is an efficient transport for bulking heart tissues when mixed in solution with lower molecular weight silicone oils. This experiment has indicated that dimethyl sulfoxide may also be effective in crosslinking waterlogged materials with crosslinking agents such as methylhydrocyclosiloxane.

1. Because long-term curation in this type of environment is not detrimental to wood samples, and because the presence of catalyst fumes may continue to cause additional polymerization, all of the samples were then placed into the containment chamber for 24 hours. At the end of this period, no changes were noted in any of the samples at the end of the 24 hour period. All samples however, will be evaluated at regular intervals to note any changes on dimensions, surface texture or weight.

Citation Information:

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1998, "Polymerization of Archaeological Waterlogged Wood Treated With Polyethylene Glycol", Archaeological Preservation Research Laboratory (APRL), Report 19, World Wide Web, URL, <http://nautarch.tamu.edu/APRL/report19.htm>, Nautical Archaeology Program, Texas A&M University, College Station, Texas.