

Archaeological Preservation Research Laboratory Report 16:

Polymerization of Polyethylene Glycol and Glycerine

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Over the past several decades, a variety of molecular weights of polyethylene glycol and glycerine have been used for the conservation of archaeological materials, including a wide range of organic materials such as leather, wood, and basketry. Polyethylene glycol (PEG) has been widely used by archaeological conservators because it is reasonably inexpensive as a conservation strategy. PEG treatments are reversible; this is an important consideration, since technologies developed in the future may make it desirable to reverse the process of conservation for the purpose of special study or for re-treatment using better processes.

By observing the physical state of artifacts that have been conserved using PEG in the past, it is obvious that many older artifacts that have been conserved using any number of molecular weights of PEG have become unstable over time. This is indicated by the migration of PEG to the surfaces of the artifact, which leaves voids within the cellular structure of the organic matrix of the artifact. These voids are susceptible to distortion and warpage, as well as cellular collapse, causing additional damage to the artifact.

For smaller organic specimens, re-treatment is an obvious strategy for halting the breakdown of PEG. The process of re-bulking the damaged cellular structure of an organic matrix, however, can cause additional stresses that contribute further to the instability of fragile organic artifacts. In regards to larger artifacts, such as ships' timbers, reversibility and re-treatment becomes a lengthy and difficult process. Ole Crumlin-Pedersen of the Viking Ship Museum in Roskilde, Denmark has observed the characteristic surface weeping that indicates the breakdown of PEG used to bulk the timbers of their extensive collection of vessels (personal communications, 1995). Noting that PEG has migrated to the surface of many ships' timbers and that some timbers have become misshapen due to warpage and cellular collapse caused by inter-cellular migration of the bulking media, Crumlin-Pedersen has concluded that, even in the controlled environment of the Viking Museum, the life expectancy of PEG is finite and the stability of the medium is estimated at approximately seventy years.

An assessment of the overall impact of the decomposition of PEG in large and small archaeological artifacts has not been fully assessed; the decomposition of PEG is a new issue for many conservators and the process of decomposition itself appears to be a slow and degenerative process. Migration of PEG is usually endemic of extensive cellular collapse.

The penetration of PEG into the deep matrix of large waterlogged timbers of shipwrecks poses a problem that must be addressed regarding re-treatment possibilities. First, is there a high enough degree of reversibility to ensure that the unstable PEG can be removed to the point that new PEG can be employed in the re-bulking of the ships timbers? While the application of PEG as a bulking agent has been widely used and regarded as reversible, microscopic analysis of the cross section of timbers conserved using conventional PEG treatments indicates that the bulking process itself causes some cell damage. A second issue to be considered is the question of additional cellular damage caused by re-treatment. Over time, many PEG-treated large timbers become warped and misshapen. This is due in part to their increased weight as the result of having been bulked with PEG, as well as their loss of structural integrity and load bearing ability due to the combined results of waterlogging and conservation. As a means of trying to eliminate some of the end results of PEG preservation, such as the addition of weight to structurally compromised organic materials and the resultant flexibility that has been noted in these same timbers, an experiment has been designed to assess various means of reconstituting or solidifying the bulking agent in the hopes of stabilizing the unstable media in situ, and therefore preventing additional damage to the ships timbers.

The objectives of this experiment are to determine which combination of catalysts and silane components can be combined to crosslink and solidify a variety of molecular weights of polyethylene glycol and glycerine. For this experiment, eight PEG and glycerine compounds were combined with silane components and either CT-32 or CT-30 catalyst and allowed to sit at room temperature in identical plastic containers. Once mixed, the viscosity, temperature and changes in physical appearances of each compound were observed and recorded. The eight sample combinations are listed below:

Table 1. Data for samples 1-8.

Sample	Bulking Agent (2oz).	Silane Component (2% by volume)	Catalyst (8-drops)
1	PEG 600	methyltrimethoxysilane	CT-30
2	PEG 600	methyltrimethoxysilane	CT-32
3	PEG 600	ethyltrimethoxysilane	CT-32
4	PEG 1500	methyltrimethoxysilane	CT-32
5	PEG 4000	methyltrimethoxysilane	CT-32
6	PEG 4000	ethyltrimethoxysilane	CT-30
7	PEG 400	methyltrimethoxysilane	CT-32

8	Glycerine	methyltrimethoxysilane	CT-32
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In all cases, the components were thoroughly mixed in clean plastic cups and then poured into clean plastic containers where they were allowed to stand at room temperature for the duration of the experiment. Because of their greater viscosity and higher molecular weight, the PEG 1500 and 4000 samples needed to be warmed slightly (to 35°C) so that the methyltrimethoxysilane and catalysts could be thoroughly mixed into solution. CT-32 and CT-30 catalysts are both tin catalysts. CT-32 is a liquid stannic compound which has an extremely long working time, based on silanol condensation, in which the solution never oxidizes. CT-30 catalyst is a liquid stannous compound which has a shorter working time in the polymerization process. Based on silanol-alcohol condensation, CT-30 must be controlled more closely to ensure that the catalyst does not become inactive before total polymerization has occurred. The resultant polymer created using CT-30 catalyst is more stable since continued polymerization is not possible once the catalyst is rendered inactive.

Observations:

Sample 1

After thirty minutes of curing at room temperature, the solution remained cloudy and translucent in appearance with evidence of very fine crystallized deposits on the sides of the container. After seven hours of curing, the solution remained essentially unchanged in appearance. After six days of curing, the solution had become a non-flowing mass which appeared thick and pasty.

Sample 2

After thirty minutes of curing, sample 2 appeared to have developed a considerably larger crystalline structure than had been noted with the CT-30 catalyst in Sample 1. After one and one half hours of curing time, Sample 2 had become non-flowing in viscosity and was translucent and milky-white in coloration. After seven days, the solution had solidified to the point that it had become a firm malleable paste.

Sample 3

Unlike Samples 1 and 2, sample 3, which was a mixture of PEG 600 and ethyltrimethoxysilane, had become quite firm and non-flowing after thirty minutes of curing. After seven days of curing, the mixture was considerably harder than Sample 2, but not hard to the point of brittleness.

Sample 4

After four minutes of curing, rapid visible changes were noted in Sample 4. At this point, the PEG 1500/methyltrimethoxysilane solution had developed a hard paste consistency which was noticeably smoother in texture than the PEG 1500 that had been used as the

source of materials for the experiment. After two days of curing, the mixture had turned to an extremely hard and brittle consistency.

Sample 5

Like Sample 4, Sample 5, which was a blend of PEG 4000 and methyltrimethoxysilane, had turned to a hard, non-flowing paste that was milky white in color. After two minutes, the mixture was very hard and slightly grainy in texture. For the duration of the experiment, no additional changes in appearance of hardness were noted in the sample.

Sample 6

The curing time for Sample 6 was considerably longer than that of sample 5, using CT-32 catalyst. Throughout the experiment, sample 5 appeared to have a finer crystalline structure and after seven days of curation, the resultant mixture was powdery, somewhat brittle and less firm than sample 5.

Sample 7

After two and one half hours of curation, there were no visible signs that polymerization was occurring in sample 7, which was a mixture of PEG 400 and methyltrimethoxysilane. After seven days of curation however, the solution had turned to a non-flowing, firm compound with a small amount of clear liquid floating on its surface. Initial examinations of this liquid suggested that it was methyltrimethoxysilane that had not bonded with the glycol molecules.

Sample 8

After two hours of curation, the glycerin/methyltrimethoxysilane solution was slightly milky white in color and small trails of what appeared to be hardened material were observed when the solution was stirred. After seven days of curation, the mixture had become a very viscous, opaque white compound. After one month of curation, sample 7 has remained in a viscous state and largely unchanged in texture or appearance.

Discussion

It was assumed that the PEG 400 and glycerine samples (samples 7 & 8) would be incapable of supporting extensive crosslinking due to their smaller molecular size. It was expected that minimal to no increases in viscosity would be observed in these samples. Sample 7 however, had hardened substantially after several days of curation, suggesting that adequate bonding had occurred between the glycol and methyltrimethoxysilane molecules. The presence of clear liquid on the surface of the hardened mixture suggests that either the small molecular size of PEG 400 rendered it less capable of fully bonding with methyltrimethoxysilane, or that a smaller percentage of methyltrimethoxysilane was needed to initiate the crosslinking process.

A comparison of Samples 1 and 2 is noteworthy. Sample 1, which was cured with CT-30, formed a visibly smaller crystalline structure in the compound and, overall, the resultant compound was not as hard and rigid as Sample 2, which had been cured with CT-32. The rate of cure for Sample 2 was considerably faster than the longer time frame required for polymerization in Sample 1. CT-32, which is a liquid stannic compound, appears to have a generally faster reaction time than CT-30 catalyst, which is a stannous compound.

Polymerization appeared to take place extremely quickly in Samples 4 and 5 (PEG 1500 and 4000 respectively). The use of heat during the mixing process was undoubtedly responsible, in part, for the accelerated polymer reaction. Because the resultant compounds were very firm, brittle and noticeably altered from their pre-treatment states, it is assumed that the polymerizing process was more efficient and complete, due in part to the larger molecular size and weight of these compounds. Degree of polymerization attributed to each sample was assessed upon the basis of observations regarding changes in color, texture, viscosity, expansion, contraction and other physical changes within and between each of the samples.

Because inter-cellular migration of PEG, which applies stress to cell walls, is directly related to the deterioration that occurs in many wooden artifacts, the focus of this experiment has been to determine ways to stabilize old PEG by in situ crosslink polymerization processes. Arguably, the viscosity and indeed, the physical nature of many of the PEG compounds tested were successfully reconstituted into compounds that were less likely to migrate.

Citation Information:

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1998, "The Polymerization of Polyethylene Glycol and Glycerine", Archaeological Preservation Research Laboratory (APRL), Report 16, World Wide Web, URL, <http://nautarch.tamu.edu/APRL/report16.htm>, Nautical Archaeology Program, Texas A&M University, College Station, Texas.