Archaeological Preservation Research Laboratory Report 22:

Induced Flash Polymerization Using Low Neutron Flux Radiation

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Experiments conducted at the Conservation Research Laboratory (CRL) that use lower molecular weight silicone oils to bulk and conserve a wide range of organic materials and artifacts have been very successful. Using tin-based catalysts to cure the silicone-bulked cell structures of waterlogged wood, leather, corn cob, bone and glass samples, it has been possible to successfully consolidate and retain the diagnostic features of numerous historic-period waterlogged artifacts. Several waterlogged wood samples recovered from marine excavations at Port Royal, Jamaica, under the direction of Dr. D.L.Hamilton, have been successfully polymerized; the diagnostic features and original shapes of these samples have been maintained. Within these samples, however, it is obvious that the use of low molecular weight silicone oils provided only minimal levels of tensile strength, since some separation of grain layers occurred. Experimentation on larger waterlogged wood samples indicates that the use of pure silicone fluids in the di- and trimethoxysilane groups resulted in artifacts with very poor tensile strength and tear characteristics. Arthur Charlesby has noted that tensile strength can be improved by irradiating silicone oils which have been mixed with fillers such as silica powder and, possibly, carbon black (1960 Charlesby, p.307).

There are some distinct advantages in using gamma radiation for the purpose of curing silicone oils, as compared to the more traditional processes of chemical curing. In the former process, doses of radiation, controlled by exposure time and intensity, directly determine the extent of curing within the silicone compound. With the cessation of radiation exposure, the process is complete and no further chemical reaction appears to occur.

The implied controllability of this curing process, with or without filler additives, is attractive for conservation purposes. Control over the degree of polymerization that occurs within an artifact also means that the conservator can avoid any swelling that can occur as a result of crosslinking in the presence of any residual organic solvents that may linger in the organic matrix of the artifact. Osthoff has noted that during a chemical curing process, which is accelerated by elevated temperatures, a form of stress relaxation occurs (1954 Osthoff, p. 4661). This stress relaxation, he observed, was due to the fact that portions of the chemical chain fracture and re-attach in a more relaxed formation in

the presence of potassium hydroxide, which is a byproduct of some polymerization processes. By comparison, Osthoff observed that stress relaxation and alterations within the polymer chain were greatly reduced when cross-linking is induced by radiation. This suggests that less stress is exerted on the cell wall structures of the artifact during the curing process.

There is a direct correlation between incremental increases in radiation dose rate and reaching the gel point of the silicone oil, which is described by Charlesby as an average of one crosslinked unit per weight average molecule (FIX(Charlesby, p.300). With the onset of even a small degree of crosslinking, it appears that the flow rate of the polymer is altered; this inhibits the flow of the solution, even if only a small amount of insoluble crosslinked material has been formed using low doses of radiation. Charlesby suggests that this is due to the fact that the three-dimensional network established with the onset of crosslinking is capable of absorbing the remainder of the polymer, which alters its flow capabilities.

This experiment is multi-faceted; it is intended to compare variables of time and intensity as factors in the polymerization process on samples of three different molecular weight silicone oils, as well as waterlogged wood samples which were bulked using these oils. For our purposes, we are using gamma radiation for treatment of our samples; much of the research conducted at the Nuclear Research Center at Texas A&M University is uses gamma radiation. Radio chromatic dye film was exposed at each of the three power settings and time intervals as a means of calculating dose rates that were being applied to the wood and oil samples. A densitometer was used to calculate the dose rates for each of the time/power settings which were chosen for this experiment.

Samples

For purposes of comparison of treatment methods, the wide range of variability observed in waterlogged wood samples makes them difficult to evaluate. Degree of waterlogging and degradation, as well as the degree of cell wall distortion or collapse which may have occurred as the result of dehydration, are two factors which are hard to assess. Factors such as cut, species and percentage of late wood-early wood growth rings within the sample are also major factors which determine the physical characteristics of any piece of wood. Any combination of these factors adds to the extreme variability of waterlogged wood samples and must be considered in any analysis of treatment methods. Because of the potential for a high degree of variability, tongue depressors made of white birch (Betula spp.) were used for this experiment. All tongue depressors were stored in a solution of tap water and sodium hydroxide for a period of three years prior to testing; for the purpose of comparison, a sample of tongue depressors had been set aside from the original shipment to act as controls for determining dimensional and mass changes. Since numerous studies have been conducted in the conservation of waterlogged tongue depressors using acetone/rosin, polyethylene glycol, camphor, sugar, freeze-drying and chemically induced polymerization techniques at the Conservation Research Laboratory, there is the added benefit of being able to compare the results of flash polymerization experimentation with results obtained using more conventional treatment methods.

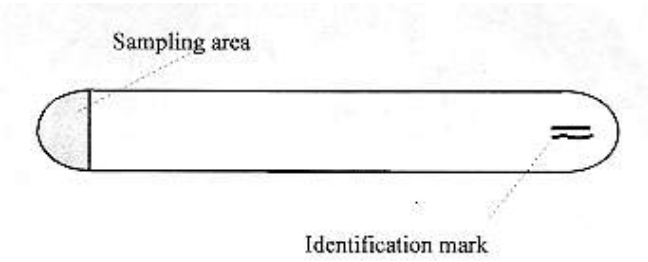


Figure 1 Tongue Depressor Sample Area.

Before treatment, all of the waterlogged tongue depressors were rinsed in a flow bath of fresh water for one hour, followed by a series of fresh water baths for a period of two days. Twelve tongue depressors were then randomly selected and each was branded with a successive identifying number. For the purposes of the first part of the experiment, the ends of one of each of the tongue depressor samples bulked with PS340, PS341 and PS343 silicone were sectioned to provide small samples of uniform size and a cross section surface (Figure 1). This was important because once the samples were treated, it was necessary to obtain uniform cross sections of each sample for microscopic analysis. Eight tongue depressors which had not undergone the waterlogging process, were set aside and the averaged dimensions and weights of these samples were used as a means of evaluating any changes in the treated samples. The treatment schedule for the waterlogged wood samples, oils and films is listed in Table 1 below.

TABLE 1 List of Samples and Treatment Schedule

Treatment	Sample Number	Treatment	Time/Power
1	**F1**	**FILM**	**2 SEC/10KW**
1	**F2**	**FILM**	**5 SEC/10KW**
1	**O1**	**PS343 OIL SAMPLE**	**5 MIN/10KW**

1	**1**	**WOOD SAMPLE/PS340**	**5 MIN/10KW**
1	**2**	**WOOD SAMPLE/PS 341**	**5 MIN/10KW**
1	**3**	**WOOD SAMPLE/PS343**	**5 MIN/10KW**
2	**F3**	**FILM**	**5 SEC/1KW**
2	**F4**	**FILM**	**10 SEC/1KW**
2	**O2**	**PS341 OIL SAMPLE**	**10 MIN/1KW**
2	**4**	**WOOD SAMPLE/PS340**	**5 MIN/1KW**
2	**5**	**WOOD SAMPLE/PS341**	**5 MIN/1KW**
2	**6**	**WOODSAMPLE/PS343**	**5 MIN/1KW**
3	**F5**	**FILM**	**10 SEC/300W**
3	**F6**	**FILM**	**20 SEC/300W**
3	**O3**	**PS 340 OIL SAMPLE**	**10 MIN/300 W**
3	**7**	**WOOD SAMPLE/ PS 340**	**10 MIN/300 W**
3	**8**	**WOOD SAMPLE/PS 341**	**10 MIN/300 W**
3	**9**	**WOOD SAMPLE/PS 343**	**10 MIN/300 W**

Bulking The Samples

After thoroughly rinsing all tongue depressors to ensure that surface dirt and as much sodium hydroxideas possible had been removed, the samples were placed into an initial dehydration bath of acetone and allowed to sit for twenty-four hours. This process was repeated two more times; for the final dehydration bath, the samples were placed in acetone within a freezer-mounted vacuum chamber, and a vacuum of 28.5 Torr was applied to the tongue depressors for twenty-four hours. After dehydration, samples 1,2 and 3 were placed on a paper towel and allowed to air-dry at room temperature for the remainder of the experiment. Samples 4,5 and 6 were quickly tamped with paper towel and immediately placed into a vat of PS343 silicone oil. Similarly, samples 7,8 and 9 were quickly blotted with paper towel and placed into PS341 silicone. Following the same processes, samples 10,1 1 and 12 were placed into a vat of PS340. Once bulked, all samples were sealed in air-tight plastic pouches and stored in a refrigerator until they were moved to the Nuclear Science Center at Texas A&M University, for the irradiation procedures.

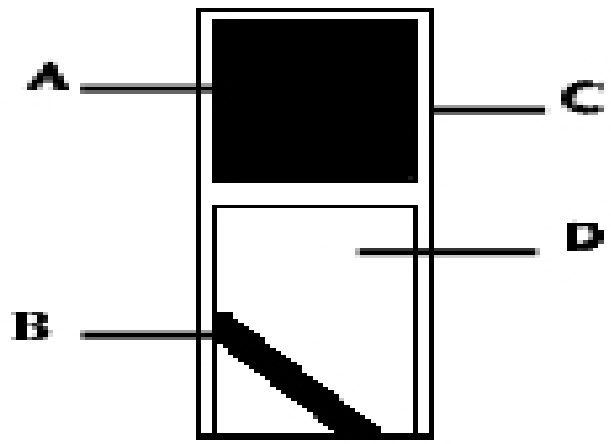
Irradiation Procedures

For our purposes, the dose rates that were applied to the samples were calibrated in terms of slowneutron flux as measured from the exposure of radio chromatic film samples at each of three power settings. Analysis of the film strips using a densitometer made it possible to more accurately determine the dose rate of gamma radiation that each of the silicone bulked samples received during the experiment. The exposure settings were 10 kilowatts, 1 kilowatt and 300 watts. Exposure times and dose rates for film samples varied and are listed in Table 1 above. Exposure times and dose rates for all wood samples are listed in Table 2 below.

Table 2 Exposure Times and Dose Rates for All Wood Samples

Sample Number	Sample/Treatment	Exposure/K/rads Total Dose	Reactor Output
1	**WOOD SAMPLE/PS340**	**65-120**	**10 K-WATTS**
2	**WOOD SAMPLE/PS341**	**65-120**	**10 K-WATTS**
3	**WOOD SAMPLE/PS343**	**65-120**	**10 K-WATTS**
4	**WOOD SAMPLE/PS340**	**25-40**	**1 K-WATT**
5	**WOOD**	**25-40**	**1 K-WATT**

	SAMPLE/PS341		
6	**WOOD SAMPLE/PS343**	**25-40**	**1 K-WATT**
7	**WOOD SAMPLE/PS340**	**40-50**	**300 WATTS**
8	**WOOD SAMPLE/PS341**	**40-50**	**300 WATTS**
9	**WOOD SAMPLE/PS343**	**40-50**	**300 WATTS**



A **Foam Spacer Plug**
B **Sample**
C **2/5 Dram Canister**
D **2 Dram Canister**

Figure 2 Sample Preparation for Irradiation

In preparation for irradiation, all wood sections were sealed in 2/5 dram polypropylene canisters which were heat sealed with a soldering iron. Each canister was then placed into a 2 dram polypropylene canister with a foam plug positioned to ensure that the smaller inner canister remained stationary within the larger outer canister. The outer canister was then heat sealed, ensuring that each sample was safely packaged for treatment. Each sample was then sent to the core of the reactor and irradiated according to the treatment schedule listed in Table 1. After exposure, each sample was inspected using a Geiger counter and, since most readings appeared to be the same as ambient readings in the treatment areas, the canisters were cut open almost immediately after exposure and sections were taken for visual inspection under a low powered microscope.

Observations

Microscopic analysis of each of the irradiated samples indicated that it was difficult to see the conservedcell structure in samples 1, 2 and 3 (Treatment One samples) which had been exposed to 65- 120 K/rads of gamma radiation. In all cases, the cell wall structures and rays were distorted and obscured. During post-exposure sectioning, all three of these samples were wet to the touch and acquiring thin uniform sections was difficult. Much of the damage to diagnostic features was undoubtedly done during the process of microtoming for slidesections.

The rate of bulking and general state of preservation of the cell structure of samples 4,5 and 6 (Treatment Two samples), which had been exposed to 25-40 K/rads of gamma radiation, were significantly better than the Treatment One group samples. While small amounts of silicone were visible in the pores and voids of sample 4, which was bulked with PS340 silicone, features such as cell walls and rays were not as well defined as in samples 5 and 6, which were bulked with higher molecular weight PS341 and PS343 respectively. In samples 5 and 6, larger deposits of silicone were visible in the pores and voids and the shape of cell walls and rays in both sections was much more clearly defined.

Cell wall structure and apparent degree of bulking was very successful in Treatment Three group samples, which were exposed to 40-50 K/rads of gamma radiation. Like Treatment One and Two samples, the Treatment Three sample bulked with PS340 silicone had less bulking in pores and voids than did samples 8 and 9, which were bulked with higher molecular weight silicone. The pores of sample 9, which was bulked with PS343 silicone, were full and there appeared to be no distortion in the shape of either the cell walls or the rays of the conserved wood. A comparison of sample 6 (bulked with PS343 and 25-40 K/rads) and sample 9 (bulked with PS343 and 40-50 K/rads) is significant. The diagnostic features of sample 6 have been preserved, but cell walls and ray structures in this sample are slightly contracted as compared to similar features in sample 9.

Conclusions

Because of the high degree of variability that can occur between wood samples, the scope of this experiment is very limited. This experiment was conducted to determine the effectiveness of three different molecular weight silicone oils and their ability to bulk and sustain the diagnostic features of waterlogged wood samples when exposed to gamma radiation-induced polymerization. Regardless of the molecular weight of the silicone oil used to bulk the Treatment One group samples, gross distortion and lack of features within these samples indicates that the dose rate of 65- 120 K/rads of gamma radiation for 5 minutes caused the situation observed by Osthoff with chemical polymerization processes: stress relaxation and alteration of the chemical chain occurred, causing distortion and potential obliteration of cellular features in the samples (1954 Osthoff, p. 461).

Treatment Two samples, which received treatment doses of 25-40 K/rads of gamma radiation for five minutes, were much more successful in preserving the diagnostic features of the wood samples. The increased bulking ability of the higher molecular weight silicone oils (PS341 and PS343) were evident since larger deposits of gelled silicone were observed in the pores of the wood samples. As already noted, a small degree of contraction was noted in the cell wall structures of these samples although distortion appeared to be minimal.

The cell wall structures of the Treatment Three samples appeared smooth and full with heavy concentrations of gelled silicone evident in all of the pores and voids of the wood samples. A comparison of samples 8 and 9, bulked with PS34 1 and PS343 silicone oils respectively, indicates that little to no distortion and contraction of cell wall structures had occurred. This suggests that the dose rate of 40-50 K/rads for a period of 10 minutes was more successful in polymerizing silicone oils in situ within the cell structure of waterlogged wood than polymerization using higher dose rates for a shorter time duration. As Charlesby has suggested, the silicone-bulked cell structure of the Treatment Two samples received a strong enough dose of gamma radiation to cause the onset of gelling which prevented any further flow of silicone from the cell structures (1960 Charlesby, p. 300). Because there was less polymerization of silicone oils in the Treatment Two samples as compared to the Treatment Three samples, this may explain the small amount of contraction that has occurred in the cell wall structures of the Treatment Two samples.

From this experiment, it appears that total dose radiation alone may not be the single factor that determines the degree of polymerization that has occurred in the waterlogged wood samples. Treatment Two samples received only slightly less total dose radiation than the Treatment Three samples, although exposure time for the Treatment Three samples was double that of the Treatment Two samples. A more accurate means of determining the total dose of gamma radiation applied to the samples, as well as experimentation to determine the relationship between reactor outputs total dose and dose rate (as measures in rods per minute) is required to better understand the processes at work in conserving waterlogged organic materials using silicone bulking techniques. From this experiment, however, it appears that lower power output, combined with lower ranges of total dose exposure, has successfully gelled silicone oils within the deteriorated matrix of the waterlogged samples.

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