STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Environmental Testing of Polyurethane Foams for use as 3-Dimensional Fixatives

DOE-FIU SCIENCE & TECHNOLOGY
WORKFORCE DEVELOPMENT PROGRAM

Date submitted:

December 10, 2021

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Submitted to:

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement # DE-EM0005213

Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

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EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2020, a DOE Fellow intern, Philip Moore, spent 10 weeks doing a summer internship at Savannah River National Laboratory under the supervision and guidance of Dr. Jennifer Wohlwend. The intern's project was initiated on May 24, 2021 and continued through July 29, 2021 with the objective of testing and characterizing polyurethane technologies in environmental chambers to simulate the varying temperatures and humidity found at Department of Energy (DOE) sites throughout the country.

In collaboration with Savannah River National Lab (SRNL), Florida International University has been investigating the use of polyurethane (PU) foams as three-dimensional fixatives for void spaces in retired DOE sites undergoing deactivation and decommissioning (D&D). However, many of these sites are left in a cold and dark state for years before reaching final disposition and no longer have environmental controls in place. To establish the ability to deploy PU foams outside of ideal conditions, SRNL performed environmental chamber testing using data taken from across the DOE Complex. In the course of this research, cure times at non-ideal temperatures and humidities were identified for Hilti Firestop Foam, Smooth-On FlexFoam-iT 7 FR, 14 and 23Fr, and evaluated for water uptake due to humidity.

Hilti and FlexFoam-iT 14 both cured as expected at all temperatures and humidities with minimal variation in cure time. FlexFoam-iT 23 FR and 7 FR both exceeded their manufacturer listed cure times at low temperatures. Based on these results, Hilti and Smooth-On FlexFoam-iT 14 are the most likely to cure according to manufacturer's instructions at any of the environmental conditions that were used in this experiment. However, only one sample of each material was able to be tested at each condition and Hilti's short cure time may also have played a factor in its performance in this experiment. Additionally, the initial weight of the foams was taken prior to curing and therefore the final weight was affected by off-gassing. Due to these factors SRNL has plans to continue this experiment with these considerations in mind.

1. INTRODUCTION

Operational Requirements

There are a number of facilities across the Department of Energy (DOE) complex that are undergoing deactivation and decommissioning (D&D) activity and contain numerous hot cells, glove boxes, pipework and other miscellaneous voids that contain contamination. This has created a need for a three-dimensional fixative technology capable of filling these void spaces and keeping the contamination from potentially being released. A foam fixative technology could also be applied to the interior of a pipe, as seen in Figure 1, to hold contamination in place during cutting or dismantling and to plug the end once the activity is complete. Polyurethane (PU) foams are a promising solution to D&D problems as they expand to many times their initial volume and have strong adhesive properties.

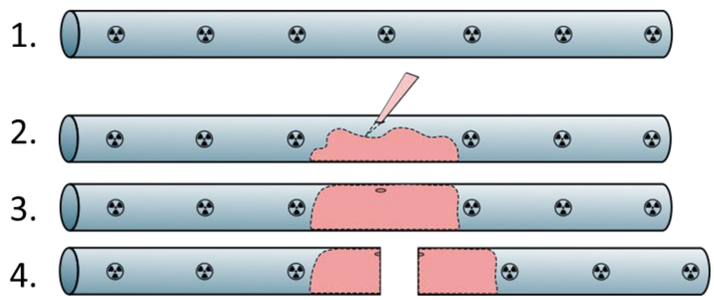

Figure 1. Diagram depicting the process of applying a PU foam plug for pipe removal.

Florida International University (FIU) and Savannah River National Laboratory (SRNL) have collaborated in the past to down-select polyurethane foams with the best physical properties most suitable for typical facility conditions during D&D. A particular emphasis has been placed on incombustible foam fixatives which would help minimize the amount of flammable material being introduced to a site awaiting final disposition. This is important as fire risks are listed on the Basis of Interim Operation (BIO) documents, which enumerate contingency scenarios that can occur at DOE sites during D&D (Figure 2) [1]. Hilti Firestop foam, one of the PU foams tested extensively by FIU, is an intumescent foam, which contains graphite that causes the foam to char and expand in response to heat, forming an insulating layer.

DOE Site/Facility	Fire Events	Explosion Events	Loss of Confinement (Spill) Events	Natural Phenomena Hazards	Other Events
RFETS Bldg 440	• ***1,200 Drum Fire (EU)*** • ***15 Crate Fire (U)*** • Truck Fire (EU)		• LLW Repack Spill (U) • Drum Spill (A)	• ***Earthquake Collapse (U)***	• ***Aircraft Crash (EU)***
RFETS Bldg 664	• ***3 Drum Fire (U)*** • ***15 Crate Fire (U)*** • *336 Drums + 72 Crates Fire (EU)* • Truck Fire (EU)		• *Multi-Container Drop*	• ***Earthquake Collapse (U)***	• ***Aircraft Crash (worst-case) (EU)*** • ***Aircraft Crash (realistic case) (EU)***
SRS APSF	• *Accountability Msmt. Room Fire (U)*	• *Explosion in Repackaging Area (A)*		• *Seismic Induced Full Facility Fire (U)*	
SRS HB-Line	• Full Facility Fire (EU) • Full Facility Fire & Secondary Events (EU) • ***Intermediate Fire (U)*** • ***Intermediate Facility Fire & Secondary Events (EU)***		• Spill (A)	• Earthquake with Secondary Events (EU)	
SRS Bldg 235-F	• Fire – Best Case (U) • Fire – Worst Case (U)			• Design Basis Earthquake (EU)	
SRS SWMF	• ***TRU Pads - Internal Culvert Drum Fire (U)***	• ***TRU Pads - Culvert Explosion (U)***	• TRU Pads - High Energy Vehicle Impact (EU) • ***TRU Pads - Dropped Steel Box (A)***	• TRU Pads -Tornado (EU)	• 634-7E Buried Waste Helicopter Crash (EU)
Hanford WRAP Facility	• *4 Drum Fire (U)* • *Single Drum Fire in Glovebox (U)*	• ***Drum Explosion with 4 Drum Fire (U)*** • *Single Drum Explosion in Glovebox (U)*	• Solid Waste Box Failure (A)	• ***Design Basis Earthquake (U)*** • Beyond DBE (EU)	
INEEL RWMC	• ***Vehicle Fire (U)***	• *Drum Explosion (A)*	• *Box Spill (A)*	• Design Basis Earthquake (U)	
LANL RAMROD Facility	• Small Fire (A) • Medium Fire (EU) • Large Fire (EU)	• Small Natural Gas Explosion (A) • Large Natural Gas Explosion (EU)	• Coring Glovebox Spill (A)	• Design Basis Earthquake (U)	• Aircraft Crash (EU)

Note: Scenarios in *Italics* are risk dominant events, based on Risk Class I or II for the collocated worker. ***Bold Italics*** denotes that it is also risk dominant for the public.

Figure 2. Basis of Interim Operations document.

The use of commercial-off-the-shelf (COTS) polyurethane foams for this purpose is established in the ASTM E3191 *Standard Specification for Permanent Foaming Fixatives Used to Mitigate Spread of Radioactive Contamination* (Figure 3) [2]. This recently developed standard lays out the selection and definition of a permanent foam fixative.

Designation: E3191 – 18

Standard Specification for Permanent Foaming Fixatives Used to Mitigate Spread of Radioactive Contamination[1]

4.1 This specification establishes performance specifications for permanent foaming fixatives that are intended to immobilize or isolate, or both, dispersible contamination deposited within a void space as might result from anticipated to unanticipated events to include normal operating conditions, decommissioning, and radiological release.

4.2 The foaming fixative is intended to be a permanent, non-removable, long-term material used for decommissioning and operations. It is intended to isolate the contamination from active working areas. It may also enable reduction in building requirements such as induced airflow or negative air pressure.

4.3 The foaming fixative is intended to be used for filling contaminated 3-dimensional void spaces of various volumes that would be difficult to otherwise coat with conventional 2-dimensional fixatives.

Figure 3. Section 4 of ASTM E3191 which defines a permanent foaming fixative.

Past Research

The baseline material properties of these PU foams have been established in prior testing. A 2005 study conducted in Germany defined three states of failure of PU foams adhered to a substrate: adhesive failure, breaking, and cohesive failure [3]. Adhesive failure occurs when a foam delaminates completely from the substate. Breaking is when the adhesion interface is stronger than the foam itself and the foam tears away leaving a layer adhered to the substrate. Cohesive failure is a combination of failures, when part of the foam peels away cleanly and others break apart leaving foam on the substrate.

FIU found that the adhesive and compressive strengths of the of Hilti firestop foam were exceeded at very similar loads. While this primarily produced cohesive failure, occasionally adhesive or breaking failure occurred instead. For this reason, FIU defined the operationally relevant term “plug strength”. Plug strength is the force level that failure occurs in which the foam fixative no longer acts as a plug, in units of pounds force (lbf). This was tested by applying Hilti to a 304-stainless steel pipe. This pipe was then placed in a lipped bucket piece and a plunger the size of the inner diameter of the pipe was compressed downward until failure occurred (Figure 4).

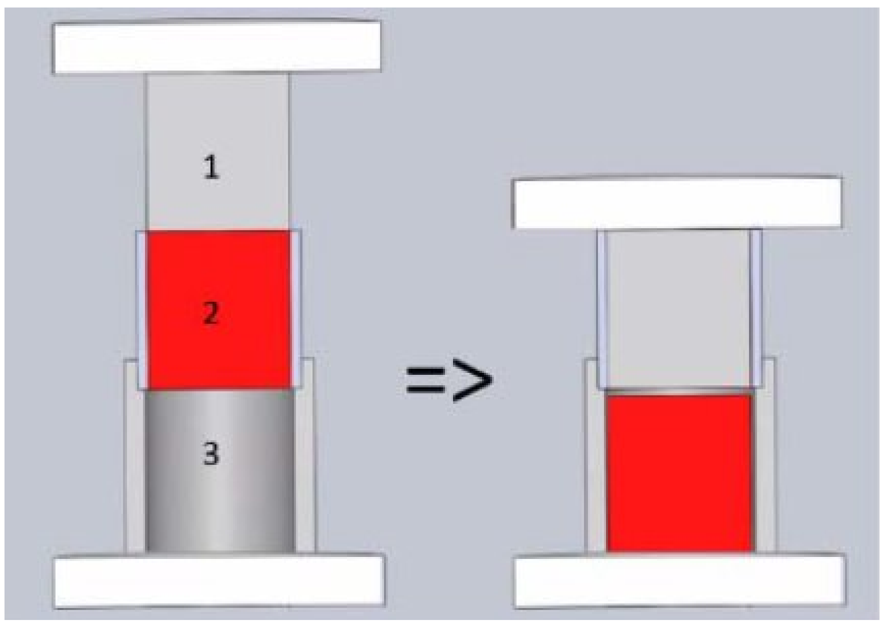

Figure 4. Plug strength test design: 1) plunger, 2) pipe sample, 3) bucket.

The bucket piece was made of 3D printed acrylonitrile butadiene styrene (ABS) for samples with a diameter of 3 inches or less (Figure 5), or stainless steel for those with a diameter greater than 3 inches. The plunger was made of aluminum for samples with a diameter of 3 inches or less and stainless steel for samples with a diameter greater than 3 inches.

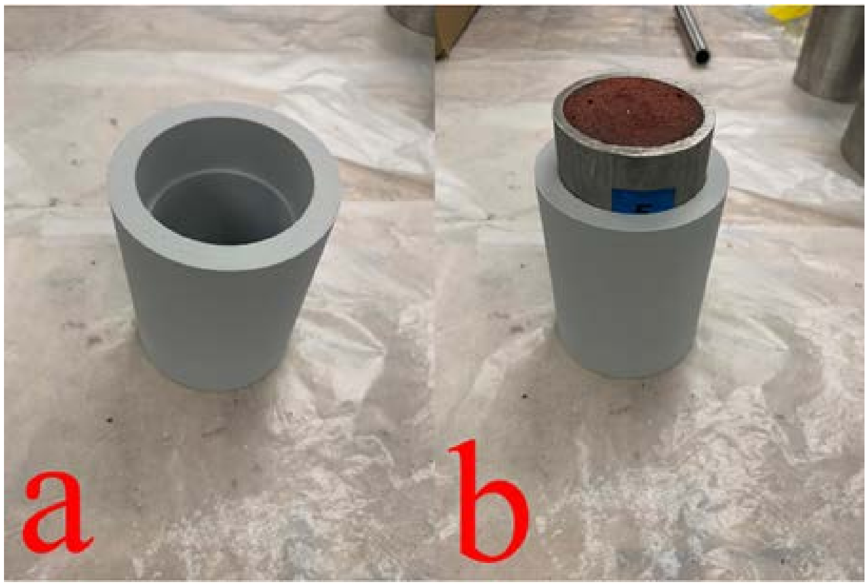

Figure 5. a) ABS Bucket piece printed in ABS plastic; b) Bucket piece with a 2" diameter sample.

This test was accomplished using an MTS Criterion Series 43 Tensile Tester equipped with compression plates (Figure 6). Plug strength is reached when the tensile tester detects failure.

Figure 6. MTS Criterion Tensile Tester Series 43 with aluminum plunger and ABS bucket.

Testing protocols were made in compliance with Normal Conditions of Transport and Hypothetical accident conditions outlined by the United States Nuclear Regulatory Commission (NRC). These stressors involved a drop test, water submersion, and direct flame conditions. Drop testing was performed by dropping samples from heights of 4, 8, and 12 feet onto a stainless steel plate (Figure 7a). Water submersion was accomplished by submerging samples under 3 feet of water for 8, 12, and 24 hrs. (Figure 7b). The direct flame test was completed by placing a propane torch at each end of the samples for 30 minutes (Figure 7c) [4].

Figure 7. Experimental design of stressors: a) water immersion, b) free drop impact, c) direct flame.

The findings for 2-inch diameter, 2-inch tall pipe samples are displayed in Figure 8. The water submersion samples' failure loads ranged from 1,144 to 1,335 lbf. The samples that had longer exposure to water had lower failure loads, and one of the 24-hr submersion samples had water inside of it. These foams are closed-celled foams so they should block the transport of water, but water still permeated the sample. This raised concerns about whether the foams might uptake water from humidity. The fire testing performed the worst due to the foam fully intumescing and delaminating from the substrate. The drop test values ranged from 999.8 to 1419 lbf [4].

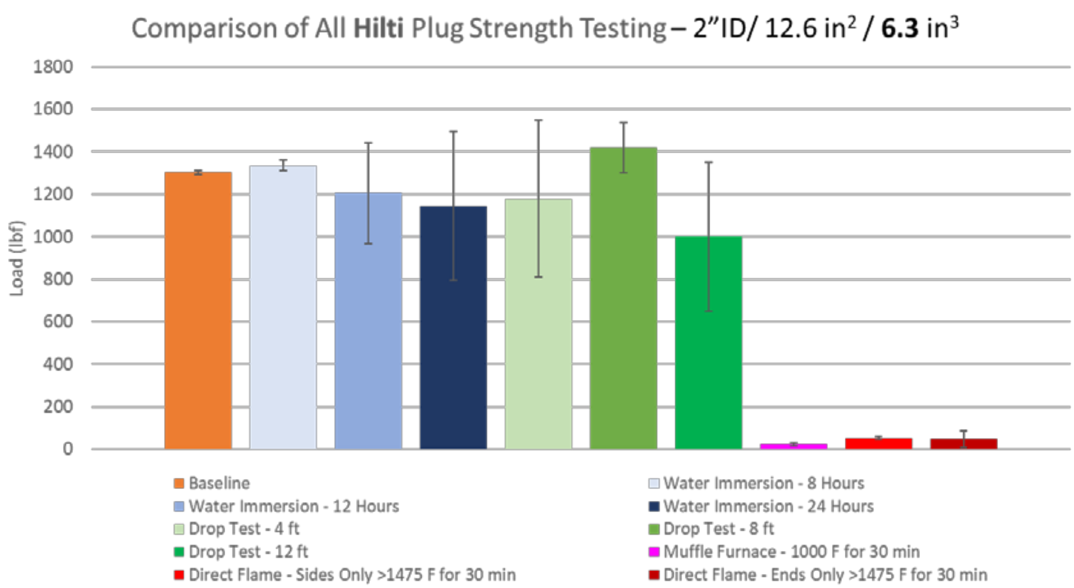

Figure 8. Hilti plug strength comparison for 2" diameter, 2" tall samples.

Larger, 3-inch diameter, 14-inch tall pipe samples were tested to verify results and test the properties of a full cartridge of Hilti. The flame test was divided into an end-focused flame test and a center-focused flame test. The end-centered flame test performed better than the smaller sample, but the center-focused flame test had different results. As seen in Figure 9, samples produced a significant amount of smoke and a single sample pushed out a 4-inch section of foam. This indicates that additional flame testing is needed to fully determine the cause [4].

Figure 9. Center-focused flame testing samples producing white smoke (left) and a single sample pushing out a section of Hilti (right).

Results from the 3-inch diameter, 14-inch tall sample testing can be viewed in Figure 10. Like in the previous testing, only the direct flame test had a significant drop in plug strength. The end-centered flame test preformed significantly better than the 2-inch diameter samples, as the larger amount of exposed foam could intumesce and insulate the pipe [4].

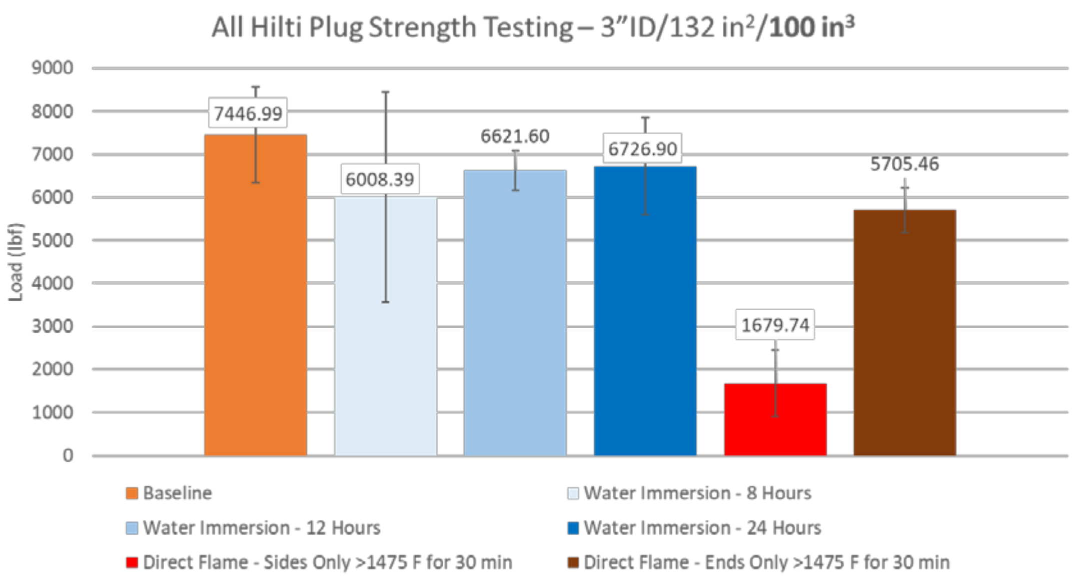

Figure 10. Hilti plug strength comparison for 3" diameter, 14" tall samples.

2. RESEARCH DESCRIPTION

Many DOE facilities undergoing D&D have been left in a cold and dark condition, meaning that the facility is without power or environmental controls. To ensure proper curing of potential permanent foaming fixatives in a variety of climates, environmental chamber testing outside ideal conditions of 25℃ and 40% relative humidity (RH) was deemed necessary. Seven environmental conditions (5℃ 50% RH, 15℃ 40% RH, 25℃ 15% RH, 25℃ 20% RH, 25℃ 40% RH, 35℃ 40% RH, 40℃ 40% RH) were selected from across the DOE complex. Testing was completed in two phases: 1) Foams were tested for set to touch, dust free, and dry to touch times according to ASTM D1640 [6] at the selected condition, and 2) samples were allowed to remain in the chamber until they had been at the selected condition for a total of 24 hours.

The foams selected for this experiment were Hilti Firestop foam, Smooth-On FlexFoam-iT 7 Fr, Smooth-On FlexFoam-iT 14, and Smooth-On FlexFoam-iT 23Fr. Hilti Firestop foam is intumescent rigid polyurethane foam that expands to 6 times its original volume [7]. Smooth-On FlexFoam-iT 14 is a flexible polyurethane foam that expands to 4 times its original volume. Smooth-On FlexFoam-iT 7 FR and 23 FR are incombustible flexible polyurethane foams that expand to 8 and 2 times respectively. FlexFoam-iT 7 FR is fire rated to *The Federal Motor Vehicle Safety Standard No. 302* and FlexFoam-iT 23 FR is fire rated to UL-94 HB. While these foams do not form a protective char layer like an intumescent foam, they are advertised to self-extinguish when exposed to flame [8].

Figure 11. Smooth-On 7 FR (top left), Smooth-On 14 (top right), Smooth-On 23 FR (bottom left), and Hilti Firestop foam (bottom left).

The first stage of testing began with portioning the parts of the two-part polyurethanes which are labeled as “part A” and “part B” by the manufacturer. It is notable that Hilti, while a two-part polyurethane, comes in a pre-portioned cartridge that can only be applied with a proprietary Hilti foam dispenser (Figure 12) [7]. Smooth-On 7 FR and 14 are both mixed by volume ratios, while Smooth-On 23 FR was portioned by mass according to the manufacturer’s specifications. The foams were then quickly mixed by hand and weighed on a balance (Figure 13). Hilti was always applied last due to its short cure time.

Figure 12. Hilti Firestop foam being applied with the Hilti foam dispenser.

Figure 13. Smooth-On foams being mixed.

The cure time was determined using a near fit standard, ASTM D1640, which describes set to touch, dust free, and dry to touch times as states that a curing coating undergoes during curing. Set to touch time is tested by rolling a finger, while wearing a clean nitrile glove, on the surface of the foam and then on a clean glass slide. When none of the polymer comes off on the slide, set to touch has been reached. Dust free time is tested by placing cotton fibers taken from a cotton ball on the fixative and blowing gently. If the cotton fibers are blown off easily and do not adhere, then the dust free time has been reached. Finally, dry to touch is tested by gently placing and removing a finger from the surface of the fixative. If the foam does not try to adhere to the glove, then dry to touch time has been reached [6] (Figure 14).

Figure 14. FlexFoam-iT 7 FR being checked for dry to touch condition.

The fixatives were removed from the environmental chamber and checked for these milestones at intervals of 20 minutes, as seen in Figure 15. The first phase of testing was concluded once all fixatives had reached the appropriate curing time.

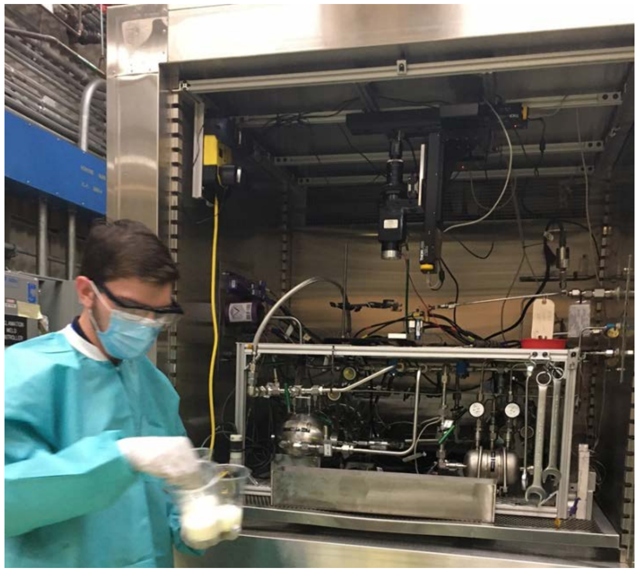

Figure 15. Foam samples being removed from the environmental chamber.

For the second stage of testing the samples were left in the environmental chamber until they had remained at the set temperature and humidity for a total of twenty-four hours. They were then removed, inspected for abnormalities, and weighed to check for water uptake.

3. RESULTS AND ANALYSIS

Of the down-selected polyurethane foams, Hilti was the most consistent. Hilti cured within a minute and a half in all but two trials and taking a maximum of 3 minutes at room temperature [7]. Of the Smooth-On foams, FlexFoam-iT 14 was the most consistent, taking an hour to cure in 4 of the 7 trials and taking significantly less time at higher temperatures without noticeable cell collapse. Both FlexFoam-iT 7 FR and 23 FR took longer to cure at colder temperatures and slightly less time to cure at higher temperatures. These two foams were the only ones tested that exceeded their manufacturer listed cure times. Moreover, at 45℃ and 40% RH, FlexFoam-iT 7 FR was observed to collapse and form a solid, rubber-like puck that cured rapidly.

Table 1. Cure Time of Polyurethane Foams at Selected Environmental Conditions

		Hilti (minutes)			7FR (minutes)			14 (minutes)			23FR (minutes)		
Temp (°C)	Humidity (%)	Set to Touch	Dust-Free	Dry to Touch	Set to Touch	Dust-Free	Dry to Touch	Set to Touch	Dust-Free	Dry to Touch	Set to Touch	Dust-Free	Dry to Touch
5	50	1.5	1.5	1.5	80	100	140	20	20	60	80	80	80
15	40	1.5	1.5	1.5	60	120	140	20	40	60	60	80	120
25	15	1.5	1.5	1.5	80	120	120	20	40	40	100	140	140
25	20	1.5	1.5	1.5	80	120	140	20	60	60	60	60	200
25	40	3	3	3	40	80	80	20	40	60	40	80	80
35	40	2	2	2	40	60	60	20	20	20	40	80	80
45	40	1.5	1.5	1.5	20	20	20	20	20	20	20	40	60

When weighed after 24 hours, water uptake from humidity was not observed in any sample. Moreover, all samples registered lighter after spending 24 hours in the chamber. This is most likely due to non-hazardous off-gassing, a known factor in the curing of polyurethane foams. The tabulated data can be viewed in the graphs below (Figure 16 - Figure 22).

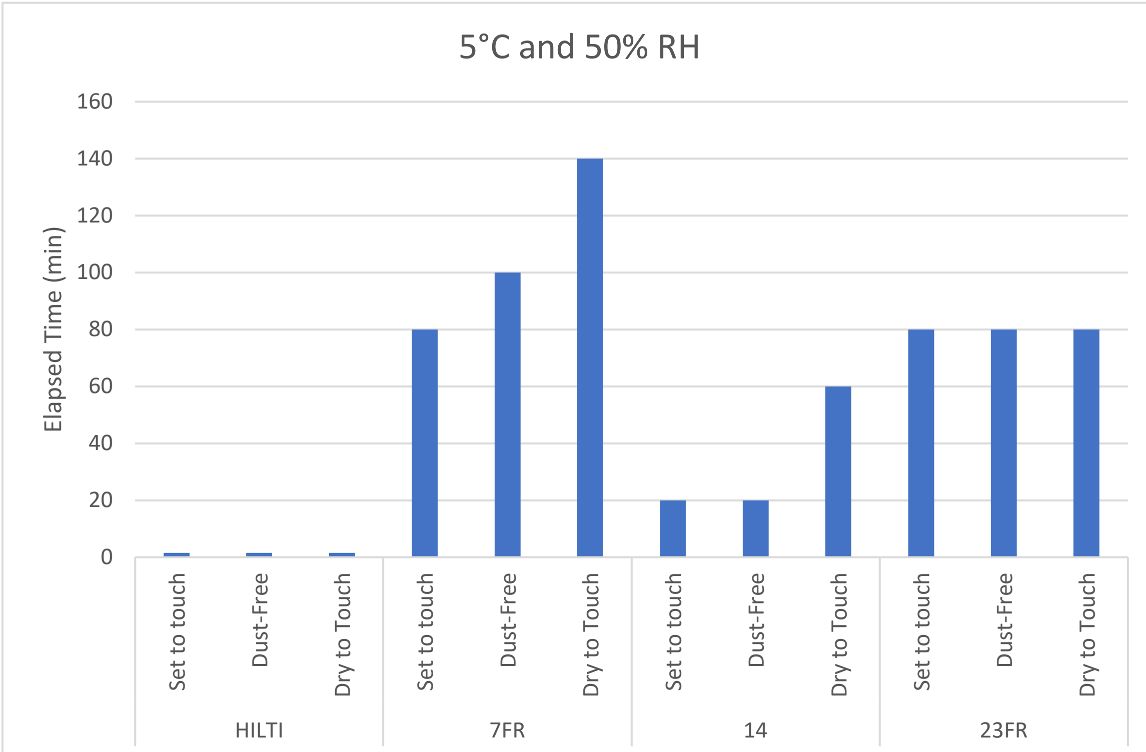

Figure 16. Cure times for polyurethane foam fixatives at 5°C and 50% RH.

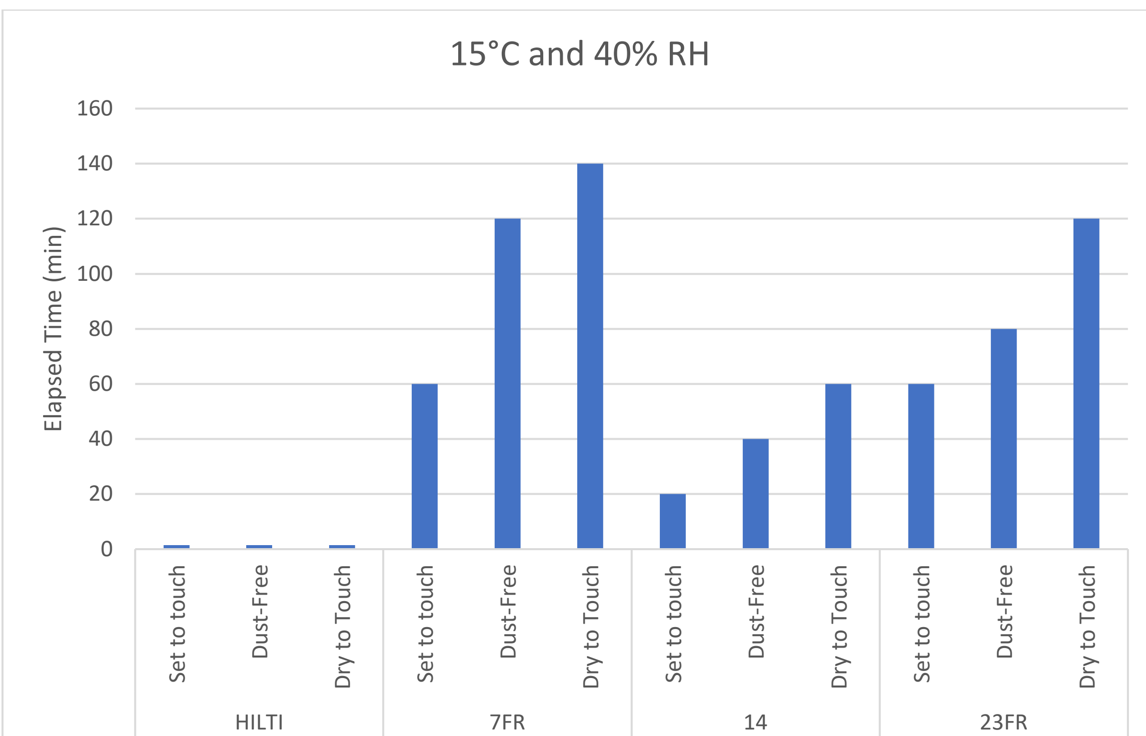

Figure 17. Cure times for polyurethane foam fixatives at 15°C and 40% RH.

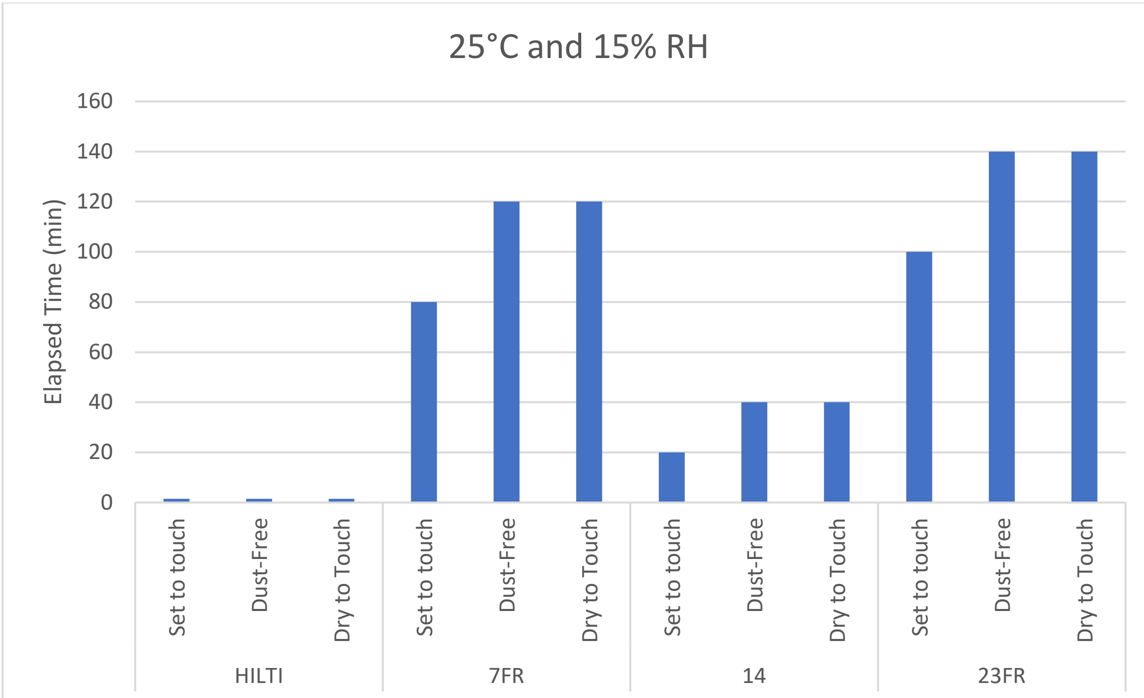

Figure 18. Cure times for polyurethane foam fixatives at 25℃ and 15% RH.

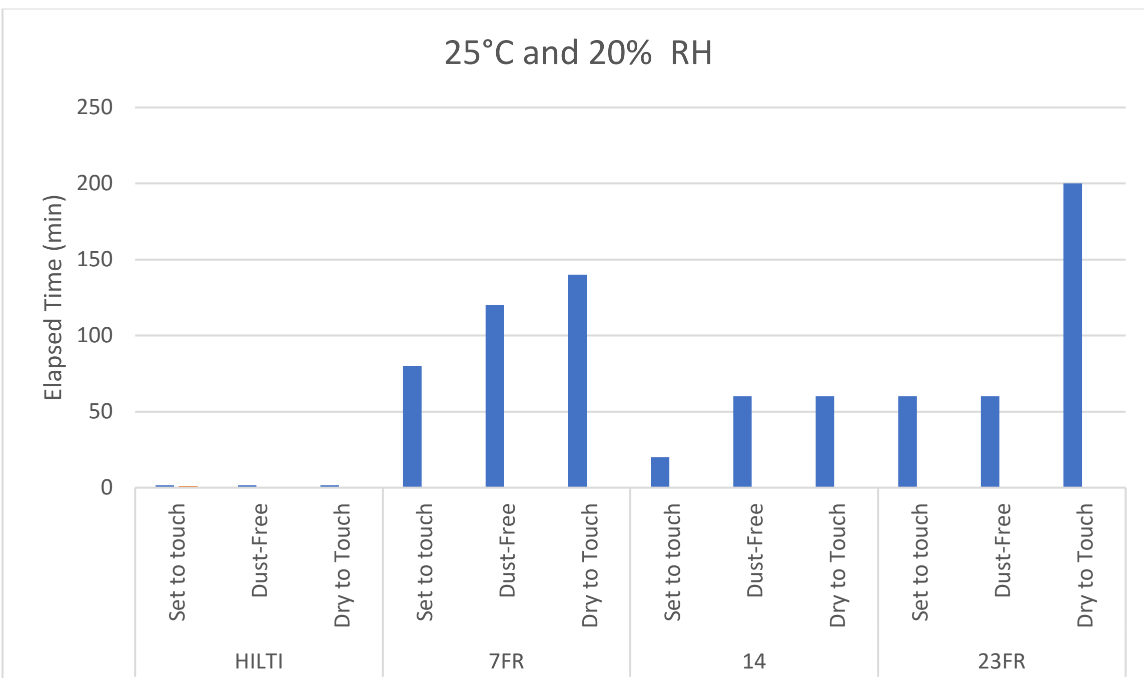

Figure 19. Cure times for polyurethane foam fixatives at 25℃ and 20% RH.

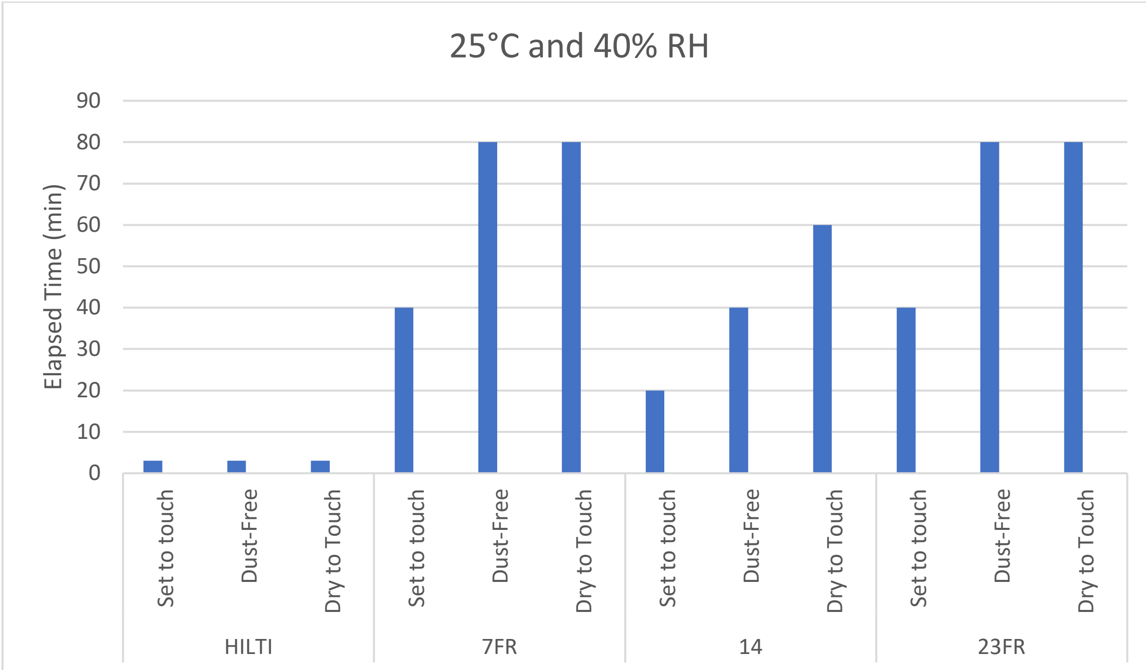

Figure 20. Cure times for polyurethane foam fixatives at 25°C and 40% RH.

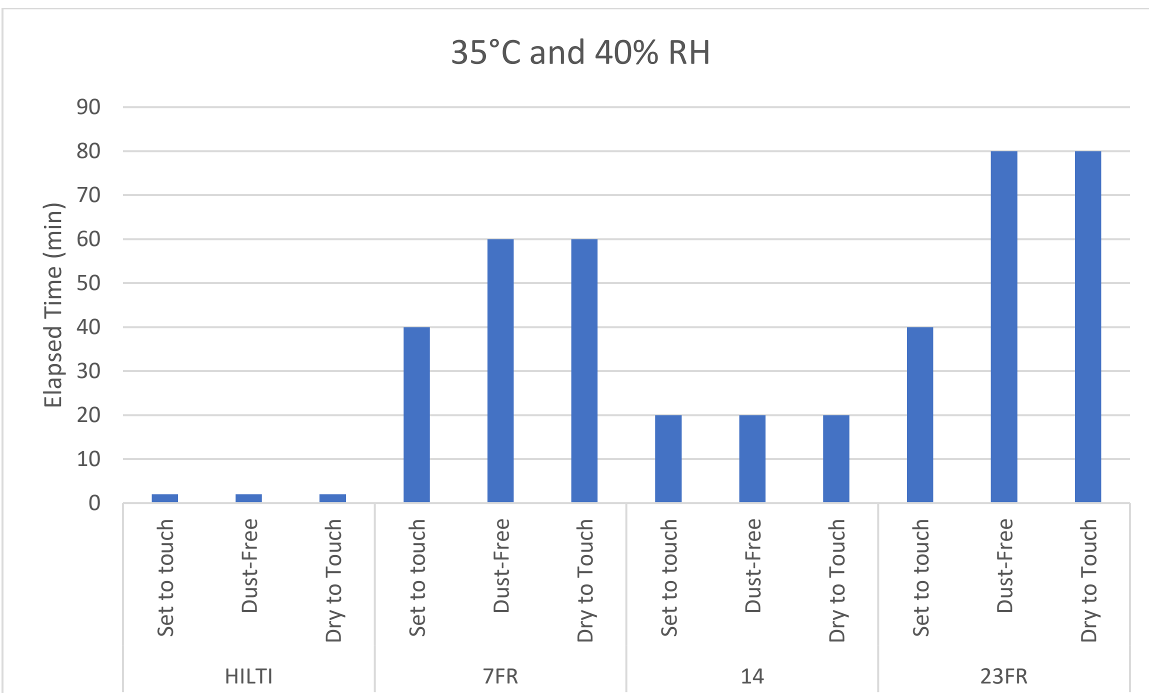

Figure 21. Cure times for polyurethane foam fixatives at 35°C and 40% RH.

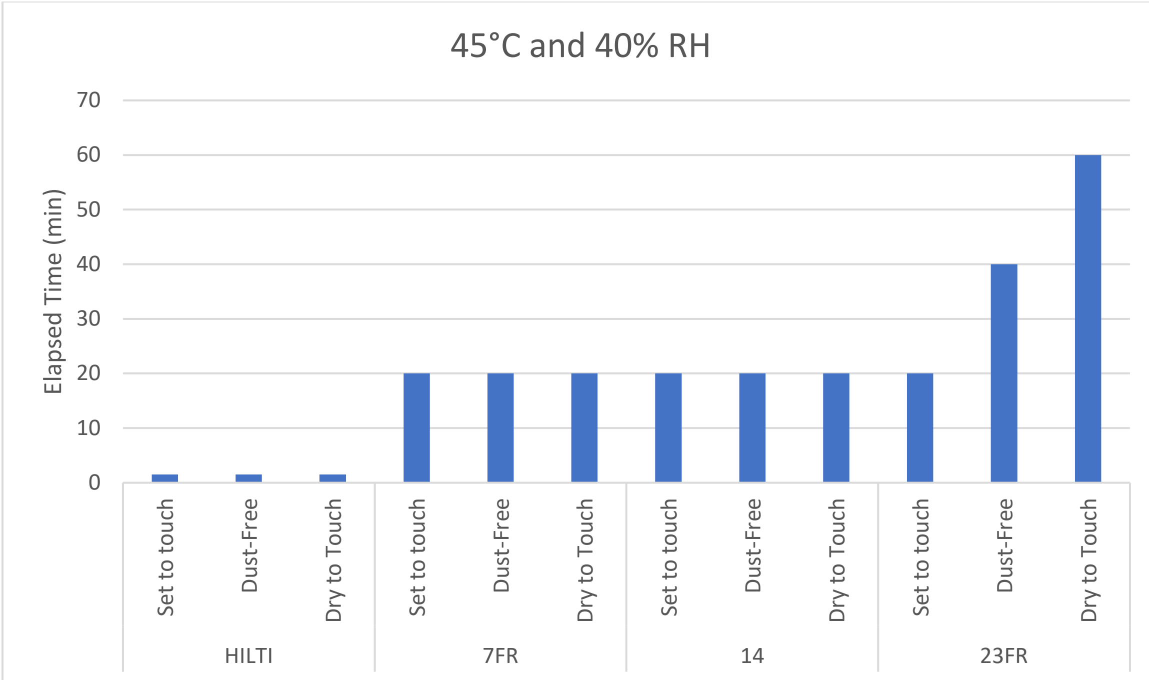

Figure 22. Cure times for polyurethane foam fixatives at 45°C and 40% RH.

4. CONCLUSION

Hilti and FlexFoam-iT 14 both cured as expected at all temperatures and humidities with minimal variation in cure time. FlexFoam-iT 14 cured faster in hotter conditions, but without noticeable loss in structure. FlexFoam-iT 23 FR and 7 FR both had wider variations in their cure time, exceeded their manufacturer listed cure time, and 7 FR had a noticeable failure at 45℃, 40% RH. None of the samples were observed to have taken up water as a result of humidity. Based on these results, Hilti and Smooth-On FlexFoam-iT 14 are the most likely to cure according to manufacturer’s instructions at any of the environmental conditions that were used in this experiment.

However, it should be considered that only one sample of each material was able to be tested at each condition and future testing with more samples may prove beneficial. It should also be noted that due to Hilti’s short cure time, the time required to move it into the environmental chamber may also have played a factor in its performance in this experiment. Additionally, the initial weight of the foams was taken prior to curing and therefore the final weight was affected by off-gassing; this led to significant uncertainty in the water uptake measurements. SRNL has plans to continue this experiment with these considerations in mind.

5. ACKNOWLEDGEMENTS

The author acknowledges the assistance and guidance of SRNL mentor Jennifer Wohlwend, PhD and SRNL collaborator Emily Fabricatore as well as FIU-ARC mentors Joseph Sinicrope and Mellissa Komninakis.

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