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# Freeze-Thawing of Polyester/E-Glass as an Evaluation of an ASTM International Test Standard Proposal

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# FREEZE-THAWING OF POLYESTER/E-GLASS AS AN EVALUATION OF AN ASTM INTERNATIONAL TEST STANDARD PROPOSAL

BY

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## ABSTRACT

American Composites Manufacturers Association (ACMA) reported in 2009 that the four major sectors currently utilizing fiber reinforced polymers (FRP) are construction, corrosion, marine, and transportation in descending order of total FRP shipped. All of these sectors are known to be billion dollar industries and they are all involved with applications subjected to freezing and thawing. FRP encompass many characteristics that are beneficial to these sectors and also in resisting this exposure. ASTM International has yet not developed a standard to test FRP materials resistance to freeze-thaw (FT) cycling exposure. The D20.18.02 committee of the ASTM is in the process of creating a test standard for freeze-thawing of FRP and has developed a draft standard. This study was conducted to assist in the development of this standard.

A pultruded mat and roving E-glass reinforced polyester with aluminum tri hydroxide (ATH) filler was used. Three sample batches were subjected to FT-cycling. Two sample batches were subjected to manual FT-cycling; one was exposed to 30 days of initial moisture exposure (30W-samples) and the other to 60 days (60W-samples). The third sample batch was exposed to 30 days of initial moisture exposure and automatic FT-cycling through the use of a programmable temperature chamber (30TC-samples).

The samples were first conditioned in distilled water at 23°C (77°F) for 30 days. Secondly they were exposed to a total of 100 FT-cycles each 6 hours long consisting of 3 hour of thawing in distilled water at 23°C and 3 hours of dry freezing at -20°C (-4°F). The ultimate tensile strength (UTS) of three sample batches was determined through ASTM D638 upon the

completion of the 100 FT-cycles. The results from the three test environments showed similar degradation. The percent reductions in the samples mean UTS of the 30W-, 60W-, and 30TC-samples was found to be 21.0%, 17.6%, and 19.1%, respectively. The test parameters were evaluated by implementing several sample batches and through the use of the preliminary research conducted. Contributions to the development of the draft from the D20.18.02 committee were made based on these findings and are presented in this study.

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# 1. INTRODUCTION

The American Composite Manufacturing Association (ACMA) reported that the construction, corrosion, marine, and transportation sectors combined for 91% of the 2.18 billion lbs total mass of thermoset fiberglass composites shipped in 2009. Exposure to different environmental conditions including corrosive, UV radiation, temperature, moisture, and freeze-thaw cycling (FT-cycling) are common for all of these sectors. Fiber reinforced polymers (FRP) are readily being utilized as a substitute to metals due to light weight with good mechanical properties and excellent corrosion resistance. Yet a FT-cycling standard has not been created to address this issue. A FT-cycling standard is needed to validate the use of FRP for this moist and harsh environment. Corrosion issues usually surface along with FT-cycling due to moisture for most metals. The direct cost of metallic corrosion in the United States was estimated to $267 billion or approximately 3.1% of the nations gross domestic product (GDP) concluded through a 2-year study by the U.S. Federal Highway Administration released in 2002 [1]. The indirect cost of corrosion is estimated to be of equal amount which results in an approximate cost of 6% of the U.S. GDP [1]. From this it is evident that a staggering amount can be saved by validating and implementing FRP for structural marine applications and other areas typically subjected to FT-cycling and prone to metallic corrosion.

## 1.1 Background Preliminary Research

FRP response to various environmental conditions have been the driving force for numerous studies [2-6] and accelerated test standards are sought for validation purposes. Several

sources for detrimental effects of moisture on FRP have been determined in previous studies. High humidity or immersion of FRP will cause water molecules to enter the FRP and establish voids in the matrix, debonding of the fiber-matrix interface, and even degradation of the fiber. This causes both reversible and irreversible damage to the FRP leading to loss of mechanical properties and premature failure [2-6]. Studies to predict long term exposure to hygrothermal environments have been conducted with promising results, especially through the use of the Arrhenius model [7, 8]. It also has been shown that increasing the temperature and exposure time in wet conditions will accelerate the degradation of FRP. Models have been devised in attempts to predict the degradation of different combinations of temperature and exposure time [9, 10]. However, the vast number of fiber and resin combinations makes this a difficult task. The effect of manufacturing processes on the response of FRP to environmental conditions has also been considered and proven to be an important parameter; i.e. to completely wet out of the fiber and to control the cure rate of the matrix [11].

Long term FT-cycling has been shown to cause detrimental effects on FRP. The damaging mechanisms are fairly well understood and are related to inertial moisture expanding through freezing in the matrix [12-17]. Debonding of the fiber and the matrix can also occur due to differences in thermal expansion. Absorbed moisture can lead to micro-cracks which will stimulate further moisture absorption and accelerate the degradation process through FT-cycling. Even though this process is well documented there has been little success in predicting the long term effects of FT-cycling. The first step towards a better understanding and comparison of future research is to develop and adopt a general test standard for FT-cycling of FRP.

ASTM International is recognized as the most utilized standards organization in the U.S., and ASTM standards are also utilized worldwide. There is already an ASTM standard available

for moisture conditioning of FRP, ASTM D5229 “Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials,” developed in 1992 and recently revised in 2010. However, there is currently no specific ASTM standard designated for FT-cycle testing of FRP. Companies and researchers are therefore forced to create their own test methods for FT-cycling of FRP to evaluate a material, product, or process. Another option is to use an existing standard designated for a different material. ASTM C666, “Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing,” has frequently been utilized to test FRP, especially for infrastructure products. ASTM C666 serves its purpose for its intended use by limiting further curing of concrete which is accelerated at higher temperatures. However, low temperature is a major drawback for FRP since it limits moisture absorption necessary to get the full detrimental effect of FT-cycling as previously discussed. Another concern is that FRP may not thaw throughout its thickness when exposed to 40°F for 30-75min as specified in ASTM C666.

It is difficult to compare results from different FT-cycling tests due to the lack of knowledge in relation to the FT-cycling response of FRP to different exposure times and temperature ranges. FT-cycling testing does in general not require high capital investments, but it can be very time consuming which can generate high labor costs. An industry accepted standard will reduce the cost to develop new products and improve the possibilities to reach other markets by providing clear comparable FT-cycling data. An ongoing effort is being made by the ASTM International’s D20.18.02 committee, a subcommittee to the D20 Plastics committee, to create an ASTM standard for freeze-thawing of pultruded shapes.

A draft has been under development and a study, “Examination of the Development of a Freeze/Thaw Test Standard for Pultruded Composites” [18], was conducted at the University of

Mississippi to evaluate the test parameters in the draft. The study was conducted as a course project and the final paper was developed through joint efforts of Michael Hougendobler, Dr. Ellen Lackey, Stefan Strandlund, and Dr. James G. Vaughan. This paper [18] was utilized as a guideline for the experimental parameters in this study. The objectives of this new standard under development are to consistently evaluate the effect of FT-cycling on the mechanical properties and also the moisture content of pultruded shapes. It is desired that the test procedure can be followed and performed without the use of expensive specialized equipment which would limit its use.

The principles of the proposed standard are as follows. The FT-cycling in this study consists, in accordance with the paper [18], of a 30 to 60 day initial moisture absorption period followed by 100 freeze-thaw cycles. The samples should be completely immersed and separated in water maintained at 23±2°C (73°F) for the initial moisture exposure. The freezing and thawing temperatures are -20±2°C (-4°F) and 23±2°C (73°F), respectively. The recommended FT-cycling environments are dry freezing and wet thawing in water. The paper proposes that the cycle time should be set to allow the samples to freeze and thaw for at least 3 hours each [18]. It has also been proposed to call for an interior temperature of -20±2°C (-4°F) for at least ½ hour, but this will require embedded thermocouples in test samples for temperature validation.

### 1.2 Specific Study Research

Table 1 is a summary of the experimental parameters of previously conducted FT-cycling studies. Dutta and Hui [12] investigated thick composites' response to low temperature and FT-cycling. A commercially available pultruded polyester/E-glass and an Army grade vacuum bag manufactured polyester/S2-glass were tested for change in shear- and Young's modulus. The FT-

cycling temperature range for this study, -60°C to 50°C (-76°F to 122°F), is one of the most extreme out of the studies investigated. 250 FT-cycles were planned for this study, but the FT-cycling of the commercial FRP was stopped after 100 cycles due to extensive surface cracking. Dutta and Hui [12] concluded that the high degradation rate of the commercial FRP was disappointing and limits its use in varying cold climates. It was also stated that their FT-cycling data is inadequate to develop predicative methodology of this degradation. Even though these test parameters provide an accelerated test, they are too extreme for implementing in a test standard. The temperature range would substantially limit the ease of testing if implemented in a standard since freezers with the capability of -60°C/-76°F settings are not readily available, and it is also more convenient to thaw at room temperature around 23°C/73°F compared to elevated temperatures to further limit necessity of temperature controlling equipment.

**Table 1. Comparison of previously conducted freeze-thaw cycling studies [11-17].**

| Study | Conditioning | Max Cycles | Cycle Times (min) | | Temperatures (°C/°F) | |
|---|---|---|---|---|---|---|
| | | | Freeze | Thaw | Freeze | Thaw |
| Dutta, Hui [12] | No conditioning | 100/250 | 120 | 120 | -60/-76 | 50/122 |
| Haramis, et al. [14] | Saturation (ASTM C666) | 500 | 90 - 225 | 30 - 75 | -17.8/0 | 4.4/40 |
| Rivera, Karbhari [15] | No conditioning | 100 | 600 [1] | 600 [1] | -10/14 | 22.5/72.5 |
| Karbhari, Rivera, Zhang [16] | No conditioning | 100 | 480 | 480 | -10/14 | 22.5/72.5 |
| Wu et al. [17] | Saturation (ASTM C666) | 625 | 90 - 225 | 30 - 75 | -17.8/0 | 4.4/40 |
| Vaughan, Lackey, Wang [13] | No conditioning | 30 [A] | 90 | 90 | -10/14 | 38/100 |
| | | 112 [B] | 90 | 90 | -10/14 | 38/100 |
| | | 56 [C] | 180 | 180 | -12/10 | 65.5/150 |
| Strandlund | 30 and 60 day moisture at 23°C | 100 | 180 [2] | 180 | -20/-4 | 23/73 |
| 1. Cycle times include 4 hour ramp, 2 hr heating and 2 hr cooling. | | | | | | |
| 2. Manual samples were kept frozen over night and for up to 2.5 days | | | | | | |

Haramis et al. [14] conducted a study to evaluate the FT-cycling response of FRP for civil infrastructure applications. The FT-cycling parameters are listed in Table 1. Three pultruded composites with similar fiber structure, but different resins (toughened vinylester, untoughened vinylester, and epoxy) were employed. Haramis et al. [14] concluded that the strain-to-failure and strength of all three materials decreased roughly 50%, the stiffness remained unchanged, and the moisture content at saturation for the three materials varied from 0.70% to 0.84%. The FT-cycling in this study was conducted through the use of ASTM C666 which as previously discussed has been utilized for infrastructure applications. As previously discussed there are drawbacks to using this standard for FRP.

Karbhari and Rivera were involved in two studies [15, 16] intended to evaluate the use of FRP for civil infrastructure and off-shore applications. A carbon/vinylester was used for the testing process in [15] and an E-glass/vinylester for [16]. Both were manufactured through wet lay-up and cured in ambient conditions. After the FT-cycling as listed in Table 1 the samples were tested for tensile strength, modulus, split D-ring strength, and transverse compression strength. The most significant conclusion of these studies is that future investigations both in controlled environments and in the field are necessary for a better understanding of the degradation process and to develop life-cycle models. As can be seen in Table 1 [15] and [16] utilized identical freeze and thaw temperatures, but different cycle times. The temperature range is suitable for a standard and similar to the ones mentioned in the previously discussed in the evaluation study of the D20.18.02 draft [18]. The cycle length, however, could be shortened to save time since it is the initial expansion of the absorbed water turning into ice that will degrade the FRP.

Wu et al. [17] performed a study on the durability of FRP bridge deck materials exposed to FT-cycling and low temperature conditions. A vinylester/E-glass skin of a honeycomb sandwich was used for testing. At the completion of conditioning, the samples were subjected to flexural strength, storage modulus, and loss factor testing. The FT-cycling was governed by ASTM C666. Wu et al. [17] concluded that 250 cycles of FT had no significant effect on the material properties tested but that a wider temperature variation could enhance the degradation. This was previously discussed concerning ASTM C666. It was also noted that the degradation seem to be more dependent on number of cycles rather than exposure time.

Vaughan, Lackey, and Wang [13] performed a study with three different FT-cycling conditions listed in Table 1. The goal of the study was to investigate techniques for laboratory testing of FRP and the results of various FT-cycling conditions. A roving and mat pultruded polyester/E-glass was tested for all conditions. Three-point flexural tests and short-beam shear tests were used to evaluate the FRP degradation. The results of this testing show that conditioning B was more detrimental than C, as detailed in Task 1, which is an indication that the number of cycles is more important than increased temperature ranges. This is desirable for testing to perform more cycles in a specific time frame and also for ease of testing.

The study presented in this thesis is intended as a contribution to the development of an ASTM standard designated for the testing of FRP subjected to FT-cycling. Numerous studies have been undertaken related to FT-cycling of FRP dating back more than 15 years, but there is still a high level of uncertainty and call for further testing. It is critical to be able to compare and validate the increasing number of FRP constituent material combinations and manufacturing processes of products intended for this form of exposure. The time and cost savings for material and process validations is also of concern. The intention is that the future standard will include

relatively short freeze and thaw cycles, the choice between manual- and automatic testing procedures, and that freeze and thaw temperatures can be sustained in a generic freezer and at room temperature, respectively. This will enhance the effectiveness and ease of use which will accelerate the standards adoption and recognition.

# 2. EXPERIMENTAL PROCEDURE

The material used for the study along with the various test parameters will be discussed in this chapter. The sections are listed in the order that they were undertaken to complete this study. Most of the experimental parameters are directly imported from the evaluation study of the draft created by the D20.18.02 committee discussed in the previous section [18].

## 2.1 Material Description

A pultruded mat and roving E-glass reinforced polyester with ATH filler was used for this study. Pultrusion is a cost competitive and easily repeatable manufacturing process that is limited to producing parts with constant cross sections. Polyester is a low cost resin and the most utilized matrix material. Polyesters can come in the form of thermosets and thermoplastics, but thermosets are usually preferred due to lower processing temperatures and lower viscosity leading to enhanced processability [19]. However, thermoplastics are gaining more attention as recyclable materials are sought by producers and end-users and due to raised awareness of volatile organic compounds such as styrene frequently present in thermosets to improve their viscosity. Polyesters are low in cost and have good corrosion resistance and good mechanical properties, but suffer from low operating temperatures (60-150°C) compared to most other thermosets [19].

E-glass is one of the cheapest and also the most produced and utilized fiber reinforcement for FRP [19]. E-glass like polyester is typically used for commercial consumer products mainly

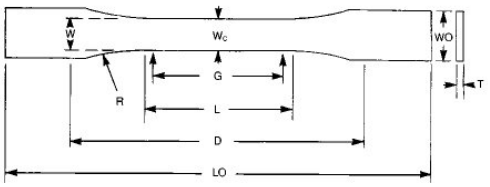
due to its low price and competitive material properties. The E stands for electrical and refers to its good electrical insulating properties. E-glass also has good mechanical properties, and when combined with a matrix system, high specific stiffness and strength can be obtained compared to metals. However, E-glass is on the heavier side of the fiber spectrum which leads to lower specific stiffness than carbon, Kevlar, and other high end market fibers [19]. Fillers are usually added to decrease the overall cost, increase the dimensional stability, and to reduce the shrinkage during molding [19]. It is common to add approximately 40% filler material by weight to commercial pultruded products.

The solid content of the polyester/E-glass used in this study was established through ASTM D2584 – 08, "Standard test method for ignition loss of cured reinforced resins." The test is performed by first machining and weighting a sample small enough to fit into a designated crucible. The sample is then ignited and allowed to burn until only ash and carbon is present. Next the residue is reduced to ash by heating in a muffle furnace at 565°C (1050°F) and lastly cooled and weighted. If glass fiber is the only reinforcement and the small amount of volatiles that may be present is ignored, the ignition loss can be considered to be the resin content of the sample and the remaining weight to be the fiber content. However, ATH filler material was a major component in the resin mixture which results in a mixture of fiber and filler left in the crucible. Therefore the result in this case is referred to as the solid content and not fiber content. Two samples were tested and resulted in an average solid content of 55.5% by weight.

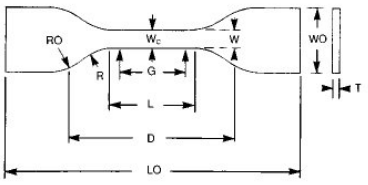
### 2.2 Sample Preparation

The pultruded polyester/E-glass that was used came in the form of wide ¼ inch thick sheets. Dog-bone samples were cut out of the sheet using CNC machining. The gage section

dimensions of the samples were selected based on ASTM D638 – 08, “Standard test method for tensile properties of plastics.” The dog-bone samples were machined to a length of 11 inches to provide sufficient grip length for tensile test gripping to prevent crushing of the samples. Figure 1 extracted from ASTM D638 – 08 is a detailed description of the dimensions of the samples which were programmed into a CNC mill. The dimensions listed for Type 1 was used in this study. The samples were sandpapered by hand to smooth out the edges after the rough CNC machining. The sandpaper residue was washed off and the samples were numbered to keep track of the individual samples throughout the remainder of the study.




TYPES I, II, III & V




TYPE IV

Specimen Dimensions for Thickness, *T*, mm [in.][A]

| Dimensions (see drawings) | 7 [0.28] or under | | Over 7 to 14 [0.28 to 0.55], incl | 4 [0.16] or under | | Tolerances |
|---|---|---|---|---|---|---|
| | Type I | Type II | Type III | Type IV[B] | Type V[C,D] | |
| *W*—Width of narrow section[E,F] | 13 [0.50] | 6 [0.25] | 19 [0.75] | 6 [0.25] | 3.18 [0.125] | ±0.5 [±0.02][B,C] |
| *L*—Length of narrow section | 57 [2.25] | 57 [2.25] | 57 [2.25] | 33 [1.30] | 9.53 [0.375] | ±0.5 [±0.02][C] |
| *WO*—Width overall, min[G] | 19 [0.75] | 19 [0.75] | 29 [1.13] | 19 [0.75] | ... | + 6.4 [ + 0.25] |
| *WO*—Width overall, min[G] | ... | ... | ... | ... | 9.53 [0.375] | + 3.18 [ + 0.125] |
| *LO*—Length overall, min[H] | 165 [6.5] | 183 [7.2] | 246 [9.7] | 115 [4.5] | 63.5 [2.5] | no max [no max] |
| *G*—Gage length[I] | 50 [2.00] | 50 [2.00] | 50 [2.00] | ... | 7.62 [0.300] | ±0.25 [±0.010][C] |
| *G*—Gage length[I] | ... | ... | ... | 25 [1.00] | ... | ±0.13 [±0.005] |
| *D*—Distance between grips | 115 [4.5] | 135 [5.3] | 115 [4.5] | 65 [2.5][J] | 25.4 [1.0] | ±5 [±0.2] |
| *R*—Radius of fillet | 76 [3.00] | 76 [3.00] | 76 [3.00] | 14 [0.56] | 12.7 [0.5] | ±1 [±0.04][C] |
| *RO*—Outer radius (Type IV) | ... | ... | ... | 25 [1.00] | ... | ±1 [±0.04] |

**Figure 1. Dog-bone sample dimensions (Type 1) from ASTM D638-08.**

### 2.3 Moisture Exposure Conditions

Two different exposure periods were conducted to compare their respective weight increase effect on the samples and evaluate if a longer period is needed for saturation purposes. It was also later investigated if this would influence the detrimental effect of the FT-cycling through mechanical testing. Thirty days and 60 days of moisture exposure were used based on the D20.18.02 draft evaluation paper [18] where it was discussed whether a 60 day moisture exposure was necessary compared to 30 day moisture exposure to ensure relative saturation. Sixty samples were exposed to a 30 day moisture exposure (from now on referred to as 30W-samples) in a 23±2°C (73°F) water bath, and 20 samples were exposed to a 60 day moisture exposure (from now on referred to as 60W-samples). The 60W-samples were submerged 30 days before the 30W-samples so that manual FT-cycling could be initiated simultaneously.

Additional samples were included in the 30 day moisture exposure for progressive mechanical tensile testing throughout the manual FT-cycling and also for automated FT-cycling through the use of a temperature chamber. However, due to issues with the control panel and fan system of the temperature chambers available, this testing was delayed. The samples designated for the temperature chamber were instead exposed to the manual FT-cycling in case the manual FT-cycling would be extended. An extra 30 day moisture exposure with a set of 15 samples was prepared to allow for the temperature chamber to be repaired (from now on referred to as 30TC-samples). The samples were kept separated and stacked on their short end through the moisture exposure to allow for equivalent and complete moisture exposure of each sample. Picture 1 [Appendix A] illustrated the samples stacked on the rack in the temperature controllable water bath utilized.

## 2.4 Weighing Procedure

All samples (30W, 60W, and 30TC) were weighed before any exposure was initiated, at the completion of the initial moisture exposure, and also before mechanical tensile testing. As previously discussed moisture is needed to get the full detrimental effect of FT-cycling, but dry freezing which was used for the manual testing will draw moisture out of the samples. Thus the samples should be weighed when tested to make sure a sufficient level of moisture has been sustained within the samples through the FT-cycling process. Different weighing procedures were conducted during the initial moisture period for the 30W-samples, 60W-samples, and 30TC-samples. For the 30W-samples a selected set were weighed after 9 days, and 17 days to evaluate the rate of the weight increase and relative saturation of the samples. The only additional weighing of the 60W-samples was conducted after 30 days of moisture exposure. The 30TC-samples were not weighed throughout the moisture exposure since sufficient data of the weight increase progress was obtained from the 30W-samples.

## 2.5 Manual Freeze-Thaw Cycling

The manual FT-cycling was performed by manually moving the samples between a cold chamber and a distilled water bath. For the 30W-samples it was conducted through the use of a temperature controlled freezer held at -20±2°C (-4°F) and a temperature controlled distilled water bath held at 23±2°C (73°F), both according to the evaluation study of the D20.18.02 draft [18]. The samples were kept in the freezer over night or during any extended period in which the samples could not be manually transferred [18]. The 60W-samples were exposed to the same freezing environment, but kept in a room temperature aluminum tin without temperature control due to lack of an additional temperature controllable water bath. The samples were kept in

separated water baths in case post analysis of the water to approximate the leaching of resin and filler material would be performed. A rack to hold the 30W-samples was constructed during the early stage of the manual FT-cycling. Without the rack the samples had to be stacked by hand every time they were moved from the freezer to the water bath and vise versa. The rack can be seen in Picture 1 [Appendix A]. A rack was not created for the 60W-samples due to the low number of samples. The samples were kept separated and stacked upright through freezing and thawing analogous to the moisture exposure.

### 2.6 Automated Freeze-Thaw Cycling

An initiative was taken in an attempt to automate the testing through the use of a Thermotron (programmable temperature chamber). This alternate automated FT-cycling process differs from the manual method in that the samples will be subjected to wet freezing. The advantages of an automated process include reduced labor and time savings. One of the obstacles is that a temperature chamber is a high capital investment not readily available to most FRP producers. The consistency issue of wet freezing of the automatic FT-cycling compared to dry for the manual FT-cycling needs to be addressed.

This issue could be solved by implementing wet freezing for the manual process. However, this would increase the labor requirements of moving a water bath with samples in and out of the freezer and it will also lengthen the cycle time necessary to reach complete freezing and thawing of the samples due to the added water mass. Identical exposure times and temperatures were used for the automated testing. However, constant water immersion and ramping of the temperature may prove more or less detrimental. In theory constant water immersion will lead to a higher water absorption which will be more detrimental, but ramping

the temperature in water compared to the rapid dry-freezing through an instant exposure to -20±2°C (-4°F) ought to be less detrimental.

The automatic FT-cycling was performed through the use of a Thermotron (temperature chamber). The samples were placed in an aluminum pan in two layers and stacked on their width, to minimize the water mass necessary to completely cover the samples. The dimensions of the aluminum pan was 11 ¾ in by 9 in. Spacers in the form of ¼ inch diameter and 8 inch long aluminum rods were positioned on the bottom of the pan and in between the layers to allow equal and complete moisture and freeze exposure of the individual samples. The automated FT-cycling differs from the manual FT-cycling in that the samples are exposed to wet freezing instead of dry freezing. To freeze the samples the entire water bath has to be frozen, so the total water mass should be minimized to optimize the required cycle time. The total cycle time was set to 6 hours to be comparable to the manual FT-cycling. The automated FT-cycling temperatures and time intervals are shown in Table 2. Note that step 1 is only used to establish a startup temperature of 23°C (73°F) before the first cycle is initiated. A loop-feature was included in Step 5 which brings the program back to Step 2 to start the next cycle. The program was set to 50 cycles to allow for mechanical tensile testing after 50 and 100-cycles.

**Table 2. Temperature chamber cycle parameters.**

| Step | Initial Temperature (°C/°F) | Final Temperature (°C/°F) | Time Interval (hrs:min) |
|---|---|---|---|
| 1 | 23/73 | 23/73 | 0:15 |
| 2 | 23/73 | -20/-4 | 0:15 |
| 3 | -20/-4 | -20/-4 | 2:45 |
| 4 | -20/-4 | 23/73 | 0:15 |
| 5 | 23/73 | 23/73 | 2:45 |
| Cycle completed. Loop back to Step 2 to initiate the next cycle | | | |

## 2.7 Mechanical Tensile Testing

Tensile testing was performed throughout the moisture and FT-cycling exposure to monitor the degradation of the samples' ultimate tensile strength (UTS). The mechanical tensile testing was performed according to ASTM D638 – 08, "Standard test method for tensile properties of plastics." The shape and dimensions of the samples, the speed, and the environment are important testing parameters that need to be controlled to obtain comparable data. The dimensions of the samples were according to Type 1 in Figure 1 with an extended grip length as previously discussed. A MTS – 810 Material Test System hydraulic machine was used. The tensile testing was conducted with a set point (maximum travel) of 0.200 inches and a constant ramp rate of 0.001 inches per second.

The UTS was determined by measuring the width and thickness of the gage section of each sample through the use of a digital caliper with an accuracy of ±0.0005 in. This data was used to determine the cross sectional area of each sample. The maximum load before failure was recorded by the software linked to the MTS – 810 Material Test System hydraulic machine. The UTS was calculated by dividing the maximum load by the cross sectional area.

An original value of the UTS of the testing material before conditioning is needed for comparison purposes. This original value is commonly referred to as a retention value. An average retention value of the UTS was obtained through mechanical tensile testing of 10 dry samples. The remainder of the mechanical tensile testing for this study is summarized in Table 3 below, listing the period and number of samples tested for each of the three conditioning procedures.

**Table 3. Mechanical tensile testing schedule.**

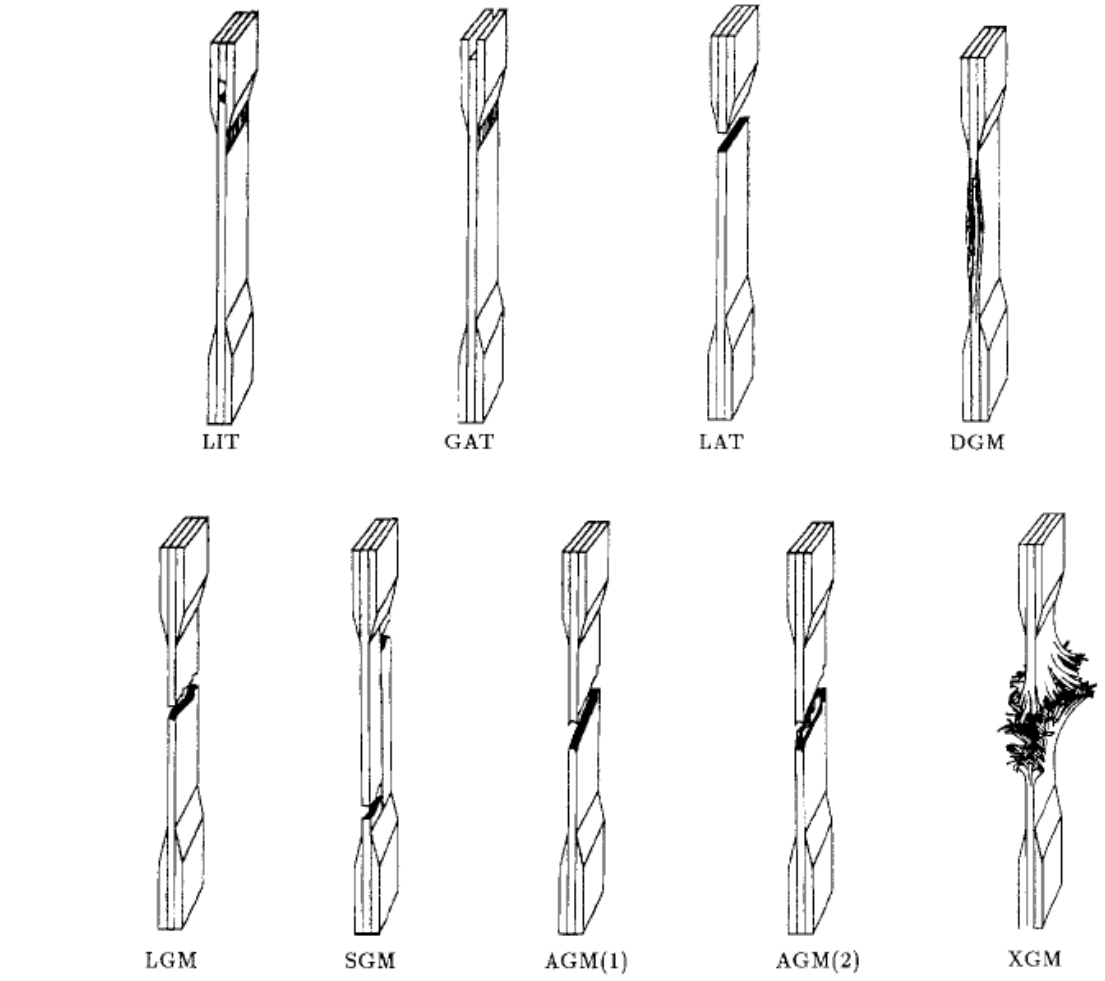
| Test Period | 30W (# samples) | 60W (# samples) | 30TC (# samples) |
|---|---|---|---|
| 30 Day Moisture | 5 | - | - |
| 60 Day Moisture | - | 5 | - |
| 25 F-T Cycles | 5 | - | - |
| 50 F-T Cycles | 5 | 5 | 5 |
| 75 F-T Cycles | 5 | - | - |
| 100 F-T Cycles | 10 | 10 | 10 |

Extensive tensile testing was performed on the 30W-samples to obtain the progressive effect of FT-cycling. This was done by performing mechanical testing after the initial moisture exposure, 25-cycles, 50-cycles, 75-cycles, and 100-cycles of freeze-thawing. The 60W-samples were tested after initial moisture exposure, 50-cycles, and 100-cycles of freeze-thawing for comparison purposes. The 30TC-samples were tested at 50-cycles and 100-cycles of freeze-thawing for validation purposes. The 30TC samples were exposed to the same initial moisture conditioning as the 30W-samples and were therefore not tested at this instance. Sufficient samples were prepared so that 10 samples could be tested for all exposure processes at the completion of 100 FT-cycles according to ASTM D7290.

The failure mode was determined through the use of ASTM D3039 - 08, “Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.” The failure mode is characterized through three letters as shown in Figure 2. The first character describes the failure type, the second character indicates the failure area, and the third character designates the failure location within the failure area. Delamination and lateral failures are most common for unidirectional FRP. Delamination failures are more common for samples with poor matrix and fiber bonding usually caused by incomplete wet out of the fibers during processing. Delamination is also more commonly seen after moisture exposure due to separation of the

matrix and the fiber. A delamination failure can be seen in Picture 2 [Appendix A]. Lateral failures are brittle failures and are more common for samples with proper wet-out which enables the matrix to transfer more of the load to the fibers. A lateral failure can be seen in Picture 3 [Appendix A].

Failures outside of the gage area are not desired as discussed in ASTM D3039. If a significant fraction of the failures of a population of samples are in the tab or grip area one should consider factors such as tab properties if tabs have been used (tabs were not used in this study), and also grip type, pressure, and alignment. As previously stated the third character defines the failure location within the failure area. Failures within the gage area usually occur at random locations. A high fraction of failures within a specific gage location other than the middle does not necessarily transpire from incorrect test parameters, but the previously listed grip and tab characteristics should be analyzed if this is the case as stated in ASTM D3039.




First Character

| Failure Type | Code |
|---|---|
| Angled | A |
| edge Delamination | D |
| Grip/tab | G |
| Lateral | L |
| Multi-mode | M(xyz) |
| long. Splitting | S |
| eXplosive | X |
| Other | O |

Second Character

| Failure Area | Code |
|---|---|
| Inside grip/tab | I |
| At grip/tab | A |
| <1W from grip/tab | W |
| Gage | G |
| Multiple areas | M |
| Various | V |
| Unknown | U |

Third Character

| Failure Location | Code |
|---|---|
| Bottom | B |
| Top | T |
| Left | L |
| Right | R |
| Middle | M |
| Various | V |
| Unknown | U |

**Figure 2. Failure mode clarification obtained from ASTM D3039 - 08.**

## 2.8 Leaching Analysis

It is quite difficult to determine the amount of leaching of FRP as stated in the evaluation study of the D20.18.02 draft [18] that residue should be noted, but not quantified. ASTM D5284,

“Standard Test Method for Sequential Batch Extraction of Waste with Acidic Extraction of Fluid,” can be used to estimate the amount of a leached constituent. The water used for the moisture exposure is intended to be analyzed for leaching constituents, but this test was not completed in time to be included.

# 3. DISCUSSION OF RESULTS

The results obtained from the water absorption and mechanical tensile testing will be discussed in this chapter. The tensile test results will be statistically analyzed to find the sample mean, standard deviation, and also to check for outliers. The results from the three different sample batches will also be compared.

## 3.1 Weight Increase Results

The initial 30 day moisture conditioning in a 23±2°C (73°F) water bath is intended to generate relatively saturated samples before the freeze-thaw cycling is initiated. The specifics of the weighing procedures of the different sample populations (30W, 60W, and 30TC) were discussed in Section 2.4. All weight increase percentages were obtained by comparing the initial 0 day weight to the weight at the respective instance through Equation 1.

$$Weight - Increase(\%) = \frac{\left(Weight_{Final} - Weight_{Initial}\right)}{Weight_{Initial}} \qquad (1)$$

The average weight increase of nine randomly selected 30W-samples through the initial 30 day moisture exposure is shown in Figure 3. From Figure 3 it can be seen that the weight increase percentage reached approximately 0.50% after 30 days of moisture exposure and increased to about 70% upon completion of the scheduled 100 FT-cycles. However, the wavy curve causes concern, especially during the initial 30 day moisture exposure. FRP subjected to

constant moisture usually display a steady initial weight increase followed by a flattened section once a relative saturation is reached. FT-cycling should be discussed separately due to the mixed exposure of wet thawing and dry freezing. Lowered average weight increase percentage during the initial FT-cycling is acceptable due to the exposure to dry freezing. However, FRP weight increase response to FT-cycling will depend on several factors such as the level of saturation achieved during initial moisture and the absorption capabilities of the resin and fiber material.

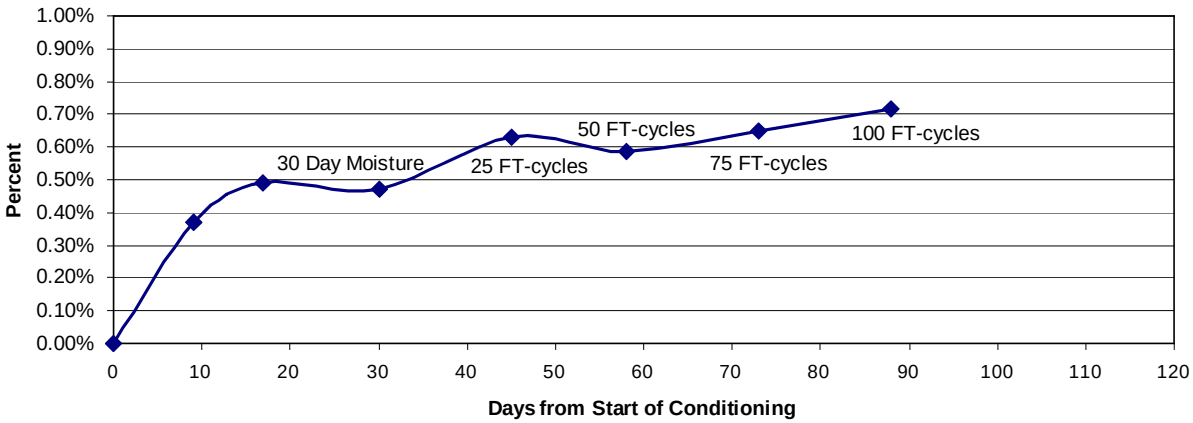



**Figure 3. Weight increase percentage of the 30W-samples through conditioning.**

From Figure 3 it can be observed that the first drop in weight increase occurred during the initial moisture exposure from the 17 day weighting to the 30 day weighting. This was most likely caused by different weighing procedures. Two different persons performed the weighing and it was found that the latter performing the 30 day moisture weighing let the samples dry out more before weighing which caused lower weights. Residue was observed in the water bath, so leaching may also be a factor in the lowered average weight increase percentage. The second minor drop in the average weight increase percentage from 25 FT-cycles to 50 FT-cycles was most likely caused by data scatter since only 5 samples were measured at each instance. It should

also be remembered that the few samples weighted before mechanical testing at these instances were most likely not included in the selected sample group producing the initial 30 day weight increase percentage.

Figure 4 displays the weight increase percentage of the 60W-samples throughout the moisture and FT-cycling conditioning. All of the 60W-samples were weighed initially and at the 30 and 60 day weighing. The 30 day weight increase percentage for the 60W-samples in Figure 4 agrees with the same period for the 30W-samples in Figure 3. The curve in Figure 4 flattens out after 30 days of moisture exposure, but there is still significant weight increase all the way through FT-cycling. The evaluation study of the D20.18.02 draft [18] proposes the use of ASTM D570, "Standard Test Method for Water Absorption of Plastics," for the weighing procedure of the samples during moisture exposure. It should also be considered to use the procedure to obtain a substantial saturation as described in ASTM D570.

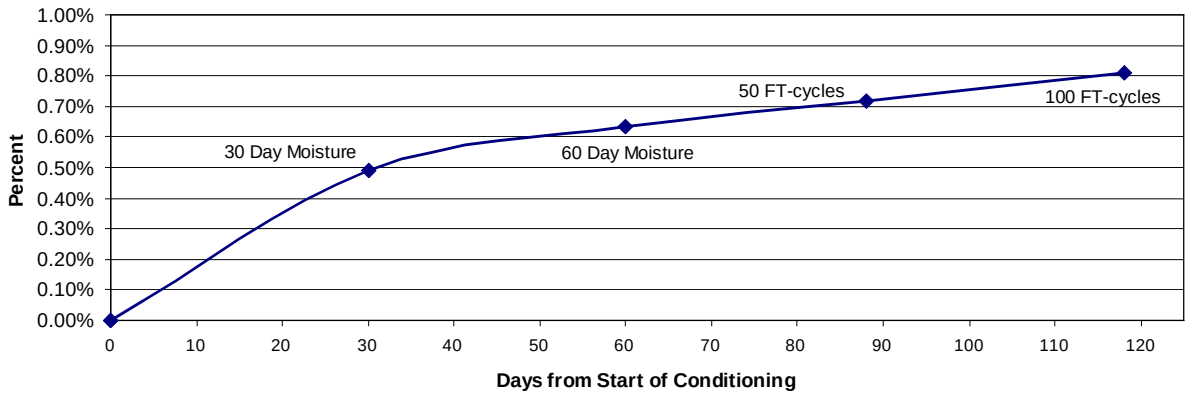



**Figure 4. Weight increase percentage of the 60W-samples through conditioning.**

The weight increase percentage of the 30TC samples are shown in Figure 5. The temperature chamber (TC) shut down several times during the FT-cycling due to inefficient ventilation; thus, it is unclear if all of the initial 50 cycles were completed. The temperature

chamber was not monitored daily and the fuse blew due to an overload/overheating. When this was discovered at the end of the 50 FT-cycles the current temperature inside the temperature chamber was close to 90°F which may have further damaged the samples. Five samples were still tested at this point and the rest of the samples were left in distilled water at room temperature until the fuse was replaced. The time between the completion of the 50 FT-cycles and the start of the 51st FT-cycle displays this down time. Several attempts to continue with the FT-cycling were made during this time interval, but the temperature chamber kept overloading and blowing the fuse.

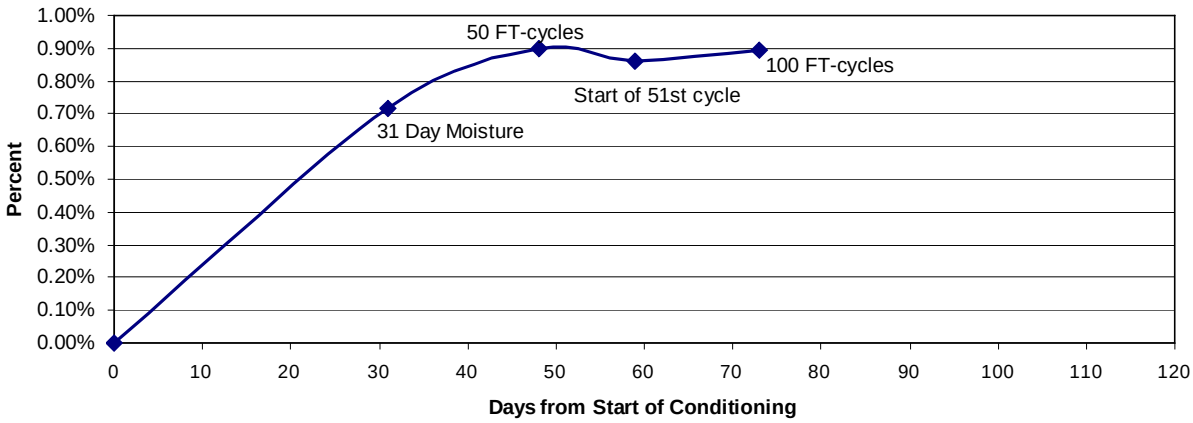



**Figure 5. Weight increase percentage of the 30TC-samples through conditioning.**

A recently repaired second temperature chamber was also tested, but it failed to reach the low freezing temperature (-20°C/-4°F). The original temperature chamber was finally repaired and the FT-cycling was reinitiated. However, the temperature chamber failed again after approximately 15 FT-cycles which was determined this time by keeping a log of the temperature. After a second major repair the remaining FT-cycles were completed to conclude the automatic FT-cycling. The automatic FT-cycling was developed as a time efficient and less labor intensive

alternative to the manual FT-cycling. Unfortunately the problems with the temperature chamber leading to unknown exposure conditions somewhat ruined the use of these samples as a source of comparison. However, the test data obtained from the 30TC-samples will still be included, but one should bear in mind that this data comes with uncertainty.

### 3.2 Mechanical Tensile Testing

As discussed in Section 2.7 a MTS – 810 Material Test System hydraulic machine was used to perform mechanical tensile testing of the samples, and ASTM D638-08 guidelines were followed. The sample dimensions can be reviewed in Figure 1 (Section 2.2) and the failure mode designation system can be seen in Figure 2 (Section 2.7). Also refer to Table 3 (Section 2.7) for the mechanical tensile testing schedules of the three different FT-cycling studies. The ultimate tensile strength (UTS) data will be discussed thoroughly as it is the basis for evaluating the degradation. The procedure used to determine the UTS was explained in Section 2.7.

For each instance the sample mean and the sample standard deviation (SSD) of the UTS will be discussed. Each sample pool will also be evaluated for outliers through the use of ASTM D7290 – 06, “Standard Practice for Evaluating Material Property Characteristic Values for Polymer Composites for Civil Engineering Structural Applications.” A possible outlier is determined by first calculating the MNR value which is done through the use of Equation 2. The MNR value is defined as the maximum absolute deviation from the sample mean divided by the sample standard deviation. The critical MNR value (CV) is calculated through the use of Equation 3. It is based on a 5% significance level and depends on the sample size. A value is classified as an outlier if its MNR value exceeds the CV of the sample size. Note that this is only

done for the value with the maximum deviation. Sub sequential evaluations can be performed to determine if there are additional outliers present if an outlier is found.

$$MNR = \max\left(\frac{|x_i - \bar{x}|}{s_{n-i}}\right) \quad (2)$$

where; $x_i$ = number with largest deviation,
$\bar{x}$ = sample mean/average,
$s_{n-i}$ = sample standard deviation

$$CV = \left(2 - \frac{8}{5\sqrt{n}}\right)^2 \quad (3)$$

where; n = sample size

The failure modes of the samples were determined in accordance with ASTM D3039 – 08 and will also be discussed. A clarification of the tensile failure modes can be found in Section 2.7, Figure 2. The moisture absorption of each individual sample will be included to evaluate if a relationship to the UTS and/or the failure mode can be established. Higher moisture content should theoretically generate lower UTS due to an increased void content by the presence of additional fluid in the sample. Higher moisture content should also produce a higher possibility of failure through delamination since extra absorbed moisture will enhance the separation of the fiber and matrix.

### 3.2.1 Retention Samples

Retention samples are as-received samples. These samples were kept in room temperature and mechanically tested to determine the materials UTS value before moisture and

FT conditioning was initiated. The test results including the UTS, outlier evaluation, and failure modes are shown in Table 4. The failure of sample 5 was initiated inside the grip/tab due to preexisting voids visible to the naked eye. The failed sample can be seen in Picture 4 and Picture 5 [Appendix A]. Because of the failure type and sample 5's low UTS it was selected to be excluded from the data set and thus the calculations of the sample mean UTS, SSD, and for being considered an outlier. This follows ASTM D3039 guidelines which states that "Values for ultimate properties shall not be calculated for any specimen that breaks at some obvious flaw." The SSD of the remaining nine samples was determined to be 2.85 ksi. It is not uncommon for commercial FRP to have a SSD of this magnitude due to its inhomogeneous structure.

**Table 4. Retention tensile test results.**

| Retention Values | | | |
|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 2.15) | Failure Mode |
| 1 | 59.56 | | DGM |
| 2 | 52.78 | 1.64 | LGT |
| 3 | 55.60 | | LGB |
| 4 | 60.49 | | LGB |
| (5) | 51.87 | | DIT |
| 6 | 58.59 | | LGB |
| 7 | 55.40 | | LGB |
| 8 | 55.12 | | LGM |
| 9 | 61.24 | | DGM |
| 10 | 58.39 | | LGT |
| Mean: | 57.46 | | |
| SSD | 2.85 | | |

The critical MNR value (CV) was determined through the use of Equation 3 discussed in the previous section. The CV for a sample size of 9 is 2.15 as shown in Table 4. Sample number 2 was determined to have the maximum absolute deviation from the sample mean and was therefore considered as a possible outlier. However, the MNR value of sample 2 was determined

to be 1.64 which does not exceed the CV; thus, it is not considered an outlier. The majority of the samples failed laterally which is expected for dry FRP due to their brittle nature. The few delamination failures may have been caused by concentrated void content areas which were observed at the surface of several samples along the center of their thickness providing a preferential path for crack initiation and propagation.

### 3.2.2 30W-Samples

The data from the 30W-samples tested after the initial 30 day moisture conditioning is shown in Table 5. The mean UTS of the tested 30W-samples after moisture exposure listed in Table 5 was found to be approximately 9.5 ksi, or 16.5%, lower than the retention mean UTS. The SSD of the UTS results from these samples was calculated to 4.12 ksi which is higher than normal. It is unclear what the major cause for this scatter is, but it is possible that random void rich areas were the cause. Voids were visible to the naked eye on the machined thickness of some of the samples even on the unexposed retention samples.

**Table 5. Test data of 30W-samples after 30 days of moisture exposure.**

| 30W-samples Moisture Only | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 1.65) | Failure Mode | Weight Increase |
| 4 | 53.81 | | DGM | 0.51% |
| 9 | 48.93 | | DGM | 0.48% |
| 22 | 47.49 | | LAT | 0.45% |
| 27 | 47.47 | | LGB | 0.49% |
| 40 | 42.28 | 1.39 | DGM | 0.49% |
| Mean: | 48.00 | | | 0.48% |
| SSD | 4.12 | | | |

The properties of FRP can fluctuate greatly depending on the process control, and the voids are probably caused by improper process parameters. The amount of fiber and resin used

for a certain pultrusion die needs to be accurately calculated to completely fill the die in order to obtain constant performance. Concentrated void-content is not desired since it will greatly affect the tensile strength by providing localized weak spots. Resin rich areas can also be created when there is not enough wet-out fiber present to fill the die. Since the fiber provides the majority of the strength and stiffness of the FRP, these areas will also become weak spots. Voids on the surface will also provide additional surface area and easier access for the fluid to enter the samples. A large pultruded sheet was the used to machine samples out of for this study. It is more difficult to produce high performance pultruded products as wide as the sheet used in this study. This may be a factor for the varying performance of the samples.

Sample 40 was determined to have the maximum absolute deviation from the sample mean and was thus evaluated as an outlier. The CV for a sample size of 5 is 1.65 and the MNR value of sample 40 was determined to be 1.39, thus not qualifying it as an outlier. The samples were expected to fail by delamination which is common after moisture exposure. The reason is that the water enters the samples and initiates separation of the fibers and the matrix. Surprisingly the samples failed both laterally and by delamination. However, sample 22 experienced a lateral failure in the tab section which must have been caused by a weak spot.

It should also be noted that another reason for lateral failures is that it was difficult to determine the starting point of failure due to its brittle nature. The lateral failures did also generally turn into a delamination failure and vise versa, so post failure analysis is not possible to determine the starting point of failure. The weight increase percentage of the individual samples was very similar, so it is difficult to establish a connection between their weight increase and their UTS or failure mode for this test instance.

The data from the 30W-samples tested after 25 manual FT-cycles is shown in Table 6. The mean UTS is approximately 7.9 ksi, or 13.7%, lower than the retention mean UTS. It may appear out of the ordinary that the mean UTS of the FRP increased after exposure to FT-cycling since it is believed to have a detrimental effect. However, 25 FT-cycles may not be enough to lower the mean UTS considerably. It has also been considered that initial dry freezing may strengthen the FRP by drying out the samples which may let them regain some of their strength. However, considering the sample mean UTS and SSD from the initial moisture exposure and after 25 FT-cycles, these data samples are very similar from a statistical standpoint.

**Table 6. Test data of 30W-samples after 25 FT-cycles.**

| 30W-samples; 25 FT-cycles | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 1.65) | Failure Mode | Weight Increase |
| 38 | 48.22 | | LGM | 0.53% |
| 54 | 50.07 | | DGB | 0.61% |
| 52 | 51.01 | | LGB | 0.70% |
| 31 | 48.13 | 1.09 | LGM | 0.67% |
| 15 | 50.45 | | DGM | 0.63% |
| Mean: | 49.58 | | | 0.63% |
| SSD | 1.32 | | | |

The SSD of the UTS of the samples listed in Table 6 is 1.32 ksi which is comparatively low for FRP. Sample 31 was determined to have the maximum absolute deviation from the sample mean and was therefore evaluated as an outlier. Its calculated MNR value of 1.09 is lower than the CV value of this sample size (1.65) and thus not considered an outlier. Again both lateral and delamination failures were observed. A higher degree of delamination failures was expected at this point, but as previously discussed the starting point of the failures was hard to determine. Sample 38 has relatively low weight increase percentage and failed laterally which would be expected. However, sample 52 which had the highest weight increase percentage out of

the samples tested also failed laterally. Sample 52 with the highest weight increase percentage did also have the highest UTS. Thus no relation can be established between the sample's individual weight increase and their UTS or failure mode.

The test data from the five tested 30W-samples after 50 FT-cycles is shown in Table 7. The mean UTS is approximately 7.7 ksi, or 13.4%, lower than the retention mean UTS. It appears that even 50 FT-cycles is not enough to substantially affect the tensile properties of the pultruded FRP utilized for this study. The UTS of the individual samples were fairly similar which generated a relatively low SSD of 1.64 ksi. Sample 57 was found to be the sample with the maximum absolute deviation from the sample mean and was therefore evaluated as an outlier. Its MNR value was calculated to be 1.47 which is lower than the CV of 1.65. Thus no outliers are present.

Four out of five samples were believed to fail laterally which was not expected, but the difficulty of determining the starting point of the failure as previously discussed should be considered. The weight increase percentage declined compared to the samples tested after 25 FT-cycles. See Section 3.1 for further discussion of this topic. No relation between the weight increase percentage of the individual samples and their UTS and failure mode was found.

**Table 7. Test data of 30W-samples after 50 FT-cycles.**

| 30W-samples; 50 FT-cycles | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 1.65) | Failure Mode | Weight Increase |
| 11 | 51.38 | | DGM | 0.55% |
| 13 | 51.05 | | LGT | 0.60% |
| 53 | 48.99 | | LGB | 0.57% |
| 55 | 50.00 | | LGM | 0.61% |
| 57 | 47.36 | 1.47 | LGM | 0.60% |
| Mean: | 49.76 | | | 0.58% |
| SSD | 1.64 | | | |

The test data from the 30W-samples tested after 75 FT-cycles is shown in Table 8. The mean UTS of the five samples tested shown in Table 8 is a reduction of approximately 9.3 ksi, or 16.2%, compared to the retention mean UTS. This is slightly lower than the mean UTS obtained from the previously tested conditioned sample batches, but it is still not low enough to statistically be proven different to the previously discussed results of conditioned 30W-samples. The SSD of the UTS data set was determined to be 1.16 ksi. Sample 34 was determined to have the maximum absolute deviation from the mean UTS. Even though sample 34's UTS is only 2 ksi higher than the mean UTS its MNR value of 1.71 classifies it as an outlier mainly due to the low SSD of the sample batch.

**Table 8. Test data of 30W-samples after 75 FT-cycles.**

| 30W-samples; 75 FT-cycles | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 1.65) | Failure Mode | Weight Increase |
| 1 | 47.18 | | LGT | 0.67% |
| 10 | 47.66 | | DGM | 0.54% |
| 26 | 47.64 | | DGM | 0.56% |
| 34 | 50.14 | 1.71 | LGB | 0.50% |
| 46 | 48.16 | | DGM | 0.97% |
| Mean: | 48.16 | | | 0.65% |
| SSD | 1.16 | | | |

It is stated in ASTM D7290 – 06 that "The possible outlier shall be investigated to determine whether there is an assignable cause for removing it from the data set. If no cause can be found, it shall be retained in the data set." The only noticeable reason for removing sample 34 is its low weight increase percentage which could theoretically lead to a higher maximum tensile strength. However, as can be seen in Table 8 there are several other samples with just slightly higher weight increase percentage compared to sample 34. As previously discussed commercial FRP are not known for providing the most consistent properties and a 2 ksi, or 4.1% deviation

from the mean UTS is not uncommon. Due to the lack of a reasonable cause it was decided to keep sample 34 in the data set.

The failure modes were split fairly even between delamination failures and lateral failures which was unexpected. However, since this has been the case for all conditioned sample batches it is possible that higher moisture content is needed before delamination will be the dominant type of failure. There is no evident connection between the weight increase of the individual samples and their UTS and failure mode other than sample 34 which has already been thoroughly discussed. However the weight increase percentage of sample 46 was found to be remarkably high. The weight data taken was reviewed, but the listed weight matched the one used for the moisture absorption calculations.

The data from the 30W-samples tested after the completion of 100 FT-cycles is shown in Table 9. The mean UTS listed in Table 9 is a 12.1 ksi, or a 21.0%, reduction compared to the retention mean UTS. There is a wide range of UTS values in this data set. Sample 19 with UTS of 51.14 ksi has only dropped 6.3 ksi, or 11.0% compared to the retention mean UTS. On the other side of the spectrum sample 8 and 12 both displayed UTS reductions of more than 25%. The lower values would be the ones to base the design of a structural component exposed to moisture and FT-cycling on since the structure will not be stronger than its weakest link. Five 30W-samples after the completion of 100 FT-cycles are illustrated in Picture 6 [Appendix A]. It can be seen that they have different degrees of external void content. A close-up of a 30W-sample can be seen in Picture 7 [Appendix A].

**Table 9. Test data of 30W-samples after 100 FT-cycles.**

| 30W-samples; 100 FT-cycles | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 2.23) | Failure Mode | Weight Increase |
| 41 | 44.29 | | DGM | 0.67% |
| 60 | 44.28 | | DGM | 0.72% |
| 3 | 47.10 | | DGM | 0.72% |
| 19 | 51.14 | 1.99 | LAT | 0.83% |
| 36 | 46.53 | | DGT | 0.65% |
| 8 | 41.89 | | DGT | 0.73% |
| 12 | 40.98 | | LGB | 0.77% |
| 25 | 47.31 | | LGM | 0.70% |
| 59 | 45.42 | | DGT | 0.65% |
| 58 | 44.92 | | DGB | 0.71% |
| Mean: | 45.39 | | | 0.71% |
| SSD | 2.89 | | | |

The standard deviation of the UTS data set was determined to be 2.89 ksi. Sample 19 was determined to have the maximum absolute deviation from the sample mean UTS and was therefore evaluated as an outlier. Its MNR value of 1.99 is not higher than the CV of the sample size listed in Table 9 and was therefore not considered an outlier. Sample 19 also displayed relatively high weight increase and failed laterally at the top tab section which is not desired. It is out of the ordinary to obtain relatively high mechanical properties when a sample fails in the tab section. The main reason is that the gage section has a smaller cross sectional area than the tab section. This leads to the conclusion that the gage section of sample 19 must have been significantly stronger than the rest of the samples. However, this is not a reason to exclude the sample from the data set.

It should be noted that FRP that are mainly reinforced with unidirectional fibers greatly depend on undamaged fibers from end to end to provide good load capability. By machining the samples into the dog bone shape as shown in Figure 1, Section 2.2, the unidirectional fibers are cut of in the tab section which substantially reduces its load capabilities. The matrix material, in

this case polyester, does not substantially add strength. The most important functions of the matrix material is to bind the fiber together, transfer the load to the fibers, slow down or stop crack propagation, provide shape and toughness, protect the fibers from wear and corrosion, and to provide ductility [19]. For these reasons FRP with a high percentage or exclusively unidirectional fibers will have a higher chance to fail in the tab section than homogenous materials. Seven out of ten samples failed through delamination. This may be a sign that the debonding of the fiber and matrix has reached a higher level which promotes delamination failures.

A progressive display of the UTS of the 30W-samples through moisture and FT-cycling is shown in Figure 6. The horizontal lines in Figure 6 depict the mean UTS. The highest and lowest point depicts the highest and lowest UTS for each data set, respectively.

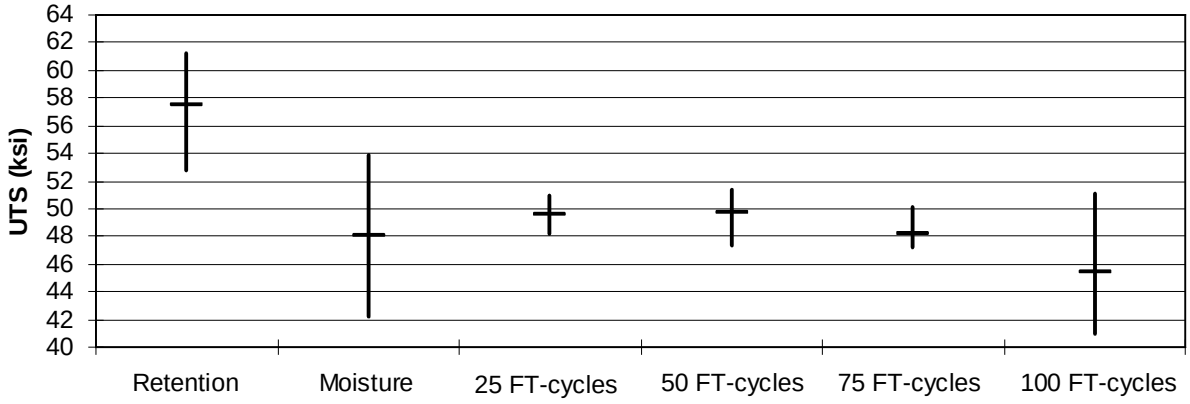



**Figure 6. Progressive UTS display of 30W-samples.**

### 3.2.3 60W-Samples

The data from the 60W-samples tested after the initial moisture exposure is shown in Table 10. The mean UTS of this data set was found to be 48.90 ksi which is an approximate

reduction of 8.6 ksi, or a 14.9%, compared to the retention mean UTS. This sample mean UTS is also 1.9% higher than the mean UTS of the 30W-samples previously discussed. It may seem surprising that the samples with a longer moisture exposure and higher moisture content displayed higher mean UTS, but the data samples' mean UTS are within one SSD; thus, considered equal statistically. It should also be noted that the UTS data set of the 30W-samples tested after moisture produced a SSD of 4.12 ksi which does raise concern about its consistency. The SSD of the UTS of this data set displayed in Table 10 was determined to be 2.13 ksi. Sample 7 was considered as a possible outlier, but its MNR value of 1.29 is lower than the CV of the sample size.

**Table 10. Test data of 60W-samples after 60 days of moisture exposure.**

| 60W-samples Moisture Only | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 1.65) | Failure Mode | Weight Increase |
| 7 | 46.15 | 1.29 | DGM | 0.72% |
| 11 | 47.77 | | LGT | 0.66% |
| 13 | 50.74 | | DGM | 0.59% |
| 16 | 48.53 | | DGM | 0.77% |
| 17 | 51.30 | | LGB | 0.57% |
| Mean: | 48.90 | | | 0.66% |
| SSD | 2.13 | | | |

Both lateral and delamination failures were observed for the samples in Table 10. A relation can be seen between the relative individual weight increase percentage and the UTS. Samples 13 and 17 are the only samples with UTS above the mean UTS and they are also the only samples with weight increase below the mean weight increase percentage. This will be considered for future data sets, but there is yet not enough supportive data to prove that the small difference in weight increase displayed in Table 10 will affect the UTS. The main reason is that

weight increase differences in previous data sets have not affected the UTS, or even proven the opposite as was seen in Table 6 comparing samples 38 and 52.

The data from the 60W-samples tested after the initial moisture exposure is shown in Table 11. The sample mean UTS was found to be 49.00 ksi which is approximately a 8.5 ksi, or 14.7%, reduction compared to the respective retention value shown in Table 4. There is a relatively high variation of UTS values, and the SSD was determined to be 2.98 ksi as shown in Table 11. Sample 12 displayed the lowest UTS with a reduction of 21.6% compared to the retention mean UTS. The UTS of sample 9 on the other hand was only lowered by 7.7% in relation to the retention mean UTS. The sample mean UTS in Table 11 is 1.5% lower than its relative value from the 30W-samples shown in Table 7. Again this small divergence is not enough to determine whether the additional 30 days of initial moisture exposure of the 60W-samples increases the detrimental effect of FT-cycling. Statistically the data sets are considered equal.

**Table 11. Test data of 60W-samples after 50 FT-cycles.**

| 60W; 50 Cycle Tensile | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 1.65) | Failure Mode | Weight Increase |
| 4 | 47.93 | | DGT | 0.81% |
| 6 | 48.40 | | DGM | 0.60% |
| 9 | 53.01 | | DGM | 0.68% |
| 12 | 45.07 | 1.32 | LAB | 0.76% |
| 18 | 50.57 | | LGT | 0.72% |
| Mean: | 49.00 | | | 0.72% |
| SSD | 2.98 | | | |

Sample 12 was found to have the maximum absolute UTS deviation from the sample mean which qualifies it as the most likely outlier. Equation 2 from Section 3.2 was used to determine its MNR value which was found to be 1.32. As seen in Table 11 this MNR value is

lower than the CV for the sample size (1.65) and thus not regarded an outlier. It should be noted that sample 12 also had relatively high weight increase percentage and more importantly that it failed in the tab section. However, this does not eliminate the sample from the data set since this type of failure has been seen in previous data sets such as the ones displayed in Table 5 and Table 9. Overall three samples failed by delamination and two laterally and no relation to the samples' individual weight increase. Once again there is a slight relation between the weight increase and the UTS. The majority of the samples with an above the sample mean UTS also displayed a below or equal sample mean weight increase percentage and vise versa. Sample 6 is excluded from this with a below mean UTS and weight increase.

The data from the 60W-samples tested after 100 FT-cycles is shown in Table 11 below. The sample mean UTS displayed in Table 11 is 10.1 ksi, or 17.6%, lower than the retention sample mean UTS. The lowest individual UTS is 26.9% lower than the relative retention value and the highest individual UTS is 9.5% lower. The SSD of the UTS data set listed in Table 12 is almost identical to the respective SSD from the 30W-samples shown in Table 9. Sample 20 with the lowest individual UTS was evaluated as an outlier. Its MNR value was determined to be 1.88 which is lower than the CV of the sample size; thus, there are no outliers present in the UTS data set.

**Table 12. Test data of 60W-samples after 100 FT-cycles.**

| 60W; 100 Cycle Tensile | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 2.23) | Failure Mode | Weight Increase |
| 15 | 44.19 | | LGM | 0.90% |
| 19 | 48.65 | | LGM | 0.68% |
| 8 | 52.01 | | DGM | 0.75% |
| 5 | 48.08 | | LGM | 0.88% |
| 3 | 46.43 | | DGM | 0.80% |
| 2 | 49.56 | | DGM | 0.78% |
| 1 | 49.33 | | LGB | 0.79% |
| 10 | 46.91 | | DGM | 0.92% |
| 14 | 46.47 | | DGM | 0.81% |
| 20 | 41.99 | 1.88 | DGM | 0.81% |
| Mean: | 47.36 | | | 0.81% |
| SSD | 2.85 | | | |

Six out of ten samples failed by delamination and the remaining four failed laterally. A few more delaminations were expected, but overall the ratio of delaminations and lateral failures is considered consistent in comparison to the previous data sets and their relative weight increase. Four out of the five samples with the highest UTS are also among the five samples with lowest weight increase percentage which supports the previously discussed relationship between UTS and weight increase. This relationship has been proven to be more true than false for the 60W-samples, but a more thorough analysis and probably even a full scale study is needed before this could possibly be predictably quantified.

A progressive display of the UTS of the 60W-samples through moisture and FT-cycling is shown in Figure 7 below. The sample mean UTS for each testing instance of the 60W-samples are comparable to that of the 30W-samples. Thus it is concluded that the extended moisture period did not have a substantial influence on the degradation due to FT-cycling for the pultruded polyester/E-glass used in this study.

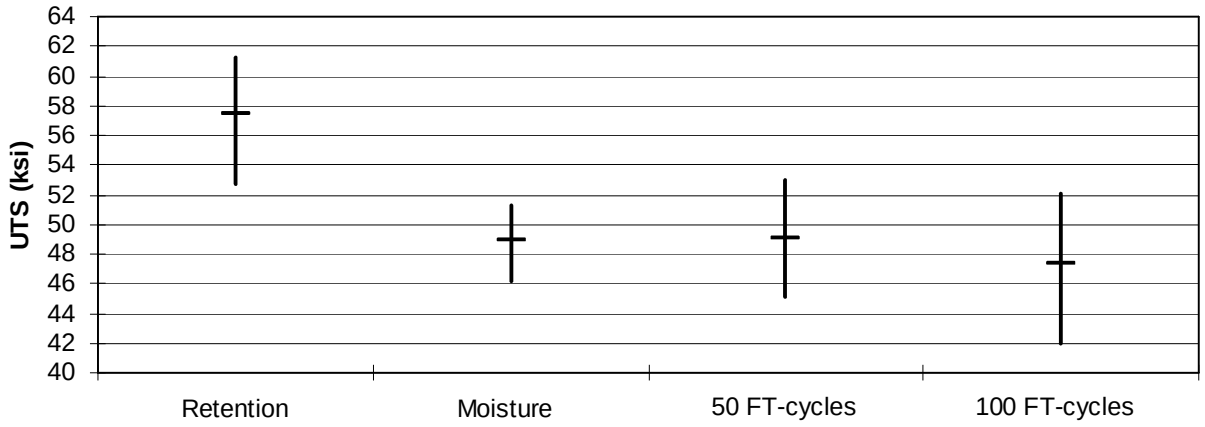



**Figure 7. Progressive UTS display of 60W-samples.**

### 3.2.4 30TC-Samples

The 30TC-samples were not tested after the initial moisture exposure since they were subjected to the same moisture exposure as the 30W-samples as previously stated in Section 2.7. It should be noted that there is a fairly high uncertainty associated with the test results of the 30TC-samples due to the problems with the temperature chamber discussed in Section 3.1. The first mechanical tensile testing of the 30TC-samples was performed after the presumed 50 FT-cycles and is shown in Table 13.

**Table 13. Test data of 30TC-samples after 50 FT-cycles.**

| TC; 50 Cycle Tensile | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 1.65) | Failure Mode | Weight Increase |
| 1 | 50.13 | | DGM | 1.07% |
| 4 | 48.44 | | DGM | 0.71% |
| 9 | 49.58 | | DGT | 0.75% |
| 10 | 49.13 | | DGT | 0.94% |
| 13 | 46.93 | 1.55 | DGM | 1.01% |
| Mean: | 48.84 | | | 0.90% |
| SSD | 1.24 | | | |

The sample mean UTS of the 30TC-samples after 50 FT-cycles is 8.6 ksi, or 15.0% lower than the retention sample mean UTS. It can be seen in Table 13 that he UTS data set is relatively consistent compared to data from previously discussed test instances. Its consistency is supported by a low SSD of 1.24 ksi. Sample 13 was determined to have the maximum absolute deviation from the sample mean. Its MNR value was found to determine if it should be considered an outlier. As can be seen in Table 13 the MNR value of sample 13 is barely below the CV of the sample size. However, it should be noted that the low SSD value enhances the MNR value. All samples failed in the gage section by delamination. It was expected that these samples would fail by delamination since they were exposed to wet freezing compared to the dry freezing conditioning of the manually FT-cycled samples. The wet freezing conditioning leads to higher moisture absorption as discussed in Section 3.1. No relation between the weight increase and the UTS can be seen from the data in Table 13.

The test data obtained from the 30TC-samples tested after 100 FT-cycles is shown in Table 14. The sample mean UTS of the data set was determined to be 46.5 ksi which is 11.0 ksi, or 19.1%, lower than the retention sample mean UTS. This sample mean value is in between the respective values from the 30W-samples and 60W-samples. This is promising in validating the automatic FT-cycling process as an alternative to the manual. The highest UTS value of the samples tested is 49.16 ksi (sample 15) which is 8.3 ksi, or 14.4%, lower than the respective retention value shown in Table 4 while the lowest UTS of the data set (sample 5) is 41.76 ksi which is 15.7 ksi, or 27.3%, lower. Sample 5 was determined to have the maximum absolute deviation from the UTS sample mean. The data set was determined to be free of outliers since sample 5’s MNR value of 1.89 is lower than the CV of the sample size.

**Table 14. Test data of 30TC-samples after 100 FT-cycles.**

| TC; 100 Cycle Tensile | | | | |
|---|---|---|---|---|
| Sample # | UTS (ksi) | MNR (CV = 2.23) | Failure Mode | Weight Increase |
| 2 | 44.61 | | DGT | 0.94% |
| 3 | 46.64 | | DGM | 1.01% |
| 5 | 41.76 | 1.89 | DGB | 1.05% |
| 6 | 47.83 | | DGM | 1.16% |
| 7 | 48.65 | | DGM | 0.74% |
| 8 | 46.03 | | DGT | 0.73% |
| 11 | 43.46 | | DGT | 0.78% |
| 12 | 48.76 | | DGM | 1.02% |
| 14 | 48.10 | | DGM | 0.69% |
| 15 | 49.16 | | DGM | 0.79% |
| Mean: | 46.50 | | | 0.89% |
| SSD | 2.51 | | | |

All samples failed in the gage section through delamination. The delamination failures were initiated in all possible locations of the gage section (bottom, middle, and top) which is desired as discussed in Section 2.7. A relatively wide range of weight increase percentages can be seen in Table 14; however, there is not a strong correlation between the relative weight increase and the UTS of the samples.

The summary of the test data of the 30TC-samples previously discussed is shown in Figure 8 below. It should be noted that the highest UTS after 100 FT-cycles in Figure 8 is lower than the respective value for the 30W-samples and 60W-samples shown in Figure 6 and Figure 7, respectively. This could have been an indication that the automatic FT-cycling process is slightly more detrimental than the manual process, but more likely is that it is caused by data scatter. The result after 100 FT-cycles of the 30TC-samples and the two manual FT-cycling processes are considered statistically equal due to their closely matching sample mean UTS and relatively high SSD.

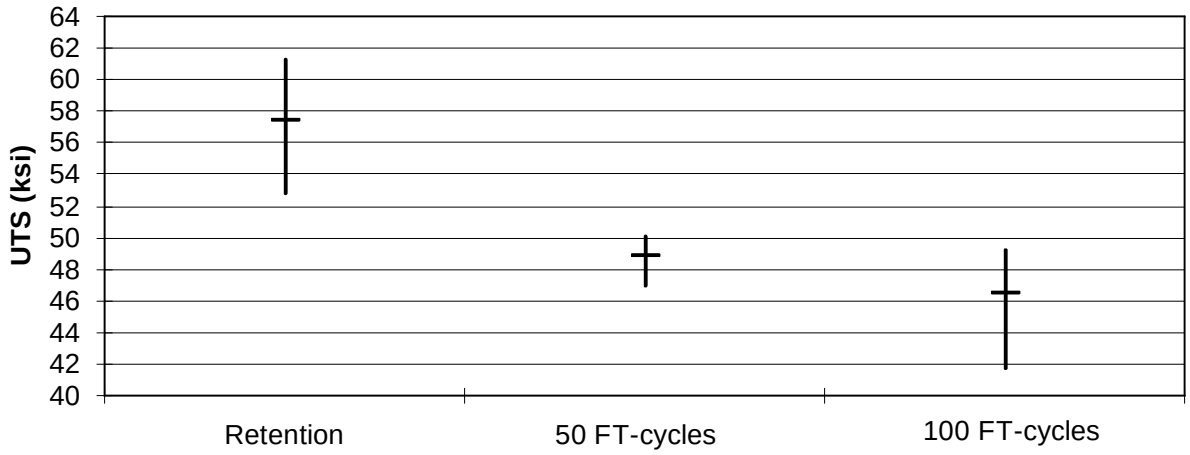



**Figure 8. Progressive UTS display of 30TC-samples.**

### 3.3 Summary of Results

Three sample batches were conditioned with different process parameters either in the initial moisture conditioning or in the FT-cycling as previously discussed in Chapter 2. The first step of the conditioning process was moisture through immersion in a 23±2°C (77°F) water bath. The 30W-samples and the 30TC-samples were both subjected to an initial 30 days of moisture exposure while this period was extended to 60 days for the 60W-samples. The results of the moisture exposure of the individual sample batches were discussed in Section 3.1. Figure 9 below includes all of the sample batches' progressive weight increase percentage results for an easier comparison.

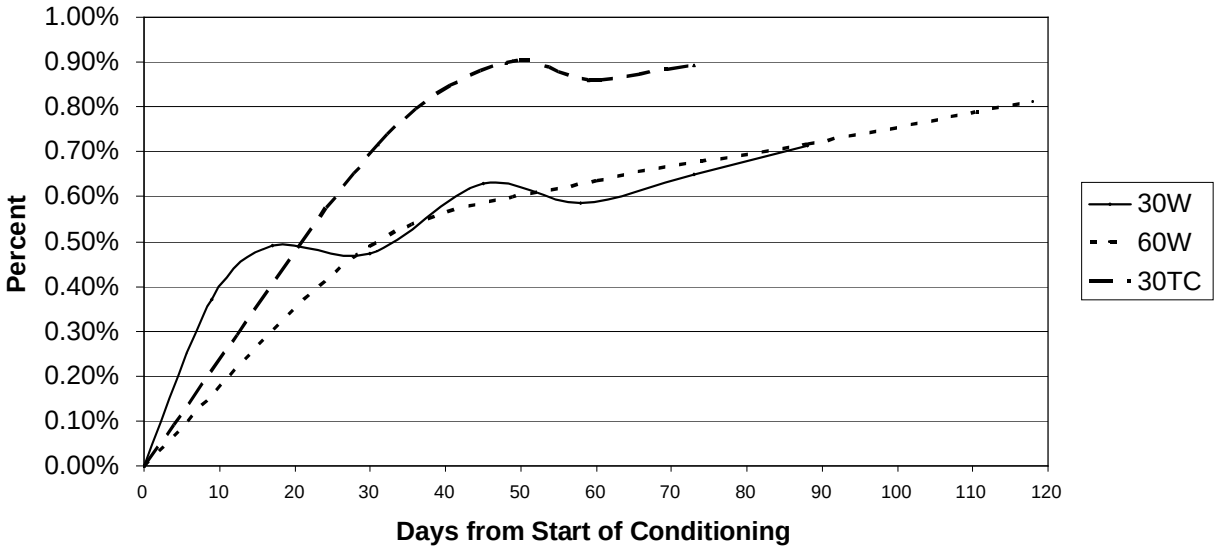



**Figure 9. Weight increase comparison of the three sample batches.**

A summary of the mechanical tensile testing data is shown in Table 15 below. All of the percent loss values listed are compared to the retention mean UTS to stay consistent with previous comparisons made in Section 3.2. Some of the data in Table 15 is also displayed in Figure 10 and it is discussed following Figure 10.

**Table 15. Mechanical tensile testing summary of the three sample batches.**

| Mechanical Tensile Testing Summary | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Test Period** | **Sample Batch** | **Min UTS** | | **Mean UTS** | | **Max UTS** | | **SSD** |
| | | **(ksi)** | **(% loss)** | **(ksi)** | **(% loss)** | **(ksi)** | **(% loss)** | **(ksi)** |
| **Retention** | Retention | 52.78 | - | 57.46 | - | 61.24 | - | 2.85 |
| **Moisture** | 30W | 42.28 | 26.4% | 48.00 | 16.5% | 53.81 | 6.4% | 4.12 |
| | 60W | 46.15 | 19.7% | 48.90 | 14.9% | 51.30 | 10.7% | 2.13 |
| | 30TC | - | - | - | - | - | - | - |
| **50 FT-cycles** | 30W | 47.36 | 17.6% | 49.76 | 13.4% | 51.38 | 10.6% | 1.64 |
| | 60W | 45.07 | 21.6% | 49.00 | 14.7% | 53.01 | 7.7% | 2.98 |
| | 30TC | 46.93 | 18.3% | 48.84 | 15.0% | 50.13 | 12.8% | 1.24 |
| **100 FT-cycles** | 30W | 40.98 | 28.7% | 45.39 | 21.0% | 51.14 | 11.0% | 2.89 |
| | 60W | 41.99 | 26.9% | 47.36 | 17.6% | 52.01 | 9.5% | 2.85 |
| | 30TC | 41.76 | 27.3% | 46.50 | 19.1% | 49.16 | 14.4% | 2.51 |

Figure 10 illustrates the sample mean UTS degradation development of the three FT-cycling processes conducted. Note that retention values were added for comparison purposes and are not linked to the three test instances displayed on the x-axis.

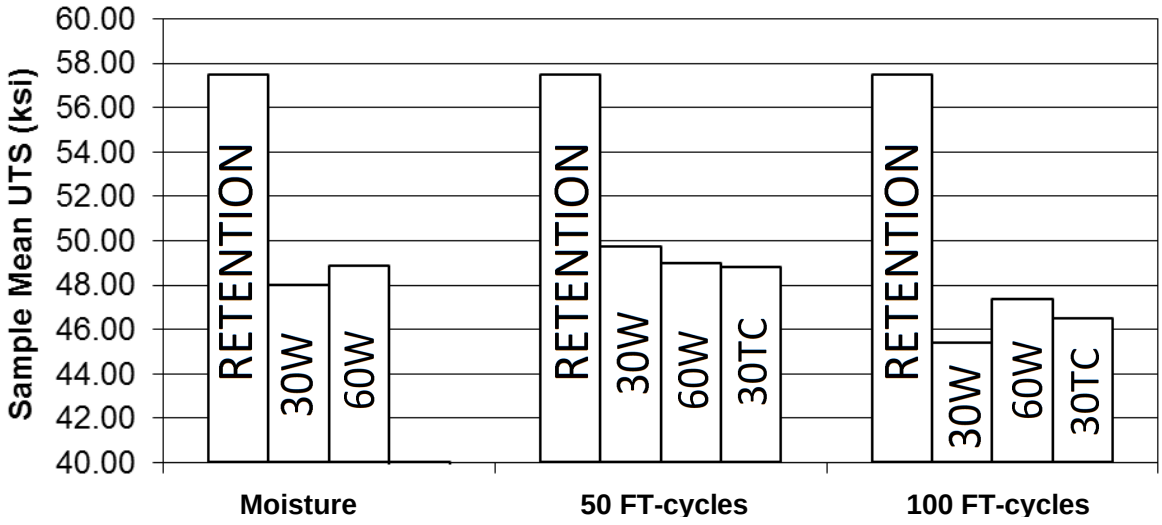



**Figure 10. Sample mean UTS degradation summary of the three FT-cycling processes.**

Five samples were tested after the initial moisture exposure. As shown in Figure 10 the degradation of the sample mean UTS after initial moisture exposure for the 30W-samples and the 60W-samples were very similar. The 60W-samples even showed slightly less degradation of its mean UTS than the 30W-samples which was unexpected. However, it should be noted that the small difference in these results fall within one sample standard deviation and is most likely caused by data scatter. The mean UTS of the 30W-samples and 60W-samples degraded by 16.5% and 14.9%, respectively, compared to the retention mean UTS as can be seen in Table 15. The 30TC-samples were not tested after moisture as previously mentioned since they were exposed to the same initial moisture exposure condition and length as the 30W-samples.

Five samples were mechanically tested for all three FT-cycling processes after 50 FT-cycles. The sample mean UTS results of the three processes were very similar with degradation compared to the retention mean UTS ranging from 13.4% to 15.0%. The possible reasons for increase in mean UTS from moisture to 50 FT-cycles were previously discussed in Section 3.2. An expected trend was seen between the three processes. The 30W-samples showed least degradation followed by the 60W-samples and finally the 30TC-samples showed the highest degree of degradation. However, the sample mean UTS of the three processes after 50 FT-cycles are all within less than 1 ksi as can be seen in Table 15, so the three processes are considered statistically equal. This is displayed in Figure 11 where it is clearly seen that the UTS of the individual samples from the three processes overlap for each test instance.

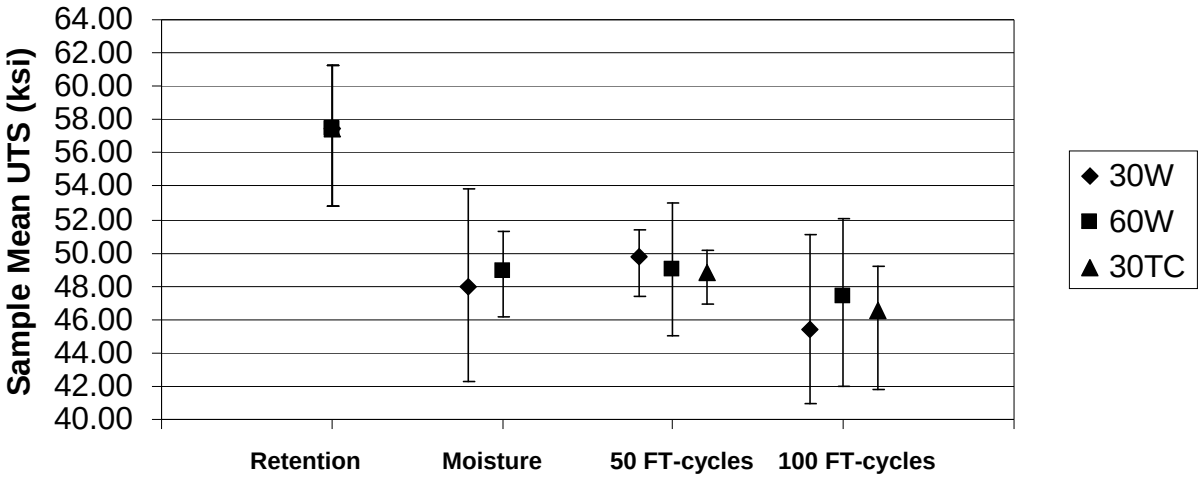



**Figure 11. Sample mean and sample range UTS summary.**

Ten samples were mechanically tested for all three processes after 100 FT-cycles in accordance with the evaluation of the D20.18.02 draft study [18]. As can be seen in Figure 10 all three processes showed mean UTS degradations lower than for the initial moisture exposure. The

degradation ranged from 17.6% to 21.0% as can be seen in Table 15. It was surprising that the 30W-samples showed the most degradation out of the three processes, but based on the sample mean UTS and SSD of the processes they are statistically equivalent. As previously stated the relative mean UTS of the three freeze-thawing processes were not as expected after moisture exposure and 100 FT-cycles as shown in Figure 10. However, there was a general trend for all three processes of a slight increase in mean UTS after 50 FT-cycles compared to the initial moisture exposure mean UTS and then a comparatively large decrease in mean UTS after 100 FT-cycles. Keeping in mind that the number of FT-cycles completed for the 30TC-samples is uncertain it is still promising for the future development of the automatic FT-cycling that the mean UTS determined after 50 and 100 FT-cycles so closely match the manually freeze-thawing procedures mean UTS. However, it is advised that future testing will be performed to confirm the automatic FT-cycling results.

Data from all of these conditions support that at the temperature and number of cycles examined in the freeze-thaw procedure, the most significant effect on the mechanical property degradation occurred due to moisture exposure. It would have been interesting to have kept samples in the water bath from the start of the initial moisture exposure to the end of the FT-cycling to compare their detrimental effects.

# 4. STANDARD PROPOSITIONS AND THOUGHTS FOR FUTURE DEVELOPMENT

This chapter is intended as a reference for the future development of an ASTM standard for determination of freeze-thaw cycling resistance of pultruded shapes. The evaluation of the D20.18.02 draft study [18] will be used as the reference and the sections that were investigated in this study are intended to be discussed and improved if possible. It should be noted that this is not a proposal of a finished ASTM standard. The discussion is intended to assist in the future development and creation of an ASTM standard as previously stated.

## 4.1 Scope

The FT-standard development discussed is lead by the D20.18.02 committee specialized in pultruded shapes and it is a subcommittee of the D20 plastics committee. Because this standard development has been undertaken by the D20.18.02 subcommittee it is aimed specifically for pultruded shapes. A single ASTM standard aimed to determine freeze-thaw cycling resistance of all possible FRP may be proven too broad. However, pultruded shapes are obviously not the only FRP exposed to FT-cycling conditions, so getting the main D20 committee, or other subcommittees involved in the development may be beneficial.

## 4.2 Normative References

In this section of a standard other referenced ASTM standards are listed that are useful in the application of the document. This study utilized most of the listed ASTM standards and a few

others that are considered beneficial and will be discussed further. ASTM D638 – 08 was used to perform the mechanical testing in this study, ASTM D3039 – 08 was used to determine the failure modes, and ASTM D7290 – 06 was used to statistically evaluate the data sets. ASTM D7290 is advised to be included while the implementation of the other two standards will be discussed in more detail.

The use of compression testing through the use of ASTM D6641 and also the possibility of tensile testing through either ASTM D638 or ASTM D3039 has been considered [18]. Implementing the ASTM D3039 standard would add complexity since tabs are often required for this test method. A comparison study between ASTM D638 and ASTM D3039 has been published through a combined effort from Owens Corning and the University of Mississippi [20] and a decision has been made to use ASTM D638 for tensile testing and ASTM D6641 for compression testing; thus, the selection between ASTM D638 and D3039 will not be discussed further. However, the consensus of the D20.18.02 committee is that compression testing is the better testing option to compare the effects of FT-cycling.

### 4.3 Principle

The general principle of how to conduct the testing starting with initial moisture exposure, followed by FT-cycling, and finally mechanical testing is explained in the evaluation study of the D20.18.02 draft [18]. The moisture and freeze-thaw conditioning parameters are also listed in this section, but they will be discussed further in Section 4.5 dealing with more detailed procedure steps.

### 4.4 Test Specimens

The test specimens should be prepared according to the respective mechanical test standard. For this study ASTM D638 – 08 was followed to create dog-bone samples of Type 1 with an extended grip length as previously discussed in Section 2.2 and illustrated in Figure 1. A 6 hour pre-conditioning at 23±2°C (73°F) and 50±5% relative humidity is asked for as the last preparation step before the initial moisture exposure [18]. This condition was not monitored for this study, but the samples were kept in an air-conditioned room which should be close or within the prescribed temperature and humidity ranges. This study has not generated any results or observations that contradict what is included in the evaluation study [18].

### 4.5 Procedure

The procedure section is a detailed description of the steps involved in the testing procedure once the samples have been prepared as discussed in the previous section. There are no objections or comments concerning the first two steps of the procedure dealing with weighting all samples and keeping the non-exposed samples in the conditioning chamber. The following steps explain how to conduct the initial moisture exposure, the freezing, and the thawing. The parameters and regulations involved in these steps will be thoroughly discussed in relation to the findings in this study along with general concerns and thoughts.

The importance of sufficient saturation has been previously discussed in Chapter 1. A proposal to possibly extend the initial moisture exposure from 30 to 60 days was discussed in the evaluation study of the D20.18.02 draft [18]. Both of these options were considered in this study through the 30W and 60W sample batches. A definite increase in the moisture content was seen by increasing the moisture conditioning period to 60 days for the exposed pultruded polyester/E-

glass. Due to the wide variety of FRP with diverse weight increase rates and magnitudes it is advised to request a relative saturation before commencing with FT-cycling.

ASTM D570, “Standard Test Method for Water Absorption of Plastics,” is one of the discussed normative references in the evaluation study of the D20.18.02 draft [18]. This standard includes specifications on how to determine a relative saturation for long term immersion in water. A relative saturation can be quantified by requesting a maximum percent of moisture absorption over a specific time. This process has not been tested in this study, so no specific numbers will be suggested based on its results. It is advised that the guidelines presented in ASTM D570 should be followed to generate a relative saturation until further evaluations have been undertaken.

Based on the result and the discussion in Section 3.3 it is strongly advised to keep a separate batch of samples in the prescribed initial moisture exposure from the start of the initial moisture exposure to the end of the final FT-cycle conducted. These samples should be mechanically tested at the same time as the final FT-cycle. As stated in Section 3.3 the results from all conditioned sample batches and test instances are considered statistically equal. These findings lead to the conclusion that the initial moisture exposure most likely caused all or most of the degradation of the samples. By keeping a separate sample batch immersed according to the initial moisture conditioning as previously discussed it can be determined if moisture is the major cause of the degradation of the FRP or not. It should be noted that the relative response to moisture and freeze-thawing will be different based on the constituent materials of the FRP.

The temperatures of freezing and thawing have been discussed previously in Chapter 1. The draft evaluation study [18] suggests a freezing temperature of -20±2°C (-4°F). This temperature was found satisfactory through this study. It was sufficient to freeze samples through

their thickness in a short period of time. This makes the standard more efficient by keeping the FT-cycle time down to a satisfactory level. This temperature is also achievable by most commercially available freezers readily available to all users which improve the standards ease of use. By requesting lower freezing temperatures the standard would become restricted to specialized testing labs, or force the user to invest in expensive equipment. It is advised to investigate if the freezing time can be lowered to make the standard more time efficient if this of interest. It is mentioned in the evaluation study of the D20.18.02 draft [18] that the samples should be kept frozen over long planned interruptions such as over night when manual FT-cycling is conducted. This was followed throughout this study as previously stated in Section 2.5.

The requested initial moisture conditioning and thawing temperature is 23±2°C (73°F) [18]. Higher temperatures have been shown to increase the moisture absorption rate of FRP as discussed in Chapter 1 [7, 8]. Figure 9 in Section 3.3 shows that the weight increase percentage of the samples kept rising after the initial moisture exposure. The 30TC-samples' weight increase percentage seem to stagnate around 0.90% weight increase, but weight increases of individual samples up to 1.16% was recorded (Table 14). Thus it can be concluded that the samples had not reached saturation even after the 60 day initial water immersion. However, it should be noted that the samples with higher weight increases did not in general display lower UTS values.

The obvious additional requirement for the user associated with a higher moisture exposure temperature is to control and maintain this temperature. This will in general require more complicated equipment, more energy will be required, and the water bath may need to be monitored more consistently due to a higher evaporation rate. The leaching rate will also be increased at elevated temperatures. Chemical testing can be performed on the water in order to

estimate the weight loss of each sample to take this into account when determining the weight increase as discussed in Section 2.8. By performing leaching tests an estimate of the actual moisture absorption instead of the weight increase can be found. However, this is difficult and time consuming to do in between each weighing which would be required if a relative saturation requirement will be used.

If a fixed time period is used for the initial moisture exposure, leaching tests can be performed at the completion of this exposure. It is noted in the evaluation study of the draft [18] that leaching should be mentioned, but not quantified. Residue was observed during this study which confirms the presence of leaching. Based on the observations during this study it is advised to consider the quantification of leaching. It is also believed that higher temperatures would require testing for leaching based on the amount of leached substance visible in the water after moisture conditioning and freeze-thaw cycling in this study. Based on the results from this study it would be beneficial to increase the temperature of the initial moisture absorption to improve the efficiency of the testing procedure, but as discussed there are too many obstacles to overcome at this point to suggest higher temperatures for initial moisture exposure and thawing.

The evaluation study of the D20.18.02 draft [18] proposes a 6 hour total cycle time split equally between freezing and thawing. There is no maximum time set for freezing or thawing, but the minimum is 3 hours to allow enough time for complete freezing and thawing throughout the thickness of the samples. It is also considered in the evaluation of the draft study [18] that the interior of the specimens should reach an internal temperature of -20±2°C (-4°F) for at least 30 min every cycle. In this study this was easily obtained for the samples subjected to dry freezing. The samples subjected to automatic FT-cycling which includes wet freezing did not reach -20±2°C (-4°F). The temperature progression of a cycle with the setup used in this study is shown

in Figure 12. The dashed line in Figure 12 represents the 32°F (0°C), or freezing point. It can be seen in Figure 12 that the samples stayed frozen for over 30 min, but the lowest temperature reached was approximately 10°F (-12°C). Based on the UTS results of this study it is believed that this temperature exposure is sufficient to cause enough detrimental effect. It should be noted that the constant water exposure of the automatic FT-cycling may have caused more degradation and that less or an insignificant amount of degradation was caused by the freezing-thawing. The possibility of moisture being the major factor for degradation of FRP was discussed in Section 3.3 and supported by Figure 11.

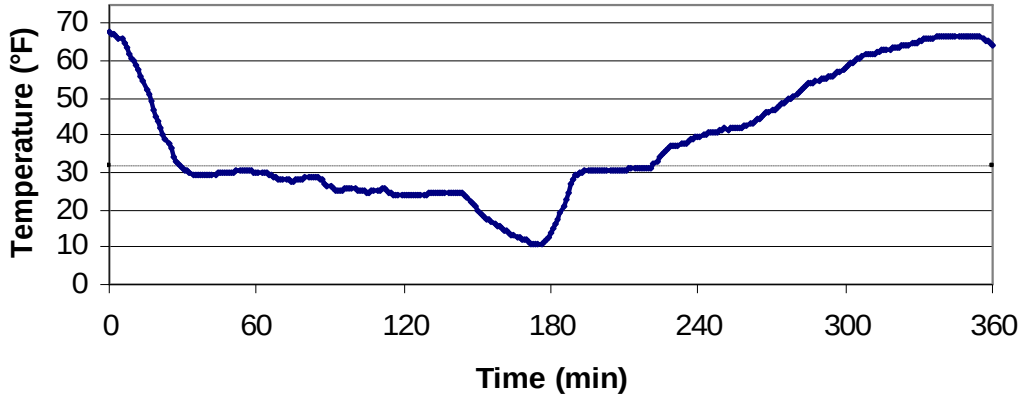



**Figure 12. One cycle of automatic FT-cycling**

The evaluation study of the D20.18.02 draft [18] suggests a total of 100 cycles, but 300 cycles had also been considered. Since this study is based on 100 cycles it is difficult to comment on the possible implementation of 300 cycles, but from the progressive degradation of the samples mechanical properties seen in this study it is evident they were just starting to drop in relation to the post moisture properties. Therefore it is advised that the number of cycles should be left open and not be restricted to 100. The theory discussed previously that moisture is the

major cause for the degradation of FRP and not freeze-thawing should also be further evaluated by performing more than 100 FT-cycles.

If automatic FT-cycling is implemented as an option it needs to be included as a separate set of procedure steps in the procedure section. The use of automatic FT-cycling is promising based on the comparison of the results of the different sample batches of this study. However, as previously discussed in Section 3.1 there are concerns about the results from the automatic FT-cycling due to the numerous breakdowns of the temperature chamber. The differences between wet and dry freezing is an issue that has been discussed in Section 2.6 and that has to be dealt with. The easiest solution would be to request wet freezing for both manual and automatic FT-cycling if both are incorporated. Due to the present issues and the uncertainty about the results from the automatic FT-cycling performed in this study it is not feasible or advised to include it as an option at this point. Further studies and solutions to the problems previously discussed may enable automatic FT-cycling as an option to manual FT-cycling in the future. The samples should be tested within 24 hrs of completion of the last FT-cycle which was followed in this study [18].

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**ASTM Standards Listed in Order of Appearance**

ASTM D5229 - “Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials.”

ASTM C666 - “Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing.”

ASTM D2584 - “Standard test method for ignition loss of cured reinforced resins.”

ASTM D638 - “Standard test method for tensile properties of plastics.”

ASTM D3039 - “Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials.”

ASTM D5284 - “Standard Test Method for Sequential Batch Extraction of Waste with Acidic Extraction of Fluid.”

ASTM D570 - “Standard Test Method for Water Absorption of Plastics.”

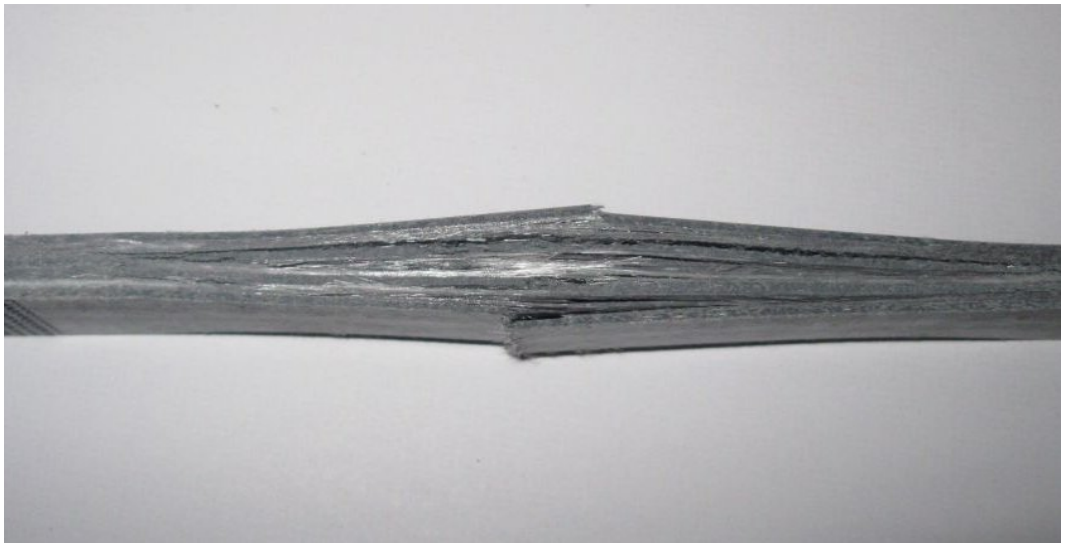
ASTM D7290 - “Standard Practice for Evaluating Material Property Characteristic Values for Polymer Composites for Civil Engineering Structural Applications.”

ASTM D6641 - “Standard Test Method for Compressive Properties of Polymer Matrix Composite Materials Using a Combined Loading Compression (CLC) Test Fixture.”

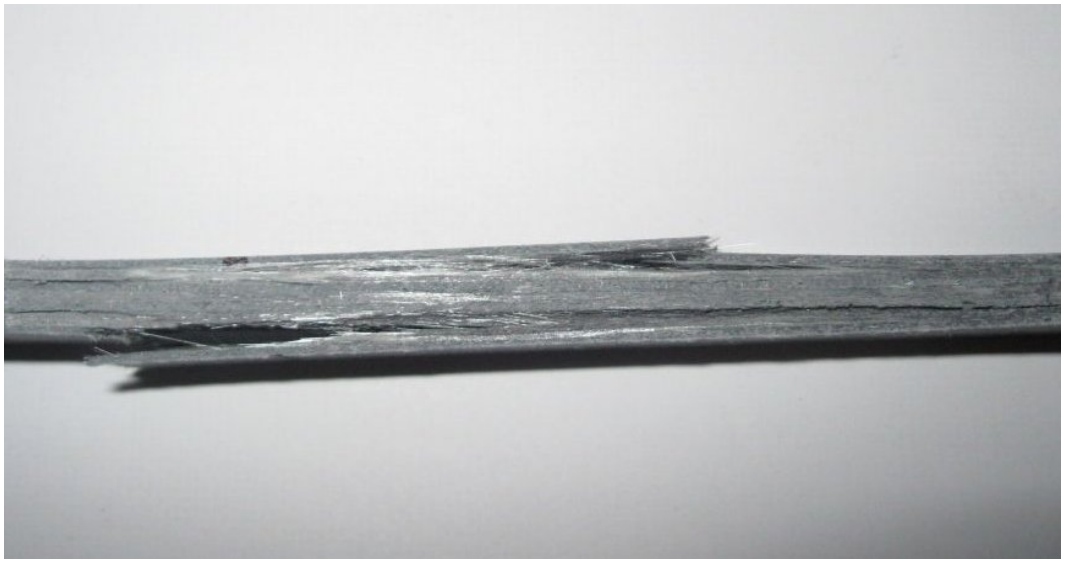
# APPENDIX A

## Illustrative Pictures

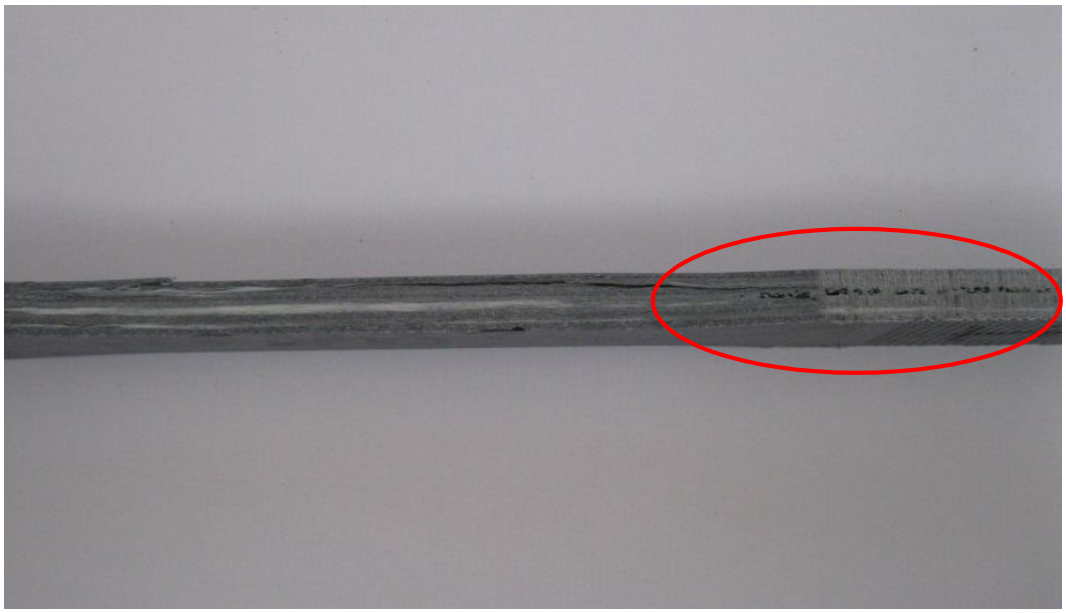
**Picture 1. Samples stacked on the rack in a temperature controlled water bath.**



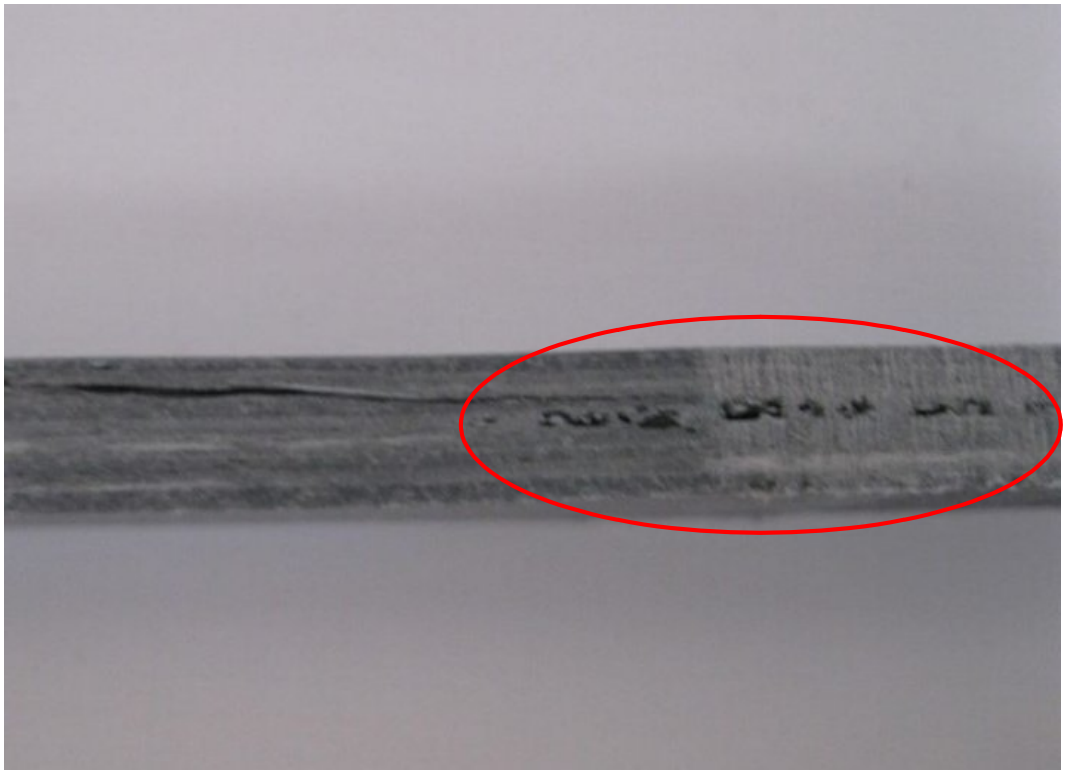
**Picture 2. Delamination failure initiated at the middle of the gage section (DGM).**



**Picture 3. Lateral failure initiated at the lower left location (LGB).**



**Picture 4. Pre-damaged retention sample 5.**



**Picture 5. Pre-damaged retention sample 5 close-up.**

**Figure 6. 30W-samples after 100 FT-cycles**

**Picture 7. Close-up of 30W-sample after 100 FT-cycles**

# VITA

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