A STUDY ON THE COMPARISON OF SAMPLE LOCATION OF PULTRUDED COMPOSITES EXPOSED TO CORROSIVE ENVIRONMENT

A Thesis

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ABSTRACT

Composite structures may experience different environments during their prolonged service life. These environments may include corrosive, acidic or both or many others that can adversely affect the mechanical properties of the structural composites. Various studies have been done on the environmental effects on the composites but only a few are on structural shaped pultruded composites. More specifically, none of the studies tell anything about the effects of corrosive media on the locations of the structural shaped pultruded composites coupon samples. Hence, this current study focused on two primary objectives, 1) the durability characterization of structural shaped pultruded composites after an extensive period of exposure (16,632 hours) with respect to their locations and 2) provide supportive data to develop a standard experimental procedure for corrosion testing of pultruded composites. Glass-fiber reinforced polyester and vinyl ester pultruded composites were examined in this present study. After 672 hours (short-term exposure) and 16,632 hours (long-term exposure) of distilled water and bleach immersion, short-beam strength was determined. The results revealed that long-term exposure of corrosive media affect the coupon samples of all locations equally while the effects of short-term exposure on sample locations were different. This demonstrated the need for specifying where the samples should be taken from during the development of an experimental procedure for the short-term exposed pultruded samples.

DEDICATION

I would like to thank the Almighty who brought me here today and keep me in good health.

My warmest gratitude to my lovely parents, my younger uncle and all family members who supported me throughout my journey, especially to my dad who taught me to become a dreamer and without whom I might not be able to fulfill my dream.

I cannot express in words my heartiest gratitude to my Adviser Dr. Ellen Lackey, who has supported me in every possible way. I would not be the person I am today without her endless supports. I dedicate my thesis to her.

LISTS OF ABBREVIATIONS AND SYMBOLS

ACMA	American Composite Manufacturers Association
ADC	Anderson-Darling Critical Value
ADK	k-sample Anderson-Darling
ASCE	American Society of Civil Engineers
ASTM	American Society of Test Methods
APWC	Average percent weight change
Avg.	Average
b	Measured Specimen Width
CACRC	Commercial Aircraft Composite Repair Committee
CERF	Civil Engineering Research Foundation
CEO	Chief Executive Officer
CLC	Combined Loading Compression
COV	Coefficient of variation
CV	Critical Value
DW	Distilled water
EDS	Energy Dispersive Spectroscopy
FRP	Fiber Reinforced Polymer
FTIR	Fourier Transform Infrared Spectroscopy
F_{ij}	The Number of Values in the ith Group Which are Less than to $z_{(j)}$ Plus One Half the Number of Values in the Combined Samples Equal to $z_{(j)}$

F_{sbs}	Short-beam Strength
GFRP	Glass Fiber Reinforced Polymer
h	Measured Specimen Height
h_j	The Number of Values in the Combined Samples Equal to $z_{(j)}$
H_j	The Number of Values in the Combined Samples Less than to $z_{(j)}$ Plus One Half the Number of Values in the Combined Samples Equal to $z_{(j)}$
ILSS	Interlaminar Shear Strength
Ksi	Kilopound per Square Inch
L	Length of the Specimen
LPA	Low Profile Additives
LRFD	Load and Resistance Factor Design
Max	Maximum
Min	Minimum
MTS	Material Test System
MNR	Maximum Normal Residual
n	Sample Size
NASA	National Aeronautic and Space Administration
NIST	National Institute of Science and Technology
OSL	Observed Significance Level
PIC	Pultrusion Industry Council
PE	Polyester

P_m	Maximum Load Observed During the Test
RH	Relative Humidity
RAAF	Royal Australian Air Force
s	Sample Standard Deviation
S^2	Sample Variance
STD	Standard Deviation
Tg	Glass Transition Temperature
TSTSP	Time-Stress-Temperature Superposition Principle
UV	Ultaviolet
US	United States
USA	United States of America
VE	Vinyl Ester
$\bar{x}$	Sample Data Mean, Average
x_i	Sample Data
$\boldsymbol{\sigma}^2$	Variance

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CHAPTER I: INTRODUCTION

With the development of new technology and improvement of the existing methods, availability of the composites in the global market is increasing. When two or more materials, which have different individual properties, are combined together, they form a new material with superior properties than the individual material. This entirely new material of desired properties is called the composite materials. There are different types of composites. Fibrous composites are one of them. In fibrous composites, fiber and resin serve as the main ingredient where fiber works as reinforcement and resin work as a binder which holds all the fibers together. While "basic" composites (such as glass fiber composites) offer better service than the bulk materials (such as metals), "advanced" composites (such as carbon, silicon, and aramid fiber reinforced composites) are the best for some of the structural applications and especially for aerospace and automotive structures. They are selected because these advanced composites show much higher modulus, higher strength and lower density than the basic composites as well as the bulk materials. Regardless of whether a structure is either strength critical or stiffness critical, it should posses a high strength-to-weight ratio or stiffness-to-weight ratio. These are the main reasons behind the extensive uses of composites in aerospace and automobile structures.

Other applications of composites in the structural field, for example I-beam, channel sections in civil infrastructure, are also gaining popularity. In civil infrastructure, FRP composite bridge decks are the fastest growing applications of composites. Since most of the civil structures experienced corrosive environments, thermal cycling, UV radiation, etc., materials used for this

purpose should have the ability to resist these environments. And composites have that inherent capability to resist those environments. These are the principal reasons for the increasing use of composites in civil infrastructures. Weight might be another major concern, but that is mostly in aerospace structures. Though composites have several advantages, manufacturing cost can limit their extensive uses. However, the fabrication process can play an important role in cost control of composites.

Due to the varieties of advantages over conventional materials, such as, higher durability, high strength-to-weight ratio, the high stiffness-to-weight ratio, etc., fiber reinforced polymeric composite materials draw the attention of the commercial industry. Though its application was limited to the aerospace industry and defense sectors at the eve of its emergence, its uses are spreading widely with the advancement of the technology. History show that the use of fiber reinforced polymer composites began in 1940s immediately after the invention of glass fibers by Owens and some polymer resins by chemical companies in the 1930s [1]. At the early stage of the composites era, glass fibers were added to the liquid polymers to make the composites. The marine industry started the earliest uses of the glass fiber reinforced polymeric (GFRP) composites to construct fiberglass boats. Fiberglass composites are lightweight and stronger than the conventional wood or metal components that are typically used for boat construction. On the other hand, they are less susceptible to being rotten or rusted when they come in contact with water, unlike wooden boats. Ease of maintenance is another advantage of GFRP composite parts over wooden or metal components. These benefits drew the attention of the marine industry to replace their wooden or metal boat components with GFRP composites parts in the early 1940s.

Today, glass fiber reinforced polymeric (GFRP) composites still make up 90 percent of the market. Though the theoretical high strength and lightweight properties drew the attention of the aerospace industry to replace their heavy metal parts with composites, they could not apply those in practice until further development was accomplished because composites are also brittle. This may have caused the catastrophic failure of the parts, which made them vulnerable to use in the aerospace structure. Hence, the use of this material in early the 1940s in the aerospace structure was not as widespread as was expected by the industry. However, these limitations were overcome by the researchers in 1960s when the aerospace and automobile industry started the rapid uses of GFRP products. For example, the Corvette sports car began the use of fiberglass-polyester to manufacture the sleek body. This era was called the high-performance composites era.

Since then the demand for composites is ever increasing. People were still looking for other materials which may perform better than the GFRP. Particularly, the space and aircraft industry continued their quest for new high modulus fibers. They started to develop a material that will provide more stiffness and strength. This continuous search enabled them to add two novel fibers, called carbon fiber and boron fiber, into the composite world, which are much stronger and stiffer than the glass fibers. Though the boron and graphite (carbon) fibers were invented at almost at the same time, and boron offers more strength than carbon, it was not as extensively used as the carbon fibers because carbon fibers are easier to process and also cheaper than boron fibers. Due to the high-cost, boron fibers are only used by the military as they are more concerned about the material properties rather than their costs. That's why carbon fibers have been leading the market since the 1960s in areas where GFRP fails to fulfill the needs. As

the cost of carbon fiber began to lessen, the markets for carbon fiber expanded into civil applications. Sports and automobile manufacturers also became regular customers of this material. They started to replace their parts with this material enormously. For instance, the wooden racket handles of tennis rackets and steel club shafts of golf clubs started to be replaced with carbon in the early 1970s. This low weight and high stiffness materials help the golfer by sending their shots to longer distance. It also benefited tennis players by returning the tennis balls at a higher speed. In 1971 Dupont introduce another new fiber to the world named "Aramid Fiber", which also has superior properties than carbon. It is commercially known as “Kevlar”[1].

In the next phase of composites development, further research by both academia and industry took the composites world to the next level which is nanocomposites. Researchers have still been trying to develop and improve nanocomposites since 1990s.

While the researchers were searching for new materials with improved performance, they were also trying to develop new methods that can help them process the materials at the highest speed but lowest cost. “Pultrusion” is one such type of process, which is faster than many other composite manufacturing processes and also its products are cheaper. There are several processes for composite manufacturing. Pultrusion started its journey in the early 1950s with a dramatic increase in market acceptance in 1980s. It is one of the most cost-effective methods of composites manufacturing in the commercial industry. The process begins when bundles of unidirectional fibers (termed as rovings) are pulled through a resin bath where the fiber bundles are impregnated with the thermosetting resins of desired properties. Then the resin impregnated fiber pass through a preheated die. Before entering the die, the fibers go through a preform which

confirms the alignment (or shape) of the fiber bundle. Resins are cured inside the heated die, which may be partially or fully cured, as a result of exothermic reaction started by the heat of the die. The pulling rate (e.g. pulling speed) is determined by the resin reactivity while the shape and size of the final product are determined by the die. Different shapes for the die cavity are available. The most common is the circular (rod type) or rectangular (flat type). There are some other customs shaped dies available in the market that can make the parts with different shapes such as I-beams, H-beams, etc. Once the solid parts come out of the die, they cool in ambient or forced air and are continuously pulled by pullers to the circular saw where the parts are cut into the desired lengths. A typical pultrusion process is shown in the Figure 1. Though pultrusion is a fast and cost-effective process, it can only make the parts of uniform cross-section. However, with the advancement of the technology, today's pultruders are manufacturing the parts with varying thickness. However, due to the use of thermoset resins, the final profile can't be reshaped. Though a technology of thermoplastic pultrusion is available that enables post-pultrusion reshaping, it has not reached a position of commercial significance yet [2].

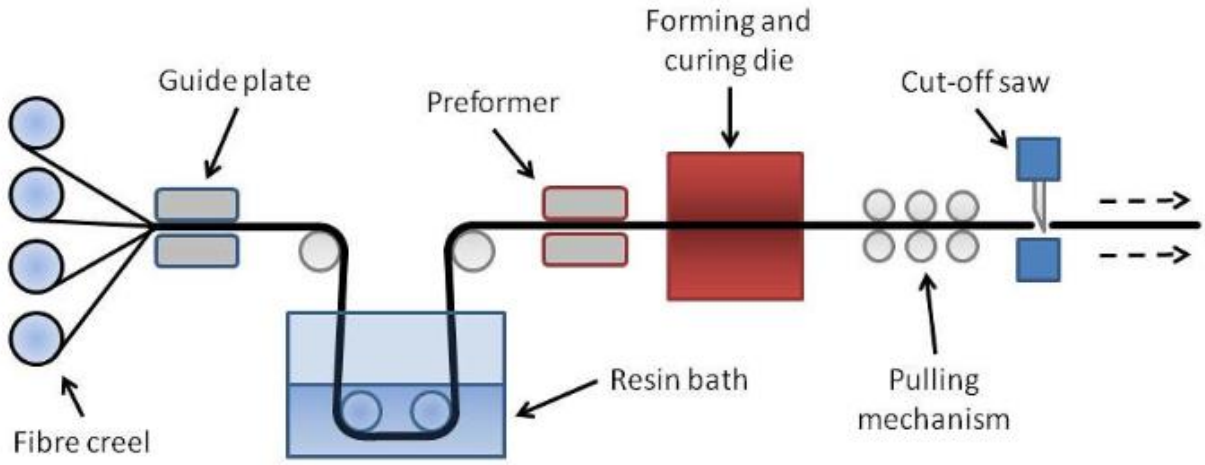


Figure 1: Typical Pultrusion Process [3]

Construction times were greatly reduced after the innovation of steel reinforcement for

concrete in the 19th century because less concrete is needed to pour into the structure if steel reinforcement is being used. It also increased the strength of the structure tremendously. This invention also made structural engineers hopeful that such reinforced structures would probably last more than 1000 years. But in reality, they found it had around 50-100 years of service life. Hence, the quest for long-lasting materials is still going on. In recent years, polymer-based composites are increasingly being used in numerous applications, especially in civil infrastructure and in hostile environments, for their long-term durability over the metals. Since the vinyl ester and isophthalic polyester (isopolyester) resin systems give desirable properties and are easy to process with fiber reinforcement, they are commonly used in constructional applications [4]. Another reason for replacing the steel and concrete structures with polymer composites is the repair costs. The writer Robert Courland mentions in his book "*Concrete Planet*" that in the future, the United States will pay trillions of dollars just for the repair and rebuilding of concrete infrastructure. In the United States, total repairing costs of corroded steel and concrete structures are around $250 billion per year [5]. Another study shows that there is $150 billion loss of money due to the corrosion of interstate highway bridges, caused by deicing and sea salts. The Transportation Research Board estimates $50-200 million for annual bridge deck repairs while substructure and other components cost $100 million per year and $50-150 million for multi-story car parks (Transportation Research Board, 1991). A more recent corrosion study estimates an annual direct cost of $8.3 billion for US highway bridge corrosion that constructed with reinforced concrete [6].

Following these statistics, the use of high-performance materials for construction is recommended by the Civil Engineering Research Foundation (CERF), which will reduce the cost by its long period of service, less maintenance, and lower mass. Fiber reinforced polymer (FRP) composites are such types of materials that would be a better choice of replacement due to their inherent corrosion resistance, high strength to weight ratio, and chemical resistance. However, these polymeric materials are susceptible to the physical damage and chemical degradation initiated by the photo-initiated oxidation [4]. As composites materials have to go through a long service life, they experience a lot of harsh weather. They are subjected to moisture ingression, thermal cycling, UV radiation, cyclic loading, and other environmental stresses during their service. All these degrade their inherent mechanical properties by altering the chemical structures as well as changing them physically and cosmetically. A better understanding of these processes is critical for the more extensive use of FRP in civil engineering application.

The development of a new test or design standard for FRP composites is challenging since it is a new and developing field where new materials are still emerging. In addition, a large number of combinations of different materials may result in varieties of properties. Composites materials show more complex structure and properties than conventional materials. Composites are said to be anisotropic (specifically orthotropic), meaning their properties vary along with directions. For example, they show different properties in X, Y and Z directions, whereas most conventional materials show the same properties regardless of the direction. The property of most metals remains the same in all the X, Y and Z planes. Hence, they are called isotropic materials.

Another obstacle preventing the wide acceptance of polymeric composites for civil infrastructure applications is the lack of adequate data. It is believed that fiber reinforced composites structure can give a better service, higher strength, and longer durability than the equivalent conventional material structures. And that is only possible if FRP can be properly designed, easily fabricated, and have sufficient data to predict their behavior. Since the pultrusion process is one of the easiest, cost-effective methods for FRP manufacturing and it has a great potential to use in structural applications, sufficient data is really needed for this material for structural applications. This need is felt by the American Society of Civil Engineers (ASCE). Hence, they are trying to develop a load and resistance factor design (LRFD) standard for pultruded fiber reinforced polymer structures [7].This project has been initiated by the Pultrusion Industry Council of the American Composites Manufacturing Associations (ACMA). This present research project is a part of that project to provide the background data that will facilitate the LRFD standard development and the development of new test standard for pultruded composites.

Natural disasters, which are pretty common in every country, especially in coastal areas, are another concern of replacing traditional materials with fiber reinforced composites used in the civil infrastructure. The infrastructures in the coastal regions need to be more disaster proof. Traditionally used reinforced concrete cannot perform well every time. They are unable to withstand most of the time even if special care is taken, such as higher factor of safety. The recent Hurricane Irma (August, 2017) resulted in caused an estimated at $50 billion which is the costliest disaster in the history of Florida, USA. Another Hurricane Maria (September, 2017), in the Virgin Island of USA, is considered the third-costliest storm in the nation’s history, causing

around $90 billion in damages. These costs are mostly associated with the infrastructures. One of the interesting findings from those hurricanes came out of a report by Shane Weyant, President and CEO of Creative Pultrusion Inc., [8]. He reported Hurricane Irma and Maria damaged all but eight utility poles in the Virginia Islands, and the undamaged poles are made out of composites. He emphasized that composites can stand in storms while other materials fail. He further mentioned that in spite of many advantages of composites, the lack of adequate standard and awareness restricts the rapid adaptation of this material into infrastructures. Most of the composite manufacturing companies are too small to fund standard development projects. This limits the availability of composite handbooks compared to the handbooks that describe the standards available for the traditional materials. However, if the government, industry, and university researchers come forward to work together, it is possible to establish more standards for advanced composite materials.

Another need for standard development for composites is also cited by Michael. J Hoke [9], owner of Abaris Training Resources Inc. He said that the information about the lack of standards of the composites industry is not entirely true. Focusing on the aircraft industry, where composites are mostly used, Hoke noted that different large aircraft manufacturing companies, such as Boeing, Airbus or Embraer, follow their own standard for almost same identical structures. They do the same repairs, but in their own way, which might confuse technicians who work for one company but move to another. Though the Commercial Aircraft Composite Repair Committee (CACRC) has been developing standards since 1990, their progress is really slow. Hence, it is necessary to develop a uniform standard by the large companies to make it easy for all practitioners.

Pultrusion products, which have a great importance to civil infrastructure applications, also urge more standards to develop for their widespread application. In spite of the significant research in pultrusion, the lack of proper standards is one of the major barriers of the growth of this industry. Pultruded composites are undoubtedly one of the high strength materials, but people of this industry still feel the lack of confidence in the durability of this product. Since the materials used in civil infrastructure require long term service time, proper durability information is indispecible for their successful application. This also urges the Pultrusion Industrial Council to establish the standards especially for the durability. It is expected that the fiber reinforced composites have the ability to compete with traditional construction materials such as concrete, steel, aluminum, wood, etc. once proper standards are developed for them. Those standards will provide more confidence for the owner, designer, and other practitioners to use in their needs [10].

CHAPTER II: BACKGROUND

Proper understanding of composite behavior is a must for its successful applications. Pultruded products are often used for structural applications. Since most of the structural materials used in civil engineering applications spend their lives in open environments, prediction of behavior in such an environment is one of the major concerns. The understanding of how pultruded composites respond to various environments is critical for the successful application of these materials in infrastructure applications that are commonly exposed to a variety of conditions. In order to design safe composites infrastructure, the proper understanding of its behavior in different environments is a must, which will facilitate the utilization of the full potential of this material.

Perhaps the first study of composites behavior in various environments was started with exposing them to the humid air. After that, researchers started to predict the response of liquid immersion composites [11], [12]. They determined various properties such as strength, fatigue, matrix cracking, interface bonding, electrical properties, etc. to compare the before and after exposure behavior. They did not confine themselves to only those two environments but rather continued their search to predict the behavior under other environments such as temperature, UV radiation, etc. They also identified the need for the evaluation of synergistic effect on composites, meaning the combined effects of two or more environments. For example, the effects of thermal cycling and relative humidity, temperature and liquid immersion, etc. were examined. This is important because composites are subjected to spend their lives where two or

more environment may be present simultaneously. Therefore, one of the purposes of this present study is to predict the durability of composites, specifically the commercially pultruded composites and to provide background data to help set a standard to measure their degraded properties.

Research related to the moisture absorption in composites started to be published in the early 1960s, and most of the published reports were concentrated on aerospace applications because that is the field where composites were used most during that period. A paper titled "Diffusion of Elastomers" by Amerogen et al. in 1964 may be consider one of the oldest published papers that discusses the moisture absorption of composite materials [13]. Since the marine industry and defense sectors were the earliest users of composites, nobody will be surprised that an analytical paper on corrosion behavior of GFRP (glass-fiber reinforced polymer) composites comes from them. In 1966, the British Navy reported the effect of water on GFRP and analyzed their corrosion behavior in an early paper on corrosion studies of composites. Halpin, one of the experts in composites who contributed in the field of composites design and analysis with his fellow researcher Tsai, studied the "Effect of Environmental Factors on Composites Materials" in 1967 and released his findings in 1968. This work was officially published in 1969. This is one of the earliest reports on environmental effects on composites which effectively explained the effects of the environments on fiber strength, interface, reversible and irreversible temperature effects on matrix, etc. Halpin not only gave some experimental data but also used an analytical approach to evaluate the environmental effects on the performance of composite structures. Interestingly, this project was also funded by the United States Air Force Materials Laboratory Wright-Patterson Air Force Base in Ohio [14].

Mass uptake in composites can take place by both absorption and adsorption. While the former is the bulk effect, the later is the surface effect. All polymers have inherent defects that are probably responsible for that absorption or adsorption. Typically those inherent defects are mainly the results of manufacturing defects that occur due to the voids, microcracks, interphase gaps, etc. Researchers also figured out how this mass uptake takes place the composites. Though there is some controversy on whether they follow the Fickian or non-Fickian laws of diffusion, they agreed that diffusion process follows Fick's Law at the composites initial stage of moisture uptake. Shen's article titled "Moisture Absorption and Desorption of Composite Materials", is one of the earliest papers published in 1976, reveals this fact of utilizing the Fourier's Law of Thermodynamics and Fick's Law. Testing the samples exposed to humid air or a water solution either on one side or both sides of the materials, Shen reported that test data gave the moisture absorption and desorption characteristics of composites and also supported the analytical results [15]. Many researchers agreed that short-term exposure follows Fickian behavior while long-term exposure showed non-Fickian behavior. Karbari (2004) reported that mass uptake shows two-staged Fickian response. Mass uptake steadily increases up to 4 to 12 weeks of exposure, when it shows a plateau. Then it continues the absorption unless it reaches the saturation point but this rate of moisture uptake is much lower than the initial uptake rate [16].

Researchers also consider temperature during their moisture uptake study to evaluate the synergistic effect of these two environments. Some of them performed experiments at a constant temperature and some of them vary it within a certain range, mostly following the service conditions or glass transition temperature as the maximum temperature the material can take.

Karbhari (2004) also showed diffusivity increases with the increase of temperature. One of the most important environmental conditions that everyone is concerned about is the hygrothermal aging scheme, which is also referred to as hot/wet condition. In this scheme, three parameters, such as temperature, moisture and time, are considered simultaneously to simulate the effects of long-term exposure. The long-term exposure is intensified by these factors. Then the mechanical properties are compared prior to and after the exposure in order to see the final outcome and thus to qualify the materials for service [16].

Time plays another important role in moisture absorption of composites. In 1980, Alfred Loos and George Springer measured the weight change of polyester-E glass composites as a function of exposure time and temperature by immersing them in various solutions. In addition, they mentioned that weight change depends on the material's composition and nature of the environment (e.g. RH of the air, type of the liquid used, etc.). They determined the weight changes of the materials by calculating the apparent maximum moisture content and apparent diffusivity, assuming diffusion followed Fick's Law [11], [12]. Loos and Springer had carried out another study with an almost identical environment but entirely different materials in the previous year, in 1979, where they found almost the same behavior (e.g. moisture absorption is a function of exposure time and temperature regardless of materials). But some dissimilarity was also noticed due to different material composition. For example, Graphite-Epoxy composites diffusivity was not affected significantly by humid air, unlike the Polyester-E glass composites. They also reported that high temperature and high moisture immersion may develop cracks on the surface of the material, which may alter the maximum moisture content and diffusivity significantly [11], [12].

Since moisture has an adverse effect on composites, it is important to know the absorption characteristics on the composites intended for infrastructure applications. Since most of the composite structures are subjected to prolonged service, it is often necessary to predict the long-term environmental effects on these materials. Therefore, today's researchers have started to develop a method that will help them evaluate the long-term effects in the laboratory. Some of them use corrosive media to obtain the same long term degradation of composites in relatively less time, which is called the "accelerated aging" because for laboratory work it is impractical to expose a sample for 50-60 years in order to get real-life data. It is better to obtain almost the same result in comparatively less time by exposing the samples in a corrosive environment. In 1980, Griffith described a method to estimate the long-term effect of unidirectional off-axis graphite/epoxy laminates from short-term laboratory exposure. Though there are many accelerating parameters, such as temperature, time, humidity, stress, etc., the author considered temperature and stress as their accelerating factors. They used the time-temperature superposition principle in their study since temperature can create one of the best accelerating environments in a shorter time frame. They concluded that the prediction of the long-term behavior of off-axis unidirectional laminates can be evaluated viably by TSTSP (Time-Stress-Temperature Superposition Principle) and orthotropic transformation equations, which can also be applicable to any other complex laminates. This project was funded by materials and the physical science branch of NASA-Ames [17]. In 1987, Ciriscioli et al., describe a two-step method to determine the accelerated moisture conditioning of graphite-epoxy composites. Upon validating the methods by mechanical testing, they compared the results with regular (non-accelerated) conditioning. Initial conditioning of 100% RH (Relative Humidity) environment

confirmed the accelerated process of moisture uptake. They found that a target moisture level of 68% was achieved in 170 days by the accelerated scheme, while it took 800 days by the regular method to reach the same target moisture level (68%). Materials experience a number of service conditions in their prolonged service life that can be reproduced in laboratories in various ways [18].

In the early stage of the composites era, composites were mostly utilized by commercial aircraft. Hence, NASA and the U.S. Army started to investigate the durability of this material over 20 years of service life in the early 1970s. Flight service environments such as moisture, thermal cycling, lighting strikes, UV, etc. were examined to predict the behavior of aerospace composites structure. In 1992, Dexter and Baker examined the different composites parts used in different locations of various flights. For example, they studied graphite/epoxy spoilers of B737, graphite/epoxy elevators of B727, and graphite epoxy ailerons of L-1011, etc. after their extended service of several years. They found a little damage in some of the parts while most of them were not damaged. Since the airplanes spend most of their time on the ground, it is prudent to examine the ground-based exposure along with flight-based exposure. The researchers of this project also concluded that coupons produced for ground-based exposure had absorbed 0.7% to 1.0% moisture in 10 years and reduced their matrix-dominated properties by 20% in 10 years [19]. The RAAF (Royal Australian Air Force) has used boron/epoxy and graphite epoxy since the 1970s to construct many airplane parts. Since the real long-term effect that the materials experience during their service life from laboratory experiment is impractical to achieve, Roger Vodicka addressed the methods that can give the same long-term effects at the laboratory but at short-time exposure for aircraft applications in his paper in 1998 [20]. The author studied the

effects of the environment under Australian climatic conditions, focusing on the materials used by the RAAF. He mentioned that special cautions should be taken while creating the accelerated testing environments which will replicate the long-term effects. He emphasized that environment selection should be carried out in such a way that it becomes a true representative of airplane flight and ground climates. If the samples used for testing are not exposed in an environment that they never sees in service, test results will reflect the real value, though it is hard to achieve the real environments in laboratory conditions. The report did not say anything about the corrosion or effect of a chemical such as fuel on the materials while addressing the durability and strength of the materials [20].

Although many researchers employ accelerated conditioning methods to simulate long-term environmental exposure, there is some controversy regarding the creation of a long-term laboratory environment. The question arises, is it really possible to obtain the same long-term effect from short term accelerated exposure? Zafari explained in his report that though high-temperature aging gives the long-term effect at a very short period, it can't confirm real long-term degradation. Because composites may undergo some additional chemical degradations at high temperature accelerated aging than they really are in actual prolonged exposure. He also mentioned accelerated aging cannot exactly replicate the long-term mechanical degradation in FRP structure what they would give in real field application for the long-term [21]. Besides, some researchers also tried to predict long term behavior by extrapolating the short-term results [22], [23].

Pultruded composites have taken the lead in structural applications over the last few decades. Hence, the study of environmental effects on this material is also important. Engineers and industrial designers often supporting pultruded structural shapes to replace metal parts because they are extremely lightweight and have a few other advantages. For example, structural pultruded products are 70% and 30% lighter than steel and aluminum, respectively. They are considerably lighter than structural timber as well [24]. Standard structural pultruded shapes offer superior long-term resistance to chemical attacks. Glass fiber reinforced pultruded composites can also resist the galvanic corrosion without any extra coatings, unlike the metal. Therefore, in the structures that are susceptible to photo-induced oxidation, pultruded composites would be a better solution. Another reason for replacing the heavy steel structures with this lightweight material is the strength to weight ratio. A pultruded structure could be three to four times stronger than the same steel structure. Besides, this great material is easy to install and requires little maintenance. Structures previously made of wood can be out of danger of rotting once this inherently chemical resistance material is used. This can also eliminate the problem of rusting or scaling associated with steel structural materials. The non-conductive nature of this material can enable them to use as insulation in electrical applications. GFRP pultrusion is transparent to radio waves and EMI/RFI transmissions, which make them a good choice for radio, radar, and antenna applications. Tailoring the strength in any direction of this orthotropic material can help the users to modify them according to their needs, unlike isotropic metal, in which the properties are the same in every direction. For example, it is possible to make a structure stronger in a particular direction rather than in all directions. Most importantly the dimensional stability of pultruded products makes them suitable for structural application compared to metals such as aluminum [24].

Though it is advantageous to use pultruded shapes in infrastructure, its behavior under various environmental short-term and long-term conditions need to be well understood. In 1994, the researchers started to evaluate the effects of simulated environments on pultruded composites with various fiber architectures and matrix compositions. In 1995, Bank identified the long-term performance of highway structural FRP composites in "Accelerated Test Methods to Determine the Long-term Behavior of FRP Composites Structures: Environmental Effects". The impact of physical and mechanical properties changes was evaluated by exposing the FRP composites into liquid, gaseous, temperature, and moisture medium. The synergistic effect of exposure conditions and mechanical loading was also determined [25]. In order to certify the materials for aircraft structure, it is important for the designers and researchers to understand the environmental conditions. This will ensure the uses of the material confidently for such a critical structure.

In 1997, the durability of these construction materials was characterized by Chin and her fellow researcher by exposing the materials in accelerated aging environments. Those environments included UV radiation, alkaline solutions, high pH environment, etc. Testing the specimen after 1300 hours of immersion, they identified little drops in tensile strength and glass transition temperature of vinylester. However, considerable changes in mechanical properties were seen for isopolyester. Both composites showed the same type of surface erosion and surface cracking but followed their own chemical mechanism to degrade [5]. In 2003, Karbhari observed the adverse effect of elevated temperature on property degradation of the composite [26]. Hence, he recommended the FRP materials with a Tg of at least 30^0C greater than the service

temperature for design purposes. Immersing the fillers and low profile additives (LPA) added polyester/E glass pultruded specimen in distilled water and seawater as a function of temperature, H. Ben Daly, et al. investigated the water absorption process of these materials [27]. At high temperature, they also noticed the composites ingressed more distilled water than sea water. Formation of microvoids by LPA, promoted a significant water uptake compared to the non-additives sample. Daly, et al identified that water absorption process followed the Fickian theory. Furthermore, they found a parabolic profile of humidity distribution across the thickness of the sample using the microtome technique, which was the most interesting findings of this study.

Vinylester and polyester composites are both suitable for civil engineering and construction applications due to their desirable properties and ease of processing. In 2015, Grammatikos et al. published two papers to assess the moisture uptake and hygrothermal aging degradation of pultruded composites used in civil applications. Grammatikos examined that the moisture uptake behavior of E-glass/polyester (isophthalic) pultruded composites under hot/wet conditions. Applying the three-dimensional Fickian theory, he revealed the fact that moisture diffusion in longitudinal (pultrusion) direction dominates transverse and through-thickness principal directions. In addition, he got some interesting findings from this long-term (224 days) exposed samples. For example, moisture uptake rate and chemical degradation were greatly influenced by the hot/wet aging. Sample size plays an important role in moisture diffusion. Small samples reach saturation at relatively earlier time periods than the large samples. Even large samples are unable to reach to the saturation conditions after 224 days. His analysis of chemical degradation of the materials was further strengthened by supplementary testing by FTIR (Fourier

Transform Infrared Spectroscopy), EDS (Energy Dispersive Spectroscopy), etc. He also suggested the computational modelers take special care during their modeling since the behaviors of the fiber-reinforced material are extremely dependent on processing and composition [28].

In his second paper, Grammatikos investigated the hydrothermal aging of this material. He noticed an increase in moisture diffusion at an elevated temperature after a certain period of immersion. While he identified the significant drops in matrix-dominated properties, such as in-plane shear strength and modulus, the tensile strength and modulus in pultrusion direction were intact after hygrothermal aging. The unchanged fiber/matrix interface was also noticed even if the materials were exposed in the most aggressive environment. Another finding of his study was the leaching out of low molecular weight material at high immersion temperature [29]. The same phenomenon of leaching out of low molecular weight polymer was also noticed by Chin et al. (2001) in her study of environmental effects on the vinylester and polyester pultruded composites. Chin observed an increase in glass transition temperature, which was the results of that hydrolysis and dissolution of low molecular weight segments of the polymer matrix. Hydrolysis of the polymer was also evident by the spectroscopy analysis in her research. She concluded that the elevated temperature reduced the interlaminar shear strength of both of the composites but to a different extent. For example, the degradation of vinylester composite is lower than the polyester due to the terminal methyl groups [12]. Xin further investigated the hydrothermal aging on pultruded composites used in bridge applications in 2016 [30]. His results followed the same trend as Grammatikos especially for degradation of strength and modulus (but in this case it is flexural strength instead of tensile) at high temperature. He noticed a higher loss

of flexural strength and modulus in a transverse direction compared to the longitudinal direction. One of the interesting outcomes from this research is the prediction of long-term effects of hygrothermal aging on flexural properties. He used Phillips equation and the Arrhenius relationship to forecast 100 years of service of FRP laminates [17].

Since the safest design is always a concern for both the designers and the users, it is important to know the pin-bearing strength of the bolted connected structure in an environment where it supposed to spend its entire life. In 2012, Zafari carried out such a study on pultruded polyester matrix in a hygrothermal aged environment to observe pin-bearing strength behavior. He observed a 20-30% drop of pin bearing strength after 3000 hours of aging compared to the non-aged values at an elevated temperature of 40C. The fiber in longitudinal direction showed a higher drop of 30%, while 45 degree and 90 degree materials orientation showed a drop of 20% of their pin-bearing strength [21].

Alkaline environments can also degrade the performance of the polymer composites. Fiber-reinforced polymer composite structures may be exposed to alkaline environments throughout their service life. Hence, it is important to understand the impact of alkali on the property degradation of polymeric composites. Studies of the effects of the alkaline environment can be found in the open literature. Alkaline environments may consist of caustic soda (NaOH) solution, potassium hydroxide (KOH) solution, calcium hydroxide (Ca(OH)2) solution, bleach solution and many others. The pH level of these environments can vary from 12.0 to 14.0 or more. When fiber-reinforced polymeric composites are immersed into any of these solutions, they absorb alkali solution, especially the polymer matrix, due to its chemical nature which

results in delamination and crack formation in the fiber-matrix interface. These delamination or cracks behave like pores which allow more chemical to pass through it which cause the degradation of the composites. As time passes, the number of cracks or size of pores or delamination increases due to the progression of degradation. When the chemical solution passes the polymer layer, it reaches to the fiber and attacks the fiber surface. This results in weakening the composite structures because both polymer matrix and fiber carry the loads together.

Researchers have evaluated the negative impact of the alkaline solution on fiber-reinforced polymer composites. Amaro et al. submerged their glass fiber/epoxy composites into the NaOH solution of pH 13.0 and evaluated the flexural properties and impact strength of the composites [31]. They noticed the aggressive behavior of alkaline solution on polymeric composites. They reported the significant reduction of both flexural properties, such as flexural strength and flexural modulus, and impact strength. Their comparison of alkali effects with acid solution revealed that alkali solution is more aggressive than the acid solution. They also observed that exposure time plays an important role in property degradation of polymer composites. Won et al. also studied the effects of alkaline solution on the glass fiber reinforced polymer (GFRP) rebar. They immersed their E-glass/vinyl ester composites in an alkaline solution of a pH 12.6 for 300 days [32]. They noticed the reduction of mechanical performance of fiber-reinforced composites rebar under the influence of the alkali solution. They examined the deformation of the GRFP rebar surfaces along with the reduction of the tensile strength of the GRFP rebar. Chin et al. also reported the adverse effects of the alkaline environment on vinyl ester and isopolyester composites [5]. They reported that the effect of alkali is more pronounced at elevated temperature (60^0C) compared to the room temperature.

Although significant efforts have been made in the last few decades, there is still a lack of data for the durability characterization of composites. Hence, insufficient data is one of the major hindrances of exploitation of FRP composites in structural applications. Even though there are some valid data, they are not standardly collected. Some of them are also not easily accessible to the designers or engineers. This limits the structural designer's and civil engineer's abilities to utilize the benefits of this material. Furthermore, many of the available data are published in different sources, and this makes it use difficult and questionable due to its dispersedness and trustworthiness. In addition, many researchers summarize the results of durability studies in their review papers instead of identifying the critical areas where data collection is required. Possibly, this is another shortcoming of the durability database for structural FRP composites.

In 2003, Karbhari performed an extensive gap analysis for fiber-reinforced composites used in civil infrastructure. He focused on prioritizing areas of need to be focused on for durability data collection. Experts from seven different fields formed a panel consisting of seven groups to serve the purpose. This gap analysis identified the fields where the data is essential and categorized the areas on a priority basis. The report mentioned that data collection for filling up the current gaps should follow certain procedures and protocols instead of collecting randomly [10]. The need for a design standard for durability characterization of pultruded composites was also identified by the Pultrusion Industry Council of American Composites Manufacturing Association (ACMA). In 2017, National Institute of Standards and Technology (NIST), U.S. Department of Commerce, reported the insufficient information about the durability and service life of FRP composites which are subjected to UV/moisture, temperature exposure, and other

environments as one of the greatest obstacles of extensive use of this material. Hence, they identified a similar need for the establishment of durability standards. Though some legacy data on the durability of composites are available, they are not open to all of the composite designers and practitioners. This was termed as another major hindrance for the exploitation of FRP composites in the report. Since the data came from various manufacturers and researchers, sometimes it is hard to get a consensus of opinion for standards development [33]. Furthermore, this consensus-based standard would take a long time to get approval. These are the few more challenges for standards development. Some standards and codes for FRP designs are available but they need to pass more engineering judgments for their acceptance.

In 2016, Lackey conducted a study related to defining a test standard for environmental characterization of pultruded composites. Her findings showed that short-beam shear (ASTM D-2344) is the preferred method to evaluate the property of pultruded composites exposed to the environmental conditions used for structured applications. She concluded that ASTM D-2344 can provide the earliest sign of property degradation of the pultruded composites intended for the use in structural design [34].

Development of a new standard or code is a long and tedious process since it needs cooperation among the industry, academia, and government. Public-private collaboration is also inevitable because the research must be commercially relevant. Hence, the relevant industry should come forward with their needs and shortcomings of the field. In addition, standard or code development may take several years. However, the end-users, engineers, architects, and designers will get the benefits of it once it is established. The American Society of Civil

Engineers (ASCE) Pre-standard for Load and Resistance Factor Design (LFRD) of Pultruded FRP Structures is one such standard that is being developed related to the need that was identified in the NIST report. This current research is a part of that project that will facilitate LRFD standard development by providing the background data for the development of durability standard for pultruded composites.

CHAPTER III: METHODOLOGY

Information on how environmental exposure might affect the mechanical properties of coupon samples taken from structural shaped exposed plates of pultruded composites is needed to help the researchers as they take samples for mechanical testing to characterize the effects of environmental conditioning on the overall properties of composites. Though many studies have been conducted that showed the effects of environmental conditioning, none of those tell anything about the degradation pattern at various locations of the samples. Numerous researchers studied the moisture uptake in pultruded composites and examined the effects of water uptake on mechanical properties of composites; however, most of the researchers studied do not indicate what location of an exposed composite part of coupon samples were taken from and whether any variation in properties due to the location was seen for the exposed sample. For instance, Grammatikos et al. (2015) identified that the diffusion coefficient in the longitudinal (pull direction) was an order of magnitude higher than in the transverse and through thickness [28]. This might suggest that samples taken from the interior of a pultruded plate would have significantly less affects from moisture, but this is not clearly mentioned in their study. Hence, the primary objective of this current project is to identify the effects of sample locations on the mechanical properties of coupon samples taken from two different locations of larger plates of pultruded composites that had been exposed to different environmental conditions. Data were taken at different time periods named as no-exposure, short-term exposure, and long-term exposure.

This present research is follow-up work done by the fellow researchers of the Pultrusion Lab of the University of Mississippi. In the previous work, researchers examined which test method gives the earliest sign of sample deterioration exposed to identical environments. They compared the test results between combined loading compression (CLC) and short beam strength and identified that short beam testing ASTM-D2344 is more suitable for this purpose [34]. Hence, only short beam testing (ASTM-D2344) will be used throughout the project for data collection and analysis. Obtained data will be utilized for the development of a novel ASTM standard for the environmental characterization of pultruded composites.

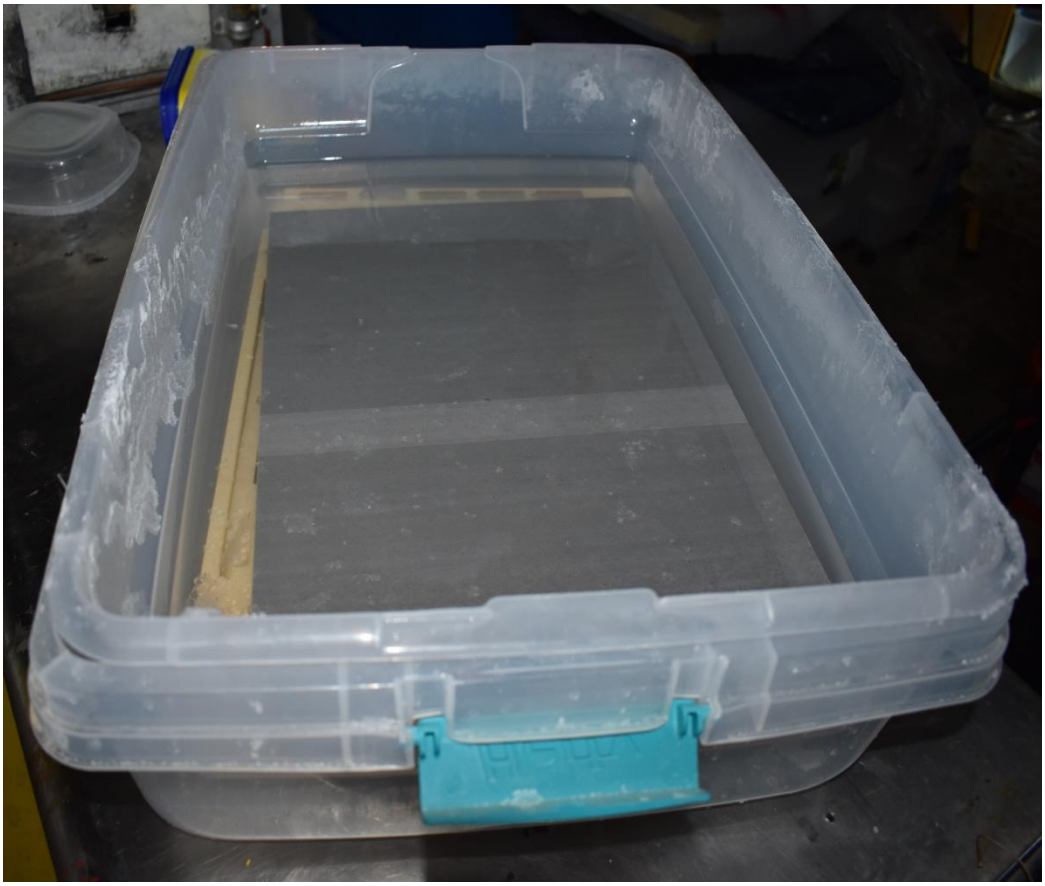
The Pultrusion Lab of the University of Mississippi is taking part in the development of standards in support of the development of the Load and Resistance Factor Design (LFRD) Pre-standard for Pultruded FRP Structures. This project is initiated by the American Composites Manufacturing Association (ACMA) and the American Society of Civil Engineers (ASCE). These groups formed a committee with various sub-committees with various industry people and researchers. The University of Mississippi is a member of this committee, and this current project will provide the supporting data for that LFRD standard development.

In order to determine the effects of short-term and long-term environmental conditioning on pultruded composites, specific pultruded parts (larger parts 18”×14”×0.25”) were immersed into two separate test mediums, namely: Great Value^{TM} Distilled water and Great Value^{TM} Easy Pour Bleach (5% weight sodium hypochlorite). It is hoped that these environments will create almost the same effects that the outdoor environment could create on fiber reinforced polymer composites used for outdoor applications. These exposure environments were chosen so that

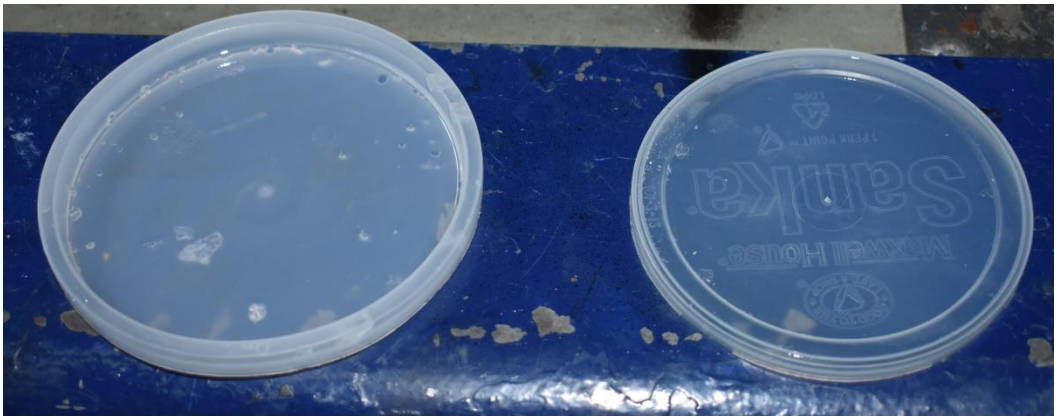
present study could provide follow-up data to the study performed by Hedgepeth [35], and both of these environments are test environments specified in the LRFD pre-standard [7].

It is a common practice to determine the environmental degradation of materials in the laboratory. Many researchers also used the same procedure to examine the environmental conditioning effects on different types of fiber-reinforced polymer composites. For example, Chin et al. (2001) used water, salt water, and an artificial concrete pore solution to characterize chemical and physical behaviors of GFRP VE and PE materials [4]. Daly et al. (2007) submerged their samples into both distilled water and seawater at different temperatures to investigate the water absorption [27]. Chu et al. (2004) exposed their specimens to deionized water and alkaline solutions at four different temperatures to characterize the durability of glass-fiber/vinyl ester systems [36]. Gautier et al. submerged their samples in water at different temperatures to determine the interface damage of GFRP polyester composites [37]. Zafari et al. (2012) simply used warm water for 3,000 hours of soaking the samples to evaluate the pin-bearing strength [21]. Grammatikos et al. (2015) used distilled water at numerous temperatures for their moisture uptake study [28]. In 2013, Lackey et al. exposed pultruded polyester/e-glass and vinylester/e-glass composites to distilled water and an alkali solution and compared baseline and experimental tensile data using ASTM D638-10 [38]. Hedgepeth (2016), used HCl, bleach, and distilled water to determine the test method which will facilitate a new standard practice to characterize the durability of the pultruded composites for structural applications [35].

Two different commercially pultruded E-glass fiber reinforced polymer composites, namely: polyester (PE) pultruded composites and vinylester (VE) pultruded composites, were used for the current study. Sample panels that were approximately 18 inches long, 14 inches wide, and 0.25 inch thick were cut from 48-inches wide commercially pultruded panels. Two plastic storage containers slightly larger than the samples with airtight-locking tops were used for the immersion of these pultruded composites plates. Both of the containers were filled with respective liquids, i.e. distilled water and bleach solution, in such a way that all the samples were completely submerged into the liquids (Figure 2a). Since each container contained two samples, i.e. one large plate of PE and another large plate of VE, one panel were placed on top of the other. The two different samples of each container were separated with four small plastic pieces (Figure 2b). They were placed underneath the four corners of each sample so that the bottom surface of the top sample did not touch the top surface of the bottom sample. And also the bottom surface of the bottom sample did not touch the container surface. Thus, all the four exposed surfaces of those two samples were ensured to be completely submerged in the exposure bath. Then the plastic storage containers were locked with airtight tops and kept at room temperature in order to obtain the short-term and long-term exposed coupon samples. The sample container is shown in Figure 3.



(a)



(b)

Figure 2: (a) Samples completely submerged into liquid, (b) Small plastic pieces used to keep panel separated

Figure 3: Plastic storage container with airtight-locking tops

Since the samples were left for a long time, the chemical level was periodically (twice a week) checked in order to make sure the samples are fully submerged into the chemicals. Sometimes extra distilled water and bleach solution needed to be poured into the container to recover their losses due to evaporation. Rapid loss of bleach solution was noticed compared to the distilled water after a couple of months, which was very unusual. Then the plastic container containing the bleached solution went through a leak test, and leaks were detected. This was the reason for the rapid loss of bleach solution. Upon replacing the container with a new one, samples were immersed into the plastic container following the aforementioned procedure. No considerable loss of bleach was noticed after that.

The first round of testing was performed on unexposed pultruded samples termed as-pultruded control samples of the same materials (PE and VE) with the same geometrical configuration (18”×14”×0.25”). Prior to testing, coupon samples were prepared from the larger plates using the abrasive water jet machine with a cutting speed of 4.8 in/min. The abrasive water jet uses a stream of water with garnet abrasive to cut samples. Two different locations of larger parts were selected to cut the samples, namely: Center and Cut Edge. At least five samples were taken from each location, and short-beam strength was determined. Before testing, samples were marked with a permanent marker (as shown in Figure 4). Since the samples were too small to write down the complete locations on each one, samples from each location were collected into separate plastic bags so that they could be easily identified. The dimension of the water jet cut sample was 6.5”×0.5”×0.25” for each material. A diamond wafering saw was then used to cut the final small samples (described later). Damage was created if the water jet was used to cut out the individual short beam samples, so the diamond wafering saw was used to cut the individual short beam samples from the strip cut out using the water jet. Sample cutting was completed within approximately four hours of removal from the exposure bath.

Following the ASTM D 2344-13 procedure, the short-beam strength of each sample was measured. A 22 kips MTS 810 Material Test System universal testing machine was used for this purpose, and it recorded the peak loads through its data acquisition system. Finally, the short-beam strength was calculated as per Eq.1 from ASTM D2344-13.

$$F_{sbs} = 0.75 \times \left(\frac{P_m}{b \times h}\right) \qquad (Eq.1)$$

Where,

F_{sbs}= *Short-beam strength (psi),*

P_m= *Maximum load observed during the test (lbf),*

b= Measured specimen wide (in.), and

h= Measured specimen height (in.)

All the data were recorded for the future analysis. Figures 5 and 6 showed the test apparatus and sample failure, respectively. The shear-type failure typically seen for each sample tested can clearly be seen in Figure 6a.

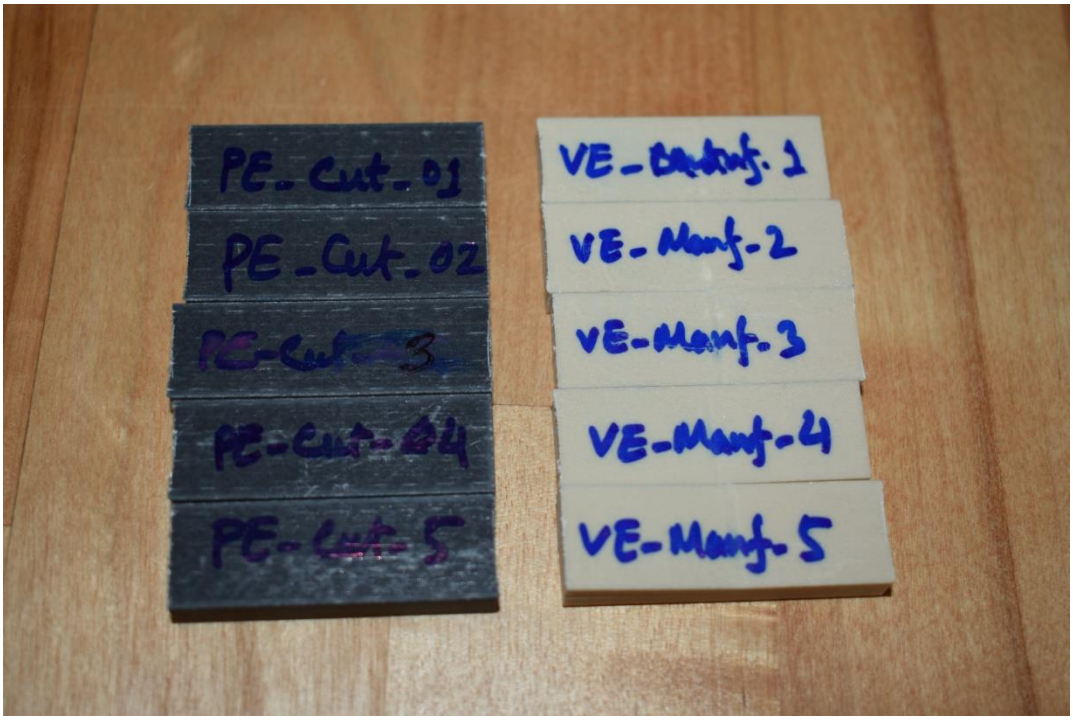
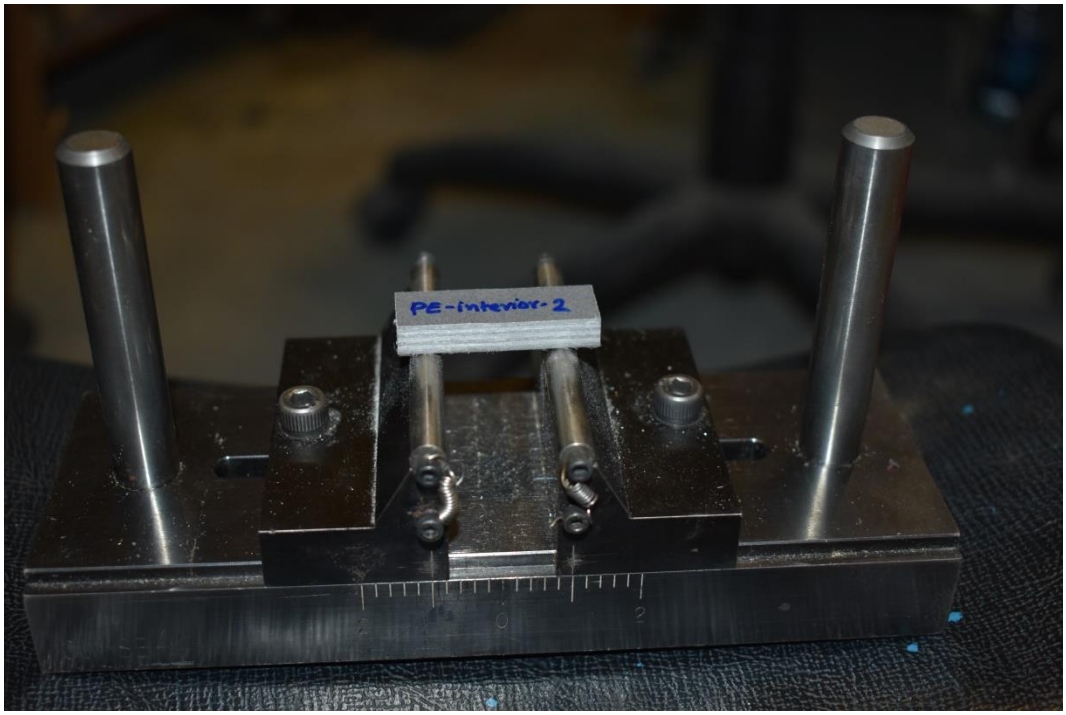
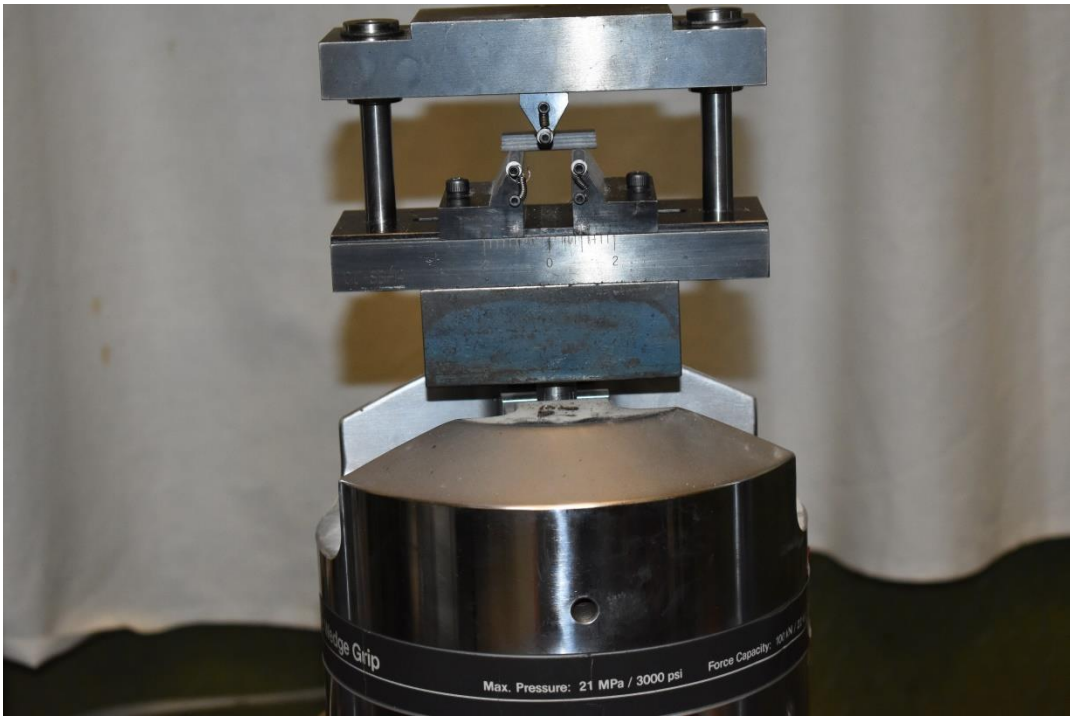


Figure 4: Samples marked with permanent marker (short beam samples nominally 1.5”×0.5”×0.25”)



(a)

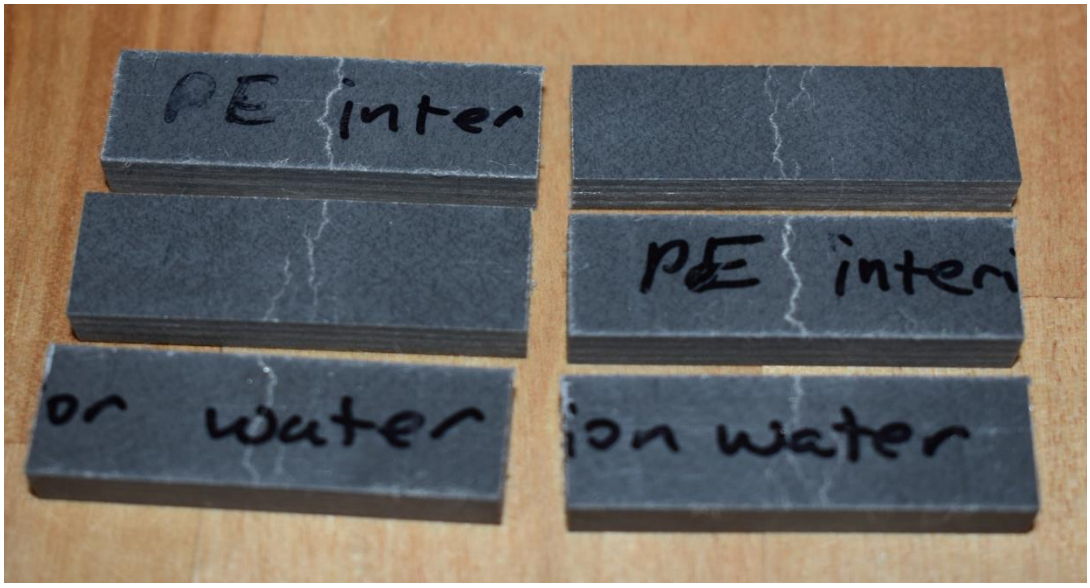


(b)

Figure 5: (a) Short-beam shear test fixture, (b) Material Test System (MTS) universal testing m/c

(a)

(b)



(c)

Figure 6: Short-beam shear failure of VE samples (a), (b) PE samples (c)

The second round of testing was performed after 28 days (672 hours) of exposure which is termed short-term exposure. For this purpose, all the samples were removed from the plastic storage containers. Distilled water samples were only dried off by simply wiping with paper towels before they were sent to the water jet. But special care was taken for bleach samples. Prior to wiping with paper towels, both PE and VE bleached exposed samples were rinsed with water. Two strips of 6.0”×0.5”×0.25” from each location were cut by the abrasive water jet with a 4.8 in/min cutting speed. Since there were two locations, i.e. Center Edge, and Cut Edge, four strips were obtained from each large plate. Thus, 8 of the 6-inch long strips of VE (four for water exposure and four for bleach exposure) and 8 of the 6-inch long strips of PE (four for water exposure and four for bleach exposure) samples were obtained. All the 16 long strips were then stored in separate zip-lock plastic bags (Figure 7) for each of the two different locations. The purpose of using this plastic bag was not only to separate the strip samples but also to avoid any further loss of water molecules from the samples by environmental temperature. Each strip was further cut using a diamond wafering saw (available at the University of Mississippi) with a speed of 250 rpm (Figure: 7) in order to obtain the coupon samples of required dimension (1.5”× 0.5”×0.25”) per ASTM D2344-13. A level was used for straight cut, and a digital vernier caliper was used to measure the required length of 1.5 inches (with a desired tolerance of ±0.005”). Then the samples were collected into the respective zip-lock plastic bags (Figure 7). Finally, 10 coupon samples were obtained from each of the plates with every exposure, e.g. water exposed VE and PE plates gave 10 coupon samples for each; bleach exposed VE and PE plates gave 10 coupon samples for each. These total 40 exposed short-beam samples were marked with a permanent marker and kept in the same zip-lock plastic bags for tracking their locations. All the coupon samples were then tested on the same day that they were removed from the exposure

bath to determine the short-beam strength using a 22 kips MTS 810 Material Test System universal testing machine (available at the University of Mississippi) as per ASTM D2344-13. A visual inspection of different failure modes, such as shear failure, compression failure or tensile flexure failure, or inelastic deformation, according to the ASTM D2344, was observed and recorded accordingly for this time only. Testing for short-term exposure coupon samples was identical to the previously described control group samples with no environmental exposure.

Figure 7: Plastic zip-locker bag with PE samples

Figure 8: Diamond wafering saw (available at the University of Mississippi)

The final testing was a performed after prolonged exposure of 693 days (16,632 hours). Following the previous procedure, all the samples were removed from their respective solutions, dried off, rinsed with water (bleach exposed plates), and cut with a water jet machine and the diamond wafering saw. Four strips from each plate were also cut using the water for the long-term exposure samples, which result in 40 coupon samples in total after the diamond saw cut. The dimensions of the exposed plates were identical to the short-term exposure sample plates (18”×14”×0.25”). All the long-term samples were tested following the same procedure identical to the testing of the short-term samples.

After gathering all the test results, the data was analyzed by calculating the average and sample standard deviation (STD). Data was collected as groups per locations, per exposure medium and per product (Table 1). Average (Avg.) and standard deviation (STD) was then calculated by the following the Eq. 2-4.

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad Eq.2$$

$$S^2 = \frac{1}{n-1}\sum_{i=1}^{n} (x_i - \bar{x})^2 \qquad Eq.3$$

$$STD = \sqrt{S^2} \qquad Eq.4$$

Where,

$$\bar{x} = Sample\ Data\ Mean, Average$$

$$x_i = Sample\ Data$$

$$n = Sample\ Size$$

$$S^2 = Sample\ Variance$$

$$STD = Standard\ Deviation$$

Table 1: Data collection as group per locations, per exposure medium and per product

Product Names	**Exposure Time**	**Sample Locations**		**Exposure Medium**
		Center of Plate	Cut Edge	
PE and VE	Short-term Exposure	5 samples	5 samples	Distilled water and Bleach solution
	Long-term exposure	5 samples	5 samples	

Coefficient of variation (COV), also known as relative sample standard deviation (STD), is a popular measure of the variability of data in the sample to the mean of the population. It is defined as the ratio of the sample standard deviation to the mean and often expressed as a percentage. Since in this particular study different samples were exposed to the different medium which has a different mean, COV may give a good comparison between the various data sets. COV will be a helpful and convenient method to compare the data for different medium and different products. The coefficient of variation is calculated by the following Eq. 5.

$$COV = \frac{STD}{\bar{x}} \qquad Eq.5$$

Where,

$$COV = Coefficient\ of\ Variation$$
$$STD = Standard\ Deviation$$
$$\bar{x} = Sample\ Data\ Mean, Average$$

As prescribed in ASTM D7290-11 [39] and MIL-HDBK-17-1F [40], a statistical analysis was also performed to identify any outlier data before any further analysis was performed. An outlier is an observation that is much lower or much higher than most other values in a data set. The outlier is often termed as an erroneous value that may occur due to an error in calculating or recording the numerical value of the data point, or a defective test specimen, or to the incorrect setting of environmental conditions during testing. As prescribed in the LFRD Pre-standard [7], identifying the outliers is one of the requirements outlined in ASTM D7290-06(11) [39]. The method used for identifying the outliers within the dataset is termed as the maximum normalized residual (MNR) method. Several methods are available for statistically analyzing the outliers in a data set but MNR is particularly used in ASTM D7290-11 due to its simplicity. By this method, a value will be called an outlier if it has an absolute deviation from the sample mean that, when compared to the sample standard deviation, is too large to be due to the chance. All values identified as outliers were investigated to determine if a valid reason exists to remove the data point from the analysis.

As specified in ASTM D7290-11, the MNR statistic is calculated Eq.6 [39].

$$MNR = \max\left(\frac{|x_i - \bar{x}|}{s_{n-1}}\right) \qquad Eq.6$$

$Where,$

$MNR = Maximum\ absolute\ deviation$

$x_i = Sample\ data$

$\bar{x} = Sample\ mean$

$s = Sample\ standard\ deviation$

And the critical value (CV) is calculated using Eq.7 [39].

$$CV = \left(2 - \frac{8}{5\sqrt{n}}\right)^2 \qquad Eq.7$$

$Where,$

$CV = Critical\ value$

$n = Sample\ size$

If the MNR ≤ CV, then no outliers are present. If MNR > CV, then a possible outlier is identified and should be investigated. The procedure was followed for each data set using the STAT17 spreadsheet associated with MIL-HDBK-17-1F [40].

Based on the Anderson-Darling test statistic (reference 8.3.2.2, MIL-HDBK-17-1F [40]), an observed significance level (OSL) was calculated for each test to identify the distribution of the data set. The OSL is the probability of obtaining a value of the test statistic at least as large as that obtained if the hypothesis that the data are actually from the distribution being tested is true. If the OSL is less than or equal to 0.05, the hypothesis is rejected (with at most a five percent risk of being in error), and one proceeds as if the data are not from the distribution being tested. All calculations described here were performed using STAT17, a macro excel program created for such statistical analysis [40].

Additional statistical analysis was again performed to test the hypothesis that the populations from which two or more groups of data were drawn are identical. The statistical test was used to determine if sample populations from different locations of the test panel were equivalent. For this purpose, a nonparametric statistical procedure called k-sample Anderson-

Darling test was considered because this is recommended as per MIL-HDBK-17-1F [40]. Following the equations mentioned in section 8.3.2.2 (Eq.8-17) of MIL-HDBK-17-1F [40], the k-sample Anderson-Darling test was performed.

The k-sample Anderson-Darling statistic is

$$ADK = \frac{n-1}{n^2(k-1)} \sum_{i=1}^{k} \left[\frac{1}{n_i} \sum_{j=1}^{L} h_j \frac{\left(nF_{ij} - n_i H_j\right)^2}{H_j(n - H_j) - nh_j/4} \right] \qquad Eq.8$$

$Where,$

$h_j = the\ number\ of\ values\ in\ the\ combined\ samples\ equal\ to\ z_{(j)}$

$H_j = the\ number\ of\ values\ in\ the\ combined\ samples\ less\ than\ z_{(j)}\ plus$

$one\ half\ the\ number\ of\ values\ in\ the\ combined\ samples\ equl\ to\ z_{(j),}\ and$

$F_{ij} = the\ number\ of\ values\ in\ the\ ith\ group\ which\ are\ less\ than\ z_{(j)}\ plus$

$one\ half\ the\ number\ of\ values\ in\ this\ group\ which\ are\ equal\ to\ z_{(j)}$

Under the hypothesis of no difference in the populations, the mean and variance of ADK are approximately 1 and

$$\sigma_n^2 = Var(ADK) = \frac{an^3 + bn^2 + cn + d}{(n-1)(n-2)(n-3)(k-1)^2} \qquad Eq.9$$

With

$$a = (4g-6)(k-1) + (10-6g)S \qquad Eq.10$$

$$b = (2g-4)k^2 + 8Tk + (2g - 14T - 4)S - 8T + 4g - 6 \qquad Eq.11$$

$$c = (6T + 2g - 2)k^2 + (4T - 4g + 6)k + (2T - 6)S + 4T \qquad Eq.12$$

$$d = (2T+6)k^2 - 4TK \qquad Eq.13$$

Where,

$$S = \sum_{i=1}^{k} \frac{1}{n_i} \qquad Eq.14$$

$$T = \sum_{i=1}^{n-1} \frac{1}{i} \qquad Eq.15$$

And

$$g = \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \frac{1}{(n-i)j} \qquad Eq.16$$

The critical value is

$$ADC = 1 + \sigma_n \left[1.645 + \frac{0.678}{\sqrt{k-1}} - \frac{0.362}{k-1} \right] \qquad Eq.17$$

And if the critical value (ADC) is less than the statistic in Eq.8, then one can conclude (with a five percent risk of being in error) that the groups were drawn from different populations. Otherwise, the hypothesis that the groups were from the identical population is not rejected, and the data may be considered unstructured with respect to the random or fixed effect in question [40].

CHAPTER IV: RESULTS AND DISCUSSION

RESULTS

Short-beam strength data was recorded for each of the samples used in this current research. Prior to recording short-beam strength, samples were cut following ASTM D2344-13. Dimensions of each sample (length, width, thickness) were measured using a digital vernier caliper. Short-beam testing was then performed per ASTM D2344-13, and peak load was recorded for each sample.

From this recorded test data, short-beam strength was calculated using the equation presented in ASTM D2344-13. Tables 1 and 2 represent the short-beam strength of non-exposed polyester (PE) and vinyl ester (VE) samples, respectively. Results of short-beam tests for each exposed sample data set are summarized in Tables 3-18. Following the mechanical testing of exposed samples per ASTM D2344-13, data for distilled water (DW) exposed PE and VE samples and data for bleach exposed PE and VE samples are grouped in the respective tables. While Tables 3-10 represent the results of the short-term (672 hour) exposure, Tables 11-18 represent the long-term (16,632 hour) data for both DW and bleach exposed samples. All the short-beam strength samples clearly showed short-beam failure.

Short-beam strength data from each individual dataset was examined for outliers (Figure 8) within that dataset using the maximum normed residual (MNR) method, as prescribed in ASTM D7290-11 [39] and MIL-HDBK-17-1F [40]. The MNR is a statistical method that

compares each data point's absolute deviation from the sample mean to the sample standard deviation to identify statistical outliers [39], [40]. Identification of outliers using the MNR method is one of the steps of the procedure in ASTM -D7290 for the calculation of characteristic values required for the LFRD Pre-standard [39].

Table 2: Short-beam shear strength (Ksi) of non-exposed polyester (PE) samples

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load Pm (lb)	Short-Beam Strength F_{sbs} = $((.75*P_m)/(b*h))$ (Ksi)
PE-01	As_Pul 1	1.495	0.504	0.248	690.0	4.14
PE-02	As_Pul 2	1.512	0.503	0.247	671.6	4.05
PE-03	As_Pul 3	1.494	0.505	0.247	613.4	3.68
PE-04	As_Pul 4	1.505	0.505	0.247	559.9	3.36
PE-05	As_Pul 5	1.482	0.505	0.247	N/A	N/A

Table 3: Short-beam shear strength (Ksi) of non-exposed vinyl ester (VE) samples

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength F_{sbs} = $((.75*P_m)/(b*h))$ (Ksi)
VE-01	As_Pul 1	1.491	0.502	0.259	899.8	5.19
VE-02	As_Pul 2	1.487	0.504	0.259	942.0	5.41
VE-03	As_Pul 3	1.515	0.505	0.260	919.5	5.25
VE-04	As_Pul 4	1.509	0.503	0.259	866.7	4.98

Table 4: Short-beam shear strength (Ksi) of short-term DW exposed polyester (PE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Center_Plate_1	1.478	0.500	0.250	799.1	4.79
PE-02	Center_Plate_2	1.487	0.500	0.249	819.4	4.94
PE-03	Center_Plate_3	1.522	0.501	0.249	850.6	5.11
PE-04	Center_Plate_4	1.478	0.499	0.249	774.6	4.68
PE-05	Center_Plate_5	1.492	0.499	0.248	781.7	4.74

Table 5: Short-beam shear strength (Ksi) of short-term DW exposed polyester (PE) samples taken from the cut edge of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Cut_Edge_1	1.495	0.500	0.248	583.5	3.53
PE-02	Cut_Edge_2	1.471	0.501	0.248	550.7	3.32
PE-03	Cut_Edge_3	1.524	0.501	0.249	519.1	3.12
PE-04	Cut_Edge_4	1.498	0.501	0.248	658.6	3.98
PE-05	Cut_Edge_5	1.476	0.501	0.247	672.3	4.07

Table 6: Short-beam shear strength (Ksi) of short-term DW exposed vinylester (VE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load Pm (lb)	Short-Beam Strength Fsbs = ((.75*Pm)/(b*h)) (Ksi)
VE-01	Center_Plate_1	1.495	0.500	0.246	753.0	4.59
VE-02	Center_Plate_2	1.485	0.501	0.246	776.4	4.72
VE-03	Center_Plate_3	1.508	0.501	0.246	796.1	4.84
VE-04	Center_Plate_4	1.505	0.501	0.246	844.3	5.14
VE-05	Center_Plate_5	1.496	0.502	0.246	804.3	4.88

Table 7: Short-beam shear strength (Ksi) of short-term DW exposed vinylester (VE) samples taken from the cut edge of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength F_{sbs} = $((.75*P_m)/(b*h))$ (Ksi)
VE-01	Cut_Edge_1	1.495	0.500	0.248	583.5	4.39
VE-02	Cut_Edge_2	1.471	0.501	0.248	550.7	4.30
VE-03	Cut_Edge_3	1.524	0.501	0.249	519.1	4.28
VE-04	Cut_Edge_4	1.498	0.501	0.248	658.6	4.42
VE-05	Cut_Edge_5	1.476	0.501	0.247	672.3	4.41

Table 8: Short-beam shear strength (Ksi) of short-term bleach exposed polyester (PE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Center_Plate_1	1.488	0.498	0.247	785.7	4.79
PE-02	Center_Plate_2	1.522	0.498	0.247	693.5	4.23
PE-03	Center_Plate_3	1.512	0.498	0.247	748.8	4.57
PE-04	Center_Plate_4	1.504	0.498	0.248	750.5	4.56
PE-05	Center_Plate_5	1.487	0.499	0.249	745.1	4.50

Table 9: Short-beam shear strength (Ksi) of short-term bleach exposed polyester (PE) samples taken from the cut edge of the exposed plate

Sample No.	Sample name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Cut_Edge_1	1.496	0.495	0.251	751.4	4.54
PE-02	Cut_Edge_2	1.481	0.496	0.251	712.8	4.29
PE-03	Cut_Edge_3	1.531	0.495	0.251	721.3	4.35
PE-04	Cut_Edge_4	1.48	0.493	0.251	719.0	4.36
PE-05	Cut_Edge_5	1.514	0.494	0.251	699.8	4.23

Table 10: Short-beam shear strength (Ksi) of short-term bleach exposed vinylester (VE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
VE-01	Center_Plate_1	1.492	0.500	0.245	738.5	4.52
VE-02	Center_Plate_2	1.543	0.499	0.245	712.6	4.37
VE-03	Center_Plate_3	1.493	0.500	0.245	707.9	4.33
VE-04	Center_Plate_4	1.48	0.498	0.245	824.0	5.07
VE-05	Center_Plate_5	1.547	0.500	0.246	810.3	4.94

Table 11: Short-beam shear strength (Ksi) of short-term bleach exposed vinyl ester (VE) samples taken from the cut edge of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
VE-01	Cut_Edge_1	1.48	0.495	0.246	670.8	4.13
VE-02	Cut_Edge_2	1.527	0.495	0.246	678.7	4.18
VE-03	Cut_Edge_3	1.495	0.496	0.246	716.7	4.41
VE-04	Cut_Edge_4	1.492	0.497	0.245	648.5	3.99
VE-05	Cut_Edge_5	1.541	0.496	0.245	673.5	4.16

Table 12: Short-beam shear strength (Ksi) of long-term DW exposed polyester (PE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Center_Plate_1	1.476	0.500	0.246	546.6	3.33
PE-02	Center_Plate_2	1.49	0.499	0.246	567.5	3.47
PE-03	Center_Plate_3	1.5	0.500	0.246	552.5	3.37
PE-04	Center_Plate_4	1.482	0.501	0.246	564.3	3.43
PE-05	Center_Plate_5	1.483	0.502	0.246	576.0	3.50

Table 13: Short-beam shear strength (Ksi) of long-term DW exposed polyester (PE) samples taken from the cut edge of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Cut_Edge_1	1.48	0.503	0.254	558.9	3.28
PE-02	Cut_Edge_2	1.477	0.502	0.253	557.3	3.29
PE-03	Cut_Edge_3	1.491	0.503	0.253	512.3	3.02
PE-04	Cut_Edge_4	1.462	0.503	0.253	519.7	3.06
PE-05	Cut_Edge_5	1.516	0.502	0.253	512.4	3.03

Table 14: Short-beam shear strength (Ksi) of long-term DW exposed vinyl ester (VE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
VE-01	Center_Plate_1	1.502	0.502	0.264	669.9	3.79
VE-02	Center_Plate_2	1.476	0.501	0.264	673.5	3.82
VE-03	Center_Plate_3	1.479	0.501	0.264	665.5	3.77
VE-04	Center_Plate_4	1.497	0.501	0.264	647.6	3.67
VE-05	Center_Plate5	1.463	0.502	0.263	706.7	4.01

Table 15: Short-beam shear strength (Ksi) of long-term DW exposed vinyl ester (VE) samples taken from the cut edge of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
VE-01	Cut_Edge_1	1.503	0.505	0.26	682.4	3.90
VE-02	Cut_Edge_2	1.468	0.504	0.26	687.4	3.93
VE-03	Cut_Edge_3	1.462	0.506	0.261	640.6	3.64
VE-04	Cut_Edge_4	1.463	0.506	0.260	665.2	3.79
VE-05	Cut_Edge_5	1.504	0.506	0.260	711.4	4.06

Table 16: Short-beam shear strength (Ksi) of long-term bleach exposed polyester (PE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Center_Plate_1	1.453	0.508	0.243	599.5	3.64
PE-02	Center_Plate_2	1.465	0.504	0.247	611.1	3.68
PE-03	Center_Plate_3	1.485	0.506	0.247	639.5	3.84
PE-04	Center_Plate_4	1.503	0.508	0.246	630.4	3.78
PE-05	Center_Plate_5	1.497	0.508	0.247	611.4	3.65

Table 17: Short-beam shear strength (Ksi) of long-term bleach exposed polyester (PE) samples taken from the cut edge of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
PE-01	Cut_Edge_1	1.475	0.520	0.245	601.7	3.54
PE-02	Cut_Edge_2	1.474	0.514	0.245	586.3	3.49
PE-03	Cut_Edge_3	1.496	0.507	0.245	591.1	3.57
PE-04	Cut_Edge_4	1.487	0.516	0.245	573.3	3.40
PE-05	Cut_Edge_5	1.526	0.506	0.244	643.3	3.91

Table 18: Short-beam shear strength (Ksi) of long-term bleach exposed vinyl ester (VE) samples taken from the center of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
VE-01	Center_Plate_1	1.498	0.507	0.268	755.8	4.17
VE-02	Center_Plate_2	1.492	0.509	0.268	698.6	3.84
VE-03	Center_Plate_3	1.488	0.509	0.268	746.0	4.10
VE-04	Center_Plate_4	1.503	0.508	0.268	842.3	4.64*
VE-05	Center_Plate_5	1.455	0.509	0.267	732.3	4.04

*-Denotes outlier due to the fixture pin displacement during the test (see MNR discussion of outliers)

Table 19: Short-beam shear strength (Ksi) of long-term bleach exposed vinyl ester (VE) samples taken from the cut edge of the exposed plate

Sample No.	Sample Name	Length L (in)	Width b (in)	Thickness h (in)	Peak Load P_m (lb)	Short-Beam Strength $F_{sbs} = ((.75*P_m)/(b*h))$ (Ksi)
VE-01	Cut_Edge_1	1.468	0.511	0.267	713.1	3.92
VE-02	Cut_Edge_2	1.490	0.511	0.268	703.8	3.85
VE-03	Cut_Edge_3	1.507	0.510	0.268	680.6	3.73
VE-04	Cut_Edge_4	1.491	0.510	0.268	704.2	3.86
VE-05	Cut_Edge_5	1.504	0.510	0.268	674.6	3.70

MIL-HDBK-17 STATISTICAL ANALYSIS FOR B-BASIS AND A-BASIS VALUES

CLEAR HEADER INFO. -->>

CALCULATE

MATERIAL:	Vinyl Ester long term bleach exposure samples
PROPERTY:	short beam str
TEST ENVIRONMENT:	
PROGRAM:	
CHARGE NO.:	
DATA SOURCE:	Lab
RUN DATE:	6/25/2019
NOTE / COMMENT:	set 1 from cut edge, set 2 from center of plate

INPUT DATA

CLEAR INPUT DATA

BATCH ID	DATA SET NO.	COUPON ID	DATA VALUES	OUTLIERS BEFORE POOLING	OUTLIERS AFTER POOLING
1	1	1	3.92		
1	1	2	3.85		
1	1	3	3.73		
1	1	4	3.86		
1	1	5	3.7		
2	2	1	4.17		
2	2	2	3.84		
2	2	3	4.1		
2	2	4	4.64		X
2	2	5	4.04		

OUTPUT RESULTS

Number of Specimens:	10
Number of Batches:	2
Number of Data Sets:	2
Minimum Data Value:	3.70
Maximum Data Value:	4.64

Results of k-sample Anderson-Darling Test	
$AD_{calculated}$	2.46
$AD_{critical}$	2.26
Same Population?	NO

Normal Distribution Statistics	
Observed Significance Level (OSL)	0.103
Mean	3.98
Standard Deviation	0.276
Coefficient of Variation (%)	6.92
B-Basis Value	3.34
A-Basis Value	2.89

Lognormal Distribution Statistics	
Observed Significance Level (OSL)	0.162

Figure 9: Results of the STAT17 analysis of the data for the long-term bleach exposure of the vinyl ester sample

Outlier testing was performed using the MNR statistic for each of the data sets using the STAT17 spreadsheet associated with MIL-HDBK-17 [38] from the conditioning short-beam strength data shown in Tables 1-18. Coupon sample #4 of the long-term bleach exposure for the vinyl ester samples shown in Table 17 was identified as one of the outliers. Results of the STAT17 analysis of the data for the long-term bleach exposure of the vinyl ester sample is shown in Figure 8. An investigation of this outlier revealed that during the testing of coupon sample #4, the test fixture pin was displaced, which showed a relatively higher value of short-beam strength. Based on this investigation showing that sample #4 for the long-term bleach exposure sample of the vinyl ester composite taken from the center of the plate was not

representative of the short-beam strength of this pultruded composite, sample #4 was removed when further analysis of this data was performed. As no other outliers were identified during the MNR analysis of the remaining data sets, all other short-beam strength data points obtained were used for the analysis of this data.

To determine the effects of environmental conditioning on pultruded composites, the short-beam strength data of each exposure method is grouped together. Before testing, one group of samples was exposed for 672 hours (short-term exposure) while another was subjected to an extensive period of exposure of 16,632 hours (long-term exposure). Results are summarized in Tables 19-20. Mean, standard deviation, and coefficient of variation were also calculated to identify any differences in the data sets. Minimum, maximum, and average for each data set of the polyester composites and the vinyl ester composites are shown in Figures 9 and 10, respectively.

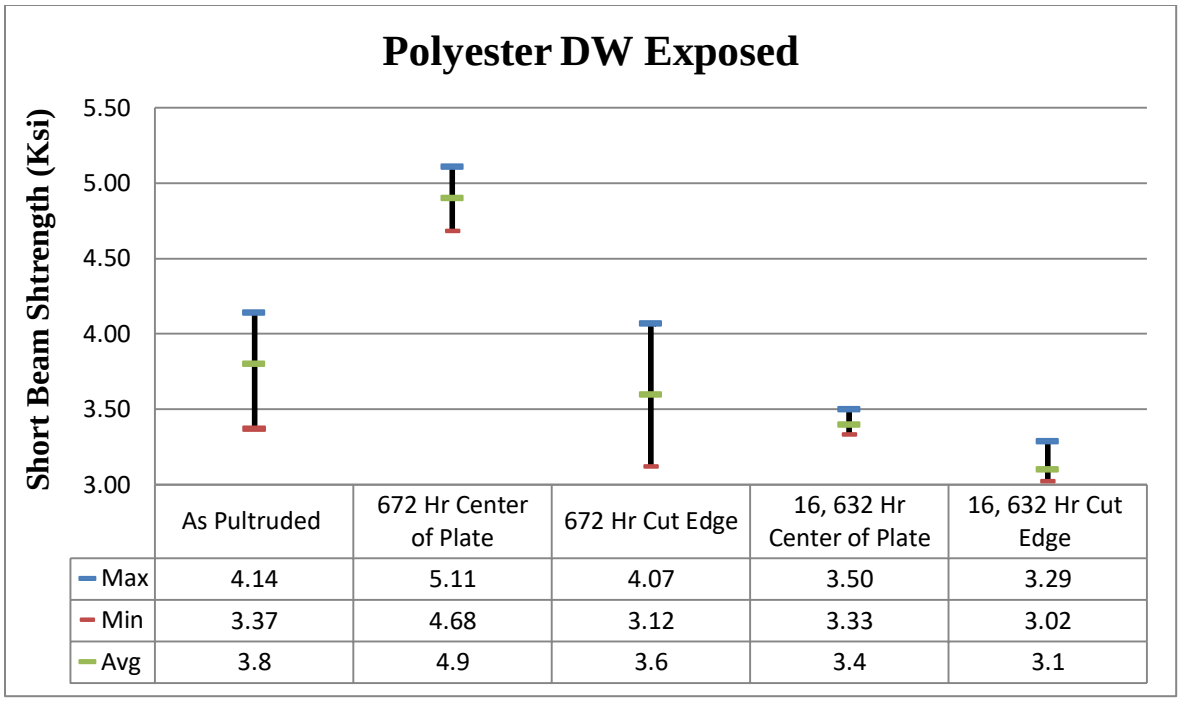
Table 20: Combined data of short-beam strength (Ksi) of distilled water exposed samples

Polyester Samples Exposed to Distilled Water Immersion					
Sample No.	As Pultruded Samples – No Exposure	672 Hr Center Of Plate Samples	672 Hr Cut Edge Samples	16,632 Hr Center of Plate Samples	16,632 Hr Cut Edge Samples
1	4.14	4.79	3.53	3.33	3.28
2	4.05	4.94	3.32	3.47	3.29
3	3.69	5.11	3.12	3.37	3.02
4	3.37	4.68	3.98	3.43	3.06
5	N/A	4.74	4.07	3.50	3.03
Mean	3.8	4.9	3.6	3.4	3.1
St. Dev.	0.4	0.2	0.4	0.1	0.1
COV	10.53%	4.08%	11.11%	2.94%	3.23%
Vinyl Ester Samples Exposed to Distilled Water Immersion					
Sample No.	As Pultruded Samples – No Exposure	672 Hr Center Of Plate Samples	672 Hr Cut Edge Samples	16,632 Hr Center of Plate Samples	16,632 Hr Cut Edge Samples
1	5.19	4.59	4.39	3.79	3.90
2	5.41	4.72	4.30	3.82	3.93
3	5.25	4.84	4.28	3.77	3.64
4	4.99	5.14	4.42	3.67	3.79
5	N/A	4.88	4.41	4.01	4.06
Mean	5.2	4.8	4.4	3.8	3.9
St. Dev.	0.2	0.2	0.1	0.1	0.2
COV	3.85%	4.17%	2.27%	2.63%	5.13%

Table 21: Combined data of short-beam strength (Ksi) of bleach exposed samples

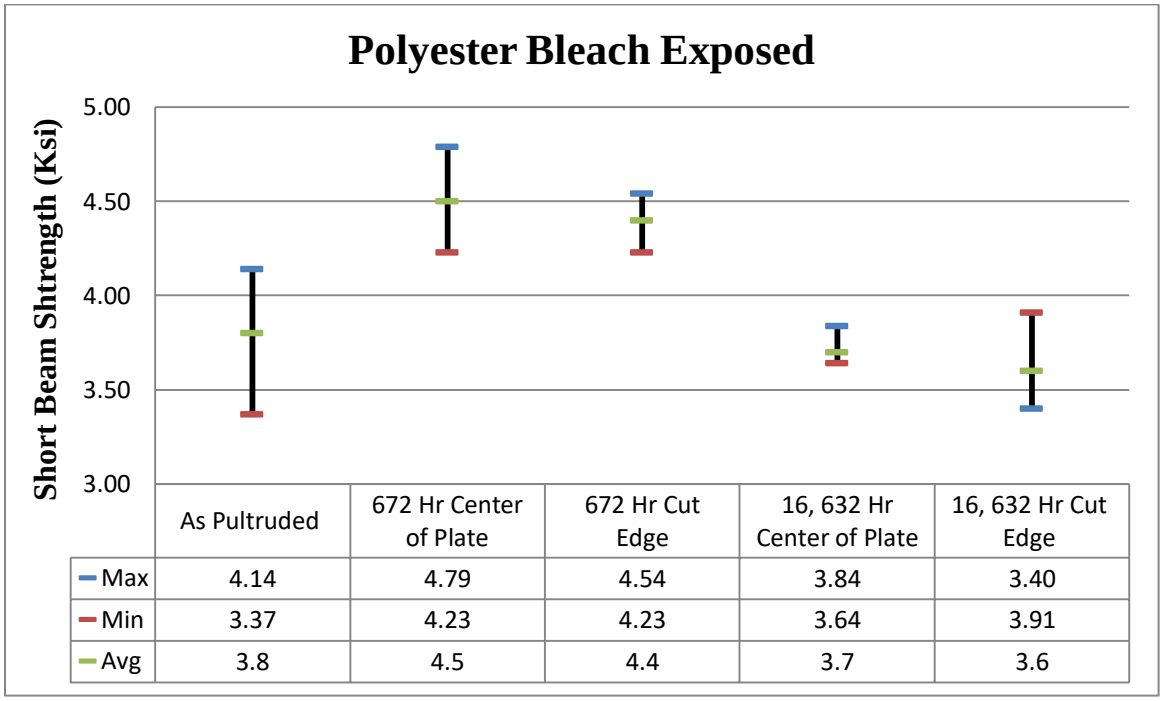
Polyester Samples Exposed to Bleach Immersion					
Sample No.	As Pultruded Samples – No Exposure	672 Hr Center Of Plate Samples	672 Hr Cut Edge Samples	16,632 Hr Center of Plate Samples	16,632 Hr Cut Edge Samples
1	4.14	4.79	4.54	3.64	3.54
2	4.05	4.23	4.29	3.68	3.49
3	3.69	4.57	4.35	3.84	3.57
4	3.37	4.56	4.36	3.78	3.40
5	N/A	4.50	4.23	3.65	3.91
Mean	3.8	4.5	4.4	3.7	3.6
St. Dev.	0.4	0.2	0.1	0.1	0.2
COV	10.53%	4.44%	2.27%	2.70%	5.56%
Vinyl Ester Samples Exposed to Bleach Immersion					
Sample No.	As Pultruded Samples – No Exposure	672 Hr Center Of Plate Samples	672 Hr Cut Edge Samples	16,632 Hr Center of Plate Samples	16,632 Hr Cut Edge Samples
1	5.19	4.52	4.13	4.17	3.92
2	5.41	4.37	4.18	3.84	3.85
3	5.25	4.33	4.41	4.10	3.73
4	4.99	5.07	3.99	N/A*	3.86
5	N/A	4.94	4.16	4.04	3.70
Mean	5.2	4.6	4.2	4.0	3.8
St. Dev.	0.2	0.3	0.1	0.1	0.1
COV	3.85%	6.52%	2.38%	2.50%	2.63%

*Outlier was removed prior to analysis of the data set



	As Pultruded	672 Hr Center of Plate	672 Hr Cut Edge	16, 632 Hr Center of Plate	16, 632 Hr Cut Edge
Max	4.14	5.11	4.07	3.50	3.29
Min	3.37	4.68	3.12	3.33	3.02
Avg	3.8	4.9	3.6	3.4	3.1

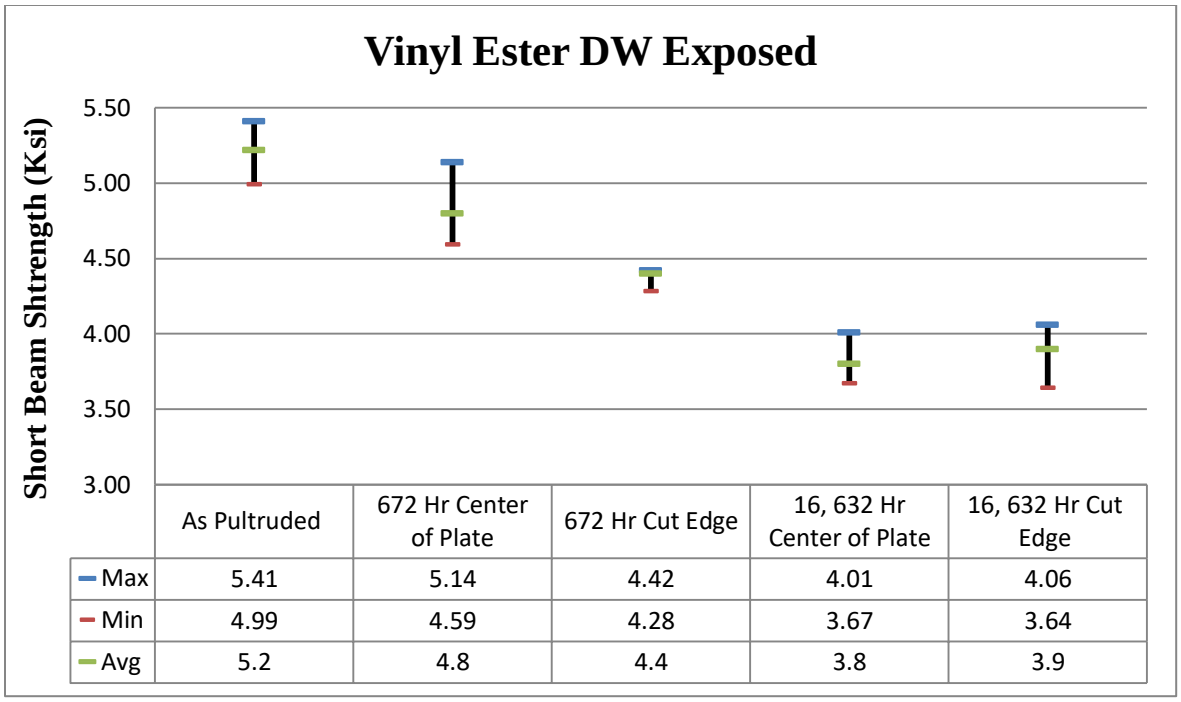
a)



	As Pultruded	672 Hr Center of Plate	672 Hr Cut Edge	16, 632 Hr Center of Plate	16, 632 Hr Cut Edge
Max	4.14	4.79	4.54	3.84	3.40
Min	3.37	4.23	4.23	3.64	3.91
Avg	3.8	4.5	4.4	3.7	3.6

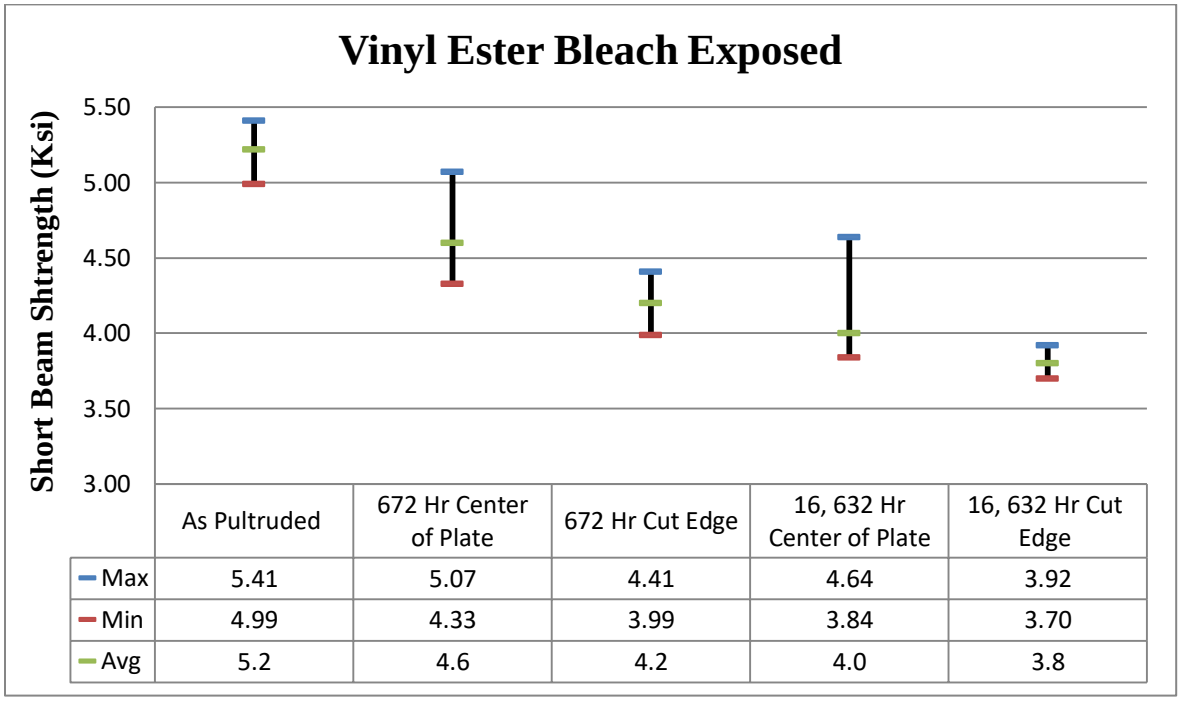
b)

Figure 10. Min, Max, and average comparison of polyester composites a) DW exposed b) Bleach exposed



	As Pultruded	672 Hr Center of Plate	672 Hr Cut Edge	16, 632 Hr Center of Plate	16, 632 Hr Cut Edge
Max	5.41	5.14	4.42	4.01	4.06
Min	4.99	4.59	4.28	3.67	3.64
Avg	5.2	4.8	4.4	3.8	3.9

a)



	As Pultruded	672 Hr Center of Plate	672 Hr Cut Edge	16, 632 Hr Center of Plate	16, 632 Hr Cut Edge
Max	5.41	5.07	4.41	4.64	3.92
Min	4.99	4.33	3.99	3.84	3.70
Avg	5.2	4.6	4.2	4.0	3.8

b)

Figure 11. Min, Max, and average comparison of vinyl ester composites a) DW exposed b) Bleach exposed

DISCUSSION

Coefficient of variation is calculated to evaluate the variation in the data. Several factors play a role in to the interpretation of the results, including time period (i.e. short-term exposure, long-term exposure); exposure medium such as distilled water (DW) or bleach water; locations of the samples and other unknown factors. Tables 19-20, which summarize the data, and Figures 9-10 give a good comparison of these different factors. Graphical representation of short-beam strength data for each exposure medium and each of the products is used to help illustrate these results. The graphs in Figures 9-10 illustrate the range in the data set for each exposure medium for each of the composite products.

COV values calculated for short-beam strength, shown in Table 19, range from 2.94% to 11.11% for distilled water exposed polyester samples and 2.27% to 5.13% for distilled water exposed vinyl ester samples. COV values calculated for short-beam strength, shown in Table 20, range from 2.27% to 5.56% for bleach exposed polyester samples and 2.38% to 6.52% for bleach exposed vinyl ester samples. COV values of control (as-pultruded-no exposure) polyester and vinyl ester samples are 10.53% and 3.85%, respectively. As shown in Tables 19 and 20, most data sets for both the polyester and vinyl ester composites exhibit COV values of less than 6%, with only the as-pultruded polyester, the polyester 672 hours distilled water immersion from the cut edge, and the vinyl ester 672 hours bleach immersion from the center of the plate having a COV of greater than 6%. Lower COV values represent less amount of spread of data within the data set. From this data, it is seen that higher COV values do not correspond to a specific type of composite, a specific immersion medium, or a specific sample location.

Scatter is commonly seen in FRP composites such as pultruded composites examined in this study. One factor for this is due to the fact that samples are being taken from various areas of the pultruded composite panel, and factors such as fiber distribution are not uniform across the width of pultruded panels. It has been seen that properties of individual samples may vary significantly with respect to their positions within a pultruded panel (Lackey et al.) [40]. Lackey illustrated this with the help of Figure 11 (Figure 7 and 8 in her study), showing that the variation in fiber volume over the width of a pultruded panel may be associated with the strength variations, with the COV of this tensile strength data from the production run I panel being 8.5% and the COV of this data from production run II panel being 11.8%. For instance, Figure 11 (Figure 8, in her study) showed higher values of mean tensile strength in the left half of the plate while the other half showed slightly lower values of the mean tensile strength. So, samples were taken from the left half of the plate will result in higher values of mean tensile strength, is due to the presence of a higher volume of fiber on this portion of the plate. Thus, this data helps explain why relatively high COV values may be seen for data sets from the pultruded composites.

Figure 7. Illustration of tensile strength across the width of the plate for the plate from Production Run I

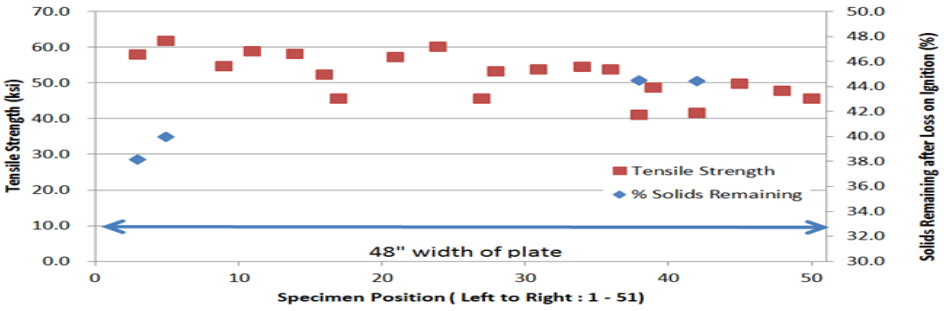


Figure 8. Illustration of tensile strength across the width of the plate for the plate from Production Run II

Figure 12. Illustration of tensile strength across the width of the plate taken from the study of Lackey [41]

With the scatter often seen for composites, statistical methods are the best approach to use for the characterization of the properties of composites. Guides such as ASTM D7290-13 [39] and MIL-HDBK-17-1F [40] recommend the use of statistical methods for analysis, and this technique will be used to evaluate the influence of sample location examined in this study. However, some general observations can be made related to the effects on the short-beam strength of samples from the polyester matrix and vinyl ester matrix composites in this study.

Short-beam strength of no exposure vs. long-term exposure samples of both polyester and vinyl ester distilled water immersion samples indicate that prolonged exposed samples are generally seen to lose strength compared to the non-exposure samples, and this was expected. This is illustrated in Figures 9 and 10. This reduction may occur due to the fact of moisture absorption. When moisture is induced into the polymer chain, it may enter into the inherent free space of the polymer matrix, which develops stress into the composites. This stress is called hygrothermal stress, which may further develop/accelerate the microcracks or microvoids [42]. Thus, this hygrothermal stress adds their values to the applied load and force the samples to fail earlier than when they are supposed to fail. Thus, it plays a role in decreasing the value of short-beam strength.

In addition, the reduction of short-beam strength of the long-term samples may be caused by the hydrolysis and leaching. Hydrolysis causes the detachment of side groups from polymer backbone, whereas leaching causes the breakdown of the fiber/matrix interface. Both phenomena play a great role in fiber matrix debonding, which results in the loss of properties of polymeric composites [42]. Properties of polymeric composites are adversely affected by plasticization because it causes plastic deformation and thus lowers the glass transition temperature (Tg). Joshi reported that an initial moisture uptake of 0.1 weight % increased the ILSS (interlaminar shear strength) of carbon/epoxy fiber composites, but ILSS reduced to 25% when they absorb only 2 weight % of moisture [43]. Phifer et al, have investigated the effect of fresh water on E-glass/vinyl ester composites and reported that tensile strength and stiffness of this FRP composite is reduced by 60% and 10%, respectively [44]. Doxsee et al, also examined the reduction of ILSS in aramid/epoxy composites as a result of moisture absorption [45]. Whitney

et al, and Drzal et al, illustrated that poor interfacial bond and moisture accumulation in the composites, which is responsible for changing the failure mode, are the main reasons for a large drop of flexural strength and interlaminar strength values [46], [47]. Furthermore, immersion time also attributes to the amount of moisture absorption and thus to composites properties. For example, long-term exposure increases the moisture ingression into the composites. After prolonged exposure, the maximum amount of moisture accumulated into the FRP composites, which attributed to the dimensional instability of composites such as swelling, decreased the glass transition temperature (Tg), and reduced the fiber matrix interface properties of the composite [27].

Mean values of short-beam strength of prolonged exposure (16,632 hours) distilled water exposed polyester composite vs. prolonged exposure (16,632 hours) bleached water polyester composites samples, shown in Tables 19 and 20, indicate that distilled water samples have the lower short-beam strength value than the bleach water samples after the same period of immersion. For 16,632 hours distilled water exposed polyester composite the mean values of short-beam strength ranges from 3.1 Ksi to 3.6 Ksi (Table 19), whereas for 16,632 hours bleach water exposed polyester composite, the mean values of short-beam strength ranges from 3.6 Ksi to 3.7 Ksi (Table 20). Similar trends are also noticed for vinyl ester composites samples. Tables 19 and 20 show that for 16,632 hours distilled water exposed vinyl ester composite the mean values of short-beam strength ranges from 3.8 Ksi to 3.9 Ksi (Table 19), whereas for 16,632 hours bleach water exposed polyester composite, the mean values of short-beam strength ranges from 3.8 Ksi to 4.0 Ksi (Table 20).

Overall, the vinyl ester samples offer superior properties after environmental exposure e,g, short-beam strength of vinyl ester samples are higher than the polyester which was expected (Hedgepeth) [33]. Harper and Naeem also noticed the similar behavior of vinyl ester composites when they compared moisture absorption between glass fiber reinforced polyester and vinyl ester composites [48]. Though they did not test the mechanical properties of the composites, they studied the moisture uptake behavior. They reported that vinyl ester composites absorb less moisture than polyester due to availability of less ester groups for hydrolysis. This indicates the better performance of the vinyl ester compared to the polyester composites when they were subjected to the environmental exposure. Both Tables 19 and 20 shows that regardless of the exposure time and exposure medium, vinyl ester samples retain more short-beam strength compared to the polyester. For example, short-beam strength (mean value) of the center plate of 16,632 hours bleach exposed vinyl ester composite is 4.0 Ksi, whereas for the same exposure medium (bleach) at the same exposure time (16,632 hours) at the same location (center of the plate) of polyester, short-beam strength (mean value) degrades 0.3 Ksi (3.7 Ksi for PE). This is because the methyl groups of the vinyl ester form the terminal of the vinyl ester chains, which makes them less susceptible to hydrolysis. Chin J.W. et al. mentioned that methyl groups of vinyl ester act as a shield for ester linkage; thus, they make the vinyl ester more stable against hydrolysis than isopolyester. Harper also reported that methyl groups of vinyl ester composites shield the ester linkage in the polymer chain that increases the resistance of hydrolysis of the composites [48]. The seawater durability of carbon and glass fiber reinforced polyester and vinyl ester composites was also studied by Kootsookos et al, [49]. They observed that carbon and glass fiber reinforced vinyl ester composites exhibit higher levels of environmental resistance than carbon and glass fiber reinforced polyester composites due to the greater resistance to hydrolytic

degradation of vinyl ester matrix compared to polyester matrix. On the other hand, ester groups in isopolyester are distributed along the main chains, making them more available to hydrolysis reactions [5]. Thus, isopolyester is more vulnerable to chemical attacks than vinyl ester. In general, vinyl ester composites offer more resistance to degradation by water, salt solution, bleach solution, and other corrosive environments than polyester composites.

In order to perform statistical analysis of the sample sets, it is necessary to know what statistical distribution this data follows. Goodness-of-fit testing was performed as per the procedure described in section 8.3.4 of MIL-HDBK-17-1F [40] to check the unstructured data. There are several methods to determine if the data follows a Weibull, normal, or log normal distribution. For this study, the Weibull distribution was identified, and this is the preferred distribution suggested by MIL-HDBK-17-1F [40]. Theory suggests that this model is appropriate for the strength distribution of brittle materials such as composites (Reference 8.3.4(a) MIL-HDBK-17-1F) [40]. Furthermore, the Weibull distribution is also recommended by ASTM D7290-06(11) [39]. It also mentioned in Figure 8.3.1 of MIL-HDBK-17-1F [40] that, a Weibull model is recommended to use if it adequately fits the data, even if other models apparently fit the data better. However, if this model fails to adequately fit data, then normal and lognormal tests are performed in succession.

After performing the Anderson-Darling goodness of fit test for each data set using the STAT17 spreadsheet associated with Mil Handbook 17, the OSL indicated that each data set in this study followed a Weibull distribution as expected. Examples of this analysis are shown in Figures 12 and 13.

As the primary objective of this study was to determine if the samples taken from the cut edge of an exposed plate were equivalent to samples taken from the interior of an exposed plate, statistical analysis of the data for each exposure condition was performed using the k-sample Anderson-Darling test to determine if the cut edge data set and the center of the plate data set for a given exposure condition were from the same population of data. This non-parametric test is appropriate for use with the Weibull distribution data. If the data had followed a normal distribution, a t-test could have been used to evaluate the data, but a t-test is not appropriate to use for a Weibull distribution. If the k-sample Anderson-Darling test indicated that the cut edge data set and the center of the plate data set were from the same population, this indicated that the exposure environment had an equivalent effect on the sample taken from either the cut edge of the sample or from the interior of the exposed plate.

CLEAR HEADER INFO. -- >>

CALCULATE

MATERIAL:	Polyester Short term DW exposure samples
PROPERTY:	short beam str
TEST ENVIRONMENT:	
PROGRAM:	
CHARGE NO.:	
DATA SOURCE:	Lab
RUN DATE:	7/3/2019
NOTE / COMMENT:	set 1 from cut edge, set 2 from center of plate

INPUT DATA

CLEAR INPUT DATA

BATCH ID	DATA SET NO.	COUPON ID	DATA VALUES
1	1	1	3.53
1	1	2	3.32
1	1	3	3.12
1	1	4	3.98
1	1	5	4.07
2	2	1	4.79
2	2	2	4.94
2	2	3	5.11
2	2	4	4.68
2	2	5	4.74

OUTLIERS	
BEFORE POOLING	AFTER POOLING

OUTPUT RESULTS

Number of Specimens:	10
Number of Batches:	2
Number of Data Sets:	2
Minimum Data Value:	3.12
Maximum Data Value:	5.11

Results of k-sample Anderson-Darling Test	
$AD_{calculated}$	4.01
$AD_{critical}$	2.26
Same Population?	NO

Normal Distribution Statistics	
Observed Significance Level (OSL)	0.236
Mean	4.23
Standard Deviation	0.722
Coefficient of Variation (%)	17.1
B-Basis Value	2.53
A-Basis Value	1.35

a)

A-Basis Value	1.35

Lognormal Distribution Statistics	
Observed Significance Level (OSL)	0.193
Log Mean	1.43
Log Standard Deviation	0.178
B-Basis Value	2.74
A-Basis Value	2.05

Weibull Distribution Statistics	
Observed Significance Level (OSL)	0.223
Scale Parameter	4.52
Shape Parameter	7.60
B-Basis Value	2.54
A-Basis Value	1.46

Nonparametric Statistics	
B-Basis Method	Hans-Koop
A-Basis Method	Hans-Koop
B-Basis Value	1.97
A-Basis Value	0.877

Results of Equality of Variances Test	
$F_{calculated}$	3.10
$F_{critical}$	5.32
Variances Equal?	YES

Analysis of Variance (ANOVA) Statistics	
Sample Between-batch Variance (MSB)	3.89
Sample Within-batch Variance (MSE)	0.0999
B-Basis Value	Negative
A-Basis Value	Negative

b)

Figure 13: Results of k-sample Anderson-Darling Testing for PE Short-term DW Exposure Samples a) Samples Population is same or not b) OSL of Weibull Distribution

MIL-HDBK-17 STATISTICAL ANALYSIS FOR B-BASIS AND A-BASIS VALUES

CLEAR HEADER INFO. -- >>

CALCULATE

MATERIAL:	Polyester Long term Bleach exposure samples
PROPERTY:	short beam str
TEST ENVIRONMENT:	
PROGRAM:	
CHARGE NO.:	
DATA SOURCE:	Lab
RUN DATE:	7/3/2019
NOTE / COMMENT:	set 1 from cut edge, set 2 from center of plate

INPUT DATA

CLEAR INPUT DATA

BATCH ID	DATA SET NO.	COUPON ID	DATA VALUES
1	1	1	3.54
1	1	2	3.49
1	1	3	3.57
1	1	4	3.4
1	1	5	3.91
2	2	1	3.64
2	2	2	3.68
2	2	3	3.84
2	2	4	3.78
2	2	5	3.65

OUTLIERS	
BEFORE POOLING	AFTER POOLING

OUTPUT RESULTS

Number of Specimens:	10
Number of Batches:	2
Number of Data Sets:	2
Minimum Data Value:	3.40
Maximum Data Value:	3.91

Results of k-sample Anderson-Darling Test	
$AD_{calculated}$	2.17
$AD_{critical}$	2.26
Same Population?	YES

Normal Distribution Statistics	
Observed Significance Level (OSL)	0.755
Mean	3.65
Standard Deviation	0.159
Coefficient of Variation (%)	4.36
B-Basis Value	3.28
A-Basis Value	3.02

a)

A-Basis Value	3.02

Lognormal Distribution Statistics	
Observed Significance Level (OSL)	0.771
Log Mean	1.29
Log Standard Deviation	0.0436
B-Basis Value	3.29
A-Basis Value	3.07

Weibull Distribution Statistics	
Observed Significance Level (OSL)	0.606
Scale Parameter	3.72
Shape Parameter	25.8
B-Basis Value	3.14
A-Basis Value	2.67

Nonparametric Statistics	
B-Basis Method	Hans-Koop
A-Basis Method	Hans-Koop
B-Basis Value	3.14
A-Basis Value	2.37

Results of Equality of Variances Test	
$F_{calculated}$	0.507
$F_{critical}$	5.32
Variances Equal?	YES

Analysis of Variance (ANOVA) Statistics	
Sample Between-batch Variance (MSB)	0.0462
Sample Within-batch Variance (MSE)	0.0227
B-Basis Value	2.53
A-Basis Value	1.67

b)

Figure 14: Results of k-sample Anderson-Darling Testing for PE Long-term Bleach Exposure Samples a) Samples Population is same or not b) OSL of Weibull Distribution

Table 22: K-sample Anderson Darling Results Testing if Samples are from the Same Population

Sample Descriptions	Same Population
672 hr water PE exposure cut edge samples, center of plate samples	NO
672 hr water VE exposure cut edge samples, center of plate samples	NO
672 hr bleach PE exposure cut edge samples, center of plate samples	YES
672 hr bleach VE exposure cut edge samples, center of plate samples	NO
16,632 hr water PE exposure cut edge samples, center of plate samples	NO
16,632 hr water VE exposure cut edge samples, center of plate samples	YES
16,632 hr bleach PE exposure cut edge samples, center of plate samples	YES
16632 hr bleach VE exposure cut edge samples, center of plate samples	YES

The statistical analysis, data shown in Table 21, show that all the short-term samples (672 hours) of distilled water exposed PE and VE composites and also bleached exposed VE composites samples are not from the same population, whereas short-term bleach exposed PE composites samples are from the same population (Figure 12 (a)). This indicates that for short exposure time, the external environment (which is distilled water in this case) did not have same effect on all samples of water exposed PE and VE composites and bleach exposed VE composites. During this short exposure time, there were different effects on the samples with respect to their locations. The reason behind the different effects on different samples would be the exposure time. Since these are the short-term exposed samples, distilled water may not get enough time to diffuse through the entire plate uniformly. This phenomenon is also evident in Grammatikos et al, [28]. They reported that at the edges areas interfacial loss enhances the moisture wicking along the fiber reinforcement, which enables the four edges surfaces areas to

absorb moisture at higher rates than the two (larger) surfaces (that is the center of the plate in this present study). This makes samples from different locations of the plate of different statistical populations.

On the contrary, short-term exposure bleach exposed samples of the PE composite exhibit that they are from the sample population. This might be due to the combined effects of polyester resin and bleach solution. For example, the methyl group of PE is distributed all over the polymer chains, making it more susceptible to chemical attack. On the other hand, bleach solution can create a more corrosive environment than the distilled water. Together these two phenomenon make the bleach exposed samples of PE composite plate of the same statistical population regardless of their locations. But this was not the case for bleach exposed VE samples because the terminal of vinyl ester chains is surrounded by methyl groups that acts as a shield for inside molecules, making them less vulnerable to bleach attack compared to polyester molecules. Thus, the statistical analysis identified them as different populations.

Long-term (16,632 hours) exposed samples of each composite product (i.e. PE and VE composites) of each medium (i.e. distilled water and bleach) appeared as the same statistical population as shown in Table 21 and Figure 13 (a) after the k-sample Anderson-Darling test. This is because these samples were submerged for an adequately long time, which makes both distilled water and bleach solution ingress into the large plate of each product (i.e. PE and VE). After this long exposure time, diffusion of both solutions into the products is more uniformly distributed. This effect of sample from all locations of the plate being equivalent after long exposure time would be expected; however, the only exception was noticed for distilled water

exposed samples of PE composite. As the PE composites with long-term exposure to distilled water did not follow the expected trend of the entire plate being uniformly affected after long-term exposure, additional testing of samples under this exposure condition is recommended because all other products of all other medium (including the bleach exposed PE samples) showed the same statistical population. If more PE samples are tested, it could be determined if this was an anomaly or if this result was representative of this exposure condition.

Based on the statistical analysis showing that short-term exposed samples from the center of a plate and from the cut edge of a plate are generally not from the same statistical population, it is important to specify where samples should be taken from when developing a standard experimental procedure for short-term environmental exposure samples. However, if long-term environmental exposure is utilized, this statistical analysis showed that specification of requirement for sample locations is not as critical when developing a standard experimental procedure. This information can now be used in the development of standard procedure for corrosion testing of pultruded composites.

CHAPTER V: CONCLUSION

The primary focus of this study was to provide the background data to the pultrusion industry that will be utilized to develop a standard practice for the durability characterization of the pultruded composites used in structural applications. In addition, another major objective was to determine whether the samples from different locations of a large exposed plate have the same effect on durability or not. During this study, some general observations were also made related to the effect of exposure time on short-beam strength of environmentally exposed polyester and vinyl ester pultruded composites. The current study revealed that the following facts related to the durability of the pultruded composites:

1) Long-term exposure (16,632 hours) distilled water (DW) samples of both PE and VE pultruded composites plates showed lower short-beam strengths compared to the same no exposure samples.
2) Prolonged exposure (16,632 hours) distilled water immersed coupons of both PE and VE composites showed the degraded values of short-beam strength than the bleach exposed coupons from identical environments and identical materials.
3) Some scattered behavior was also noticed that might be the results of non-uniform fiber distribution throughout the composites and also due to the uneven diffusion of both DW and bleach into the coupon samples because shorter time did not allow them to saturate into the entire composites.

In general, vinyl ester coupons offer higher values of short-beam strength than polyester coupons of each medium and each composite.

The effects of sample locations (e.g. cut edge and center of the plate) on the durability characterization of pultruded composites were examined with the help of statistical analysis, and these are the findings:

1) Cut edge samples and samples taken from the center of large PE and VE plate exposed in both DW and bleach solution for a short period (672 hours) were not from the same population, which indicates that exposure environments affect the short-term exposed samples differently, irrespective of their locations. The only exception was noticed in the short-term bleach exposed PE samples that could be addressed by testing more coupon samples.
2) On the other hand, both long-term exposed (16,632 hours) PE and VE composites of DW and bleach exposed samples had come from the same population, which revealed that exposure environments had an equivalent effect whether the samples were taken from the cut edge or interior of the plate. Here, another exception was also found in case of long-term DW exposed PE samples, which could only be further examined by increasing the number of PE samples.

Therefore, it is clear from the above discussion that in order to develop a standard experimental procedure for short-term environmental exposure pultruded composites samples, it is important to mention the location where the sample is taken from. However, when developing a standard experimental procedure for environmentally exposed pultruded composite, the location of the sample does not matter because exposure environments will create the same effects on each sample regardless of their locations.

These interesting findings also encourage the researchers to research further. Hence, the researchers of this current study are planning to expand their work with the following objectives:

1) Study the water uptake behavior of pultruded composites, e.g. whether they follow the Fickian or non-Fickian diffusion;
2) Study the effect of long-term exposure on the chemical behavior of pultruded composites such as glass-transition temperature (Tg) and others by performing DMA, TGA and FTIR tests, which will help the designer, researcher, and users to predict the service life of the pultruded composites.

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