Highly Accelerated Lifetime for Externally Applied Bond Critical Fiber-reinforced Polymer (FRP) Infrastructure Materials

Final Report

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Principal investigator: Elliot P. Douglas

Co-Principal Investigators: H. R. Hamilton III Juan Nino

Research assistants: Andrew Stewart Jovan Tatar

Department of Materials Science & Engineering University of Florida P.O. Box 116400 Gainesville, Florida 32611

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University of Florida Department of Materials Science and Engineering Engineering School of Sustainable Infrastructure and Environment Department of Civil and Coastal Engineering

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SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL			
LENGTH							
in	inches	25.4	millimeters	mm			
ft	feet	0.305	meters	m			
yd	yards	0.914	meters	m			
mi	miles	1.61	kilometers	km			
		AREA					
in ²	square inches	645.2	square millimeters	mm ²			
ft ²	square feet	0.093	square meters	m ²			
yd ²	square yard	0.836	square meters	m ²			
ac	acres	0.405	hectares	ha			
mi ²	square miles	2.59	square kilometers	km ²			
		VOLUME					
fl oz	fluid ounces	29.57	milliliters	mL			
gal	gallons	3.785	liters	L			
ft ³	cubic feet	0.028	cubic meters	m ³			
yd ³	cubic yards	0.765	cubic meters	m ³			
NOTE: volumes greater than 1000 L shall be shown in m ³							
		MASS					
OZ	ounces	28.35	grams	g			
lb	pounds	0.454	kilograms	kg			
Τ	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")			
TEMPERATURE (exact degrees)							
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C			
ILLUMINATION							
fc	foot-candles	10.76	lux	lx			
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²			
FORCE and PRESSURE or STRESS							
lbf	pound-force	4.45	newtons	N			
lbf/in ²	pound-force per square inch	6.89	kilopascals	kPa			

APPROXIMATE CONVERSIONS TO SI UNITS

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL		
LENGTH						
mm	millimeters	0.039	inches	in		
m	meters	3.28	feet	ft		
m	meters	1.09	yards	yd		
km	kilometers	0.621	miles	mi		
		AREA				
mm ²	square millimeters	0.0016	square inches	in ²		
m ²	square meters	10.764	square feet	ft ²		
m ²	square meters	1.195	square yards	yd ²		
ha	hectares	2.47	acres	ac		
km ²	square kilometers	0.386	square miles	mi ²		
		VOLUME				
mL	milliliters	0.034	fluid ounces	fl oz		
L	liters	0.264	gallons	gal		
m ³	cubic meters	35.314	cubic feet	ft ³		
m ³	cubic meters	1.307	cubic yards	yd ³		
		MASS				
g	grams	0.035	ounces	OZ		
kg	kilograms	2.202	pounds	lb		
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	Τ		
	TEMPER	ATURE (exact degre	es)			
°C	Celsius	1.8C+32	Fahrenheit	°F		
ILLUMINATION						
lx	lux	0.0929	foot-candles	fc		
cd/m ²	candela/m ²	0.2919	foot-Lamberts	fl		
FORCE and PRESSURE or STRESS						
N	newtons	0.225	pound-force	lbf		
kPa	kilopascals	0.145	pound-force per square inch	lbf/in ²		

APPROXIMATE CONVERSIONS TO SI UNITS

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16. Abstract		4 1 4	1 :		£1	
I his report describes a resea	rcn project to investig	gate accelerated	aging prot	ocols for	ilber-reinforced	
polymer (FRP) reinforcement o	t concrete. This research	arch was condu	cted in thre	e stages.	In the first	
stage, various spectroscopic tec	hniques were used to	investigate the	chemical b	onding b	etween epoxy	
and cement. Evidence suggests	that hydrogen bonding	ng may occur at	t the epoxy-	-cement in	nterface. Next,	
degradation of epoxy properties	s and the correspondi	ng degradation	mechanism	ns during	accelerated	
aging were examined. Low tem	perature water imme	rsion resulted in	n loss of pr	operties d	ue to water	
absorption while high immersi	on temperatures or lo	w immersion te	emperature	s in comb	ination with UV	
exposure resulted in loss of properties due to chemical changes in the epoxy resin. Finally, the aging						
protocols identified for the apo	vias wara usad ta ava	mino durobilitu	of concret	o hooma r	ainforced with	
EDD L aga in hearn strongth due	to aging from this a		of concret	e deallis i	ennoiceu with	
FKP. Loss in beam strength due	to aging from this s	ludy was comb	ined with d	ata from a	a published	
NCHRP project to determine be	and durability factors	for use in desi	gn. These f	actors we	re determined to	
be 0.4 for wet layup without putty and 0.6 for wet layup with putty.						
G17. Key Word	anarata Durahility	18. Distribution Stat	ement		available to the	
Accelerated Aging, Bonding, Concrete, Duraolity, No restrictions			15.1115 doc			
public poxy, rKr, spectroscopy, public		public through	the Nation	al Techn	ical information	
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Executive Summary

FDOT currently uses fiber-reinforced polymer (FRP) composites for repair of impacted bridges and to strengthen bridge decks. Use of these advanced materials can extend the life span of existing bridges or improve the functionality of existing bridges. Prediction of long-term performance of FRP composites, however, over the design lifetime of structures (50+ years) requires accelerated and routine testing. Current durability testing, where used, typically involves accelerating degradation through elevated temperature, stress levels, and concentrations of corrosive media. However, these tests have generally been developed based on empirical considerations and do not take into account the degradation mechanisms involved. Therefore, this study was undertaken to investigate the fundamental mechanisms of degradation during accelerated aging and to identify conditioning protocols based on those mechanisms.

The first part of this work investigated the nature of the epoxy-concrete bond. The initial hypothesis was that hydrogen bonding takes place at the interface, so small molecule analogs of the epoxy molecule were adsorbed onto cement paste particles to create a more simple system to analyze. Infrared spectroscopy did not show any indication of bonding between cement and these small molecules. Solid state NMR experiments showed a weak interaction between one epoxy analog and cement, suggesting the presence of hydrogen bonding. Most likely, for these small molecules and this specific type of Portland cement with a 0.38 water-to-cement ratio, weak hydrogen bonding exists that is difficult to detect on the specific composites made.

The second part of this work focused on accelerated aging of two epoxy systems, including a model DGEBA-POPDA system and a commercial system. Mechanical testing was performed along with infrared spectroscopy and diffusion modeling to determine the change in properties and mechanisms of degradation. A decrease in tensile strength and modulus and an increase in strain to failure was found with higher exposure temperatures. Three distinct degradation mechanisms were identified, depending on exposure conditions: water absorption at low exposure temperatures; oxidation for exposure to UV radiation; and hydrolysis for combined water and UV exposure.

Based on these results, accelerated aging conditions were identified and tested on five different FRP systems bonded to small-scale concrete beams. The acquired data were grouped with data from a previous NCHRP study by that utilized the same FRP reinforced concrete test

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specimen. This formed a population of over 900 test results. Data were subjected to a rigorous statistical analysis to determine the distribution of data with respect to multiple variables.

The method used to experimentally determine a characteristic design value for adhesive anchors (ACI 355.4-11) was adapted to quantify the loss in bond capacity following accelerated conditioning. Bond durability factors of 0.4 and 0.6 were established for wet-layup with and without putty, respectively. The intent of this work was to quantify the loss in bond properties over time. However, for the durability factor to be incorporated into design standards, the findings from this study need to be confirmed on large-scale specimens and full-scale structural elements.

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1 Introduction

1.1 Background

In 2003, the American Society of Civil Engineers reported that 27.1% of U.S. bridges were structurally deficient. Therefore, they suggested significant changes needed to be made to repair America's bridges. One possible repair solution could be the use of fiber-reinforced polymers (FRPs). Compared to tearing down and rebuilding a bridge, this method represents substantial time and cost savings. The FRP can be wrapped around columns or applied to the tension side of a beam, using a wet layup approach or by bonding a precured laminate. Epoxy resins have been widely used for this application due to their high performance in strength, stiffness (Chen et al., 2004), and resistance to creep (Hu et al., 2001). Despite the advantages of FRP repair, questions still exist regarding the composite's durability, as evidenced in a recent catastrophe in 2006 where concrete panels fell on a car at the Big Dig in Boston. The concrete panels were attached to the ceiling using an adhesive anchor, which appeared to fail at the epoxy-concrete interface. Another important concern is the issue of bond degradation due to environmental exposure. Many investigations have been done on how environmental exposure affects metal-epoxy (Jones et al., 1994; Hong, 1995), glass-epoxy (Lefebvre et al., 2000, Dewimille and Bunsell, 1983), carbon-epoxy (Adams and Singh, 1996), and glass-vinylester (Chu et al., 2004; Karbhari, 2004; Chu and Karbhari, 2005; Ramirez et al., 2008) FRP, but little is known regarding the chemical nature of the bond between epoxy and concrete.

Prediction of long-term performance of FRP composites over the design lifetime of structures (50+ years) requires accelerated and routine testing. Current durability testing, where used, typically involves accelerating degradation through elevated temperature, stress levels, and concentrations of corrosive media. However, these tests have generally been developed based on empirical considerations and do not take into account the degradation mechanisms involved.

1.2 Civil Engineering vs. Chemistry Perspective

Civil engineering, by definition, deals with the design, construction, and maintenance of artificial and naturally occurring structures. Therefore, the size of the materials and dimensions they must consider can range from millimeters to kilometers. They have to have a practical consideration of the variables and components of the systems they deal with as they affect things

on the macro scale. On the other hand, chemistry is concerned with atoms and interactions at the nano scale, which determine some of the most important properties of materials. The fact that these two disciplines examine different length scales results in different theories regarding the nature of adhesion between epoxy and concrete. The two main mechanisms are mechanical interlock and chemical bonding.

The mechanical interlocking theory assumes that good adhesion between two materials occurs when an adhesive penetrates into the pores, holes, and irregularities of the surface, and locks mechanically to the substrate. Numerous investigations have shown enhanced bond strength of concrete systems as a result of rough surface preparation using a variety of test methods (Czarneck, 2008; Karbhari et al., 1997; Garbacz et al., 2005; Momayez et al., 2005). On the other hand, since good adhesion has been reported between epoxy and smooth surfaces, such as aluminum (deBruyne, 1956; Schmidt and Bell, 1986), another theory must also be considered.

It is highly possible that a chemical bond between epoxy and concrete exists. While the exact stoichiometry and chemical makeup of cement is still debated, many scientists have acknowledged that hydroxyl and silanol groups exist within the material. The presence of highly polar aliphatic hydroxyl and ether groups in epoxy chains can serve as sites for the formation of strong hydrogen bonds. A few studies that have examined the chemical nature of the interface suggested hydrogen bonds are formed between epoxy and concrete (Neves et al. 2002; Djouani et al., 2011), and water tends to cluster at the interface and form hydrogen bonds (Lefebvre et al., 2000).

1.3 Goals of This Research

This research investigates the limits of accelerated testing for carbon FRP composites that are externally bonded to concrete and near surface mounted (NSM) composites that are just below the surface of the concrete. The objectives are to 1) identify the limits for conditioning protocols; and 2) propose new conditioning protocols that can be used for accelerated testing.

In the first part of this work, interactions between epoxy analogs and cement paste were investigated to get a fundamental understanding of the elusive interfacial bond. Various spectroscopic techniques were utilized to demonstrate that a chemical bond exists (Chapter 3).

The second part of this work focused on accelerated aging of three epoxy systems. Mechanical testing was performed along with IR spectroscopy and diffusion modeling to determine the change in properties and mechanisms of degradation (Chapter 4). The result of this testing is a proposed set of conditioning protocols for accelerated testing.

The last section of this work tested these conditioning protocols using small beam tests (Chapter 5).

2 Review of the Literature

2.1 What is Cement?

The most general meaning of cement is a substance that hardens and can bind other materials together. The word "cement" was first used by the Romans to describe a masonry building material that was composed of crushed rock with burnt lime as a binder. While cement and concrete are commonly used interchangeably, there are key technical differences. Cement is the key ingredient in concrete. It is a finely made powder, that when mixed with water creates cement paste that hardens during hydration and curing. During this process it can bind with rocks, called aggregates, to form concrete. When only sand particles are used as aggregates, the cured material is referred to as mortar, while when bigger stones are used it is referred to as concrete. In 1824, Joseph Aspdin patented a cement that he called Portland due to the similarity in color with the stone quarried on the Isle of Portland off the British coast. His method of producing cement, which he developed in his kitchen, was based on a precise ratio of finely ground limestone and clay (MacLaren and White, 2003).

Current day Portland cement manufacturing is a complex process. The first step in the manufacturing process is obtaining raw materials consisting of limestone, chalk, clay, sand or iron oxide mined from a quarry. Two different methods, wet and dry, are used in the heating process. In the dry process, dry raw materials are proportioned, ground to a powder, blended together and fed to the kiln in a dry state. In the wet process, a slurry is formed by adding water to the properly proportioned raw materials. The grinding and blending operations are then completed with the materials in slurry form. After blending, the mixture of raw materials is fed into a tilted rotating, cylindrical kiln where the mixture passes through the kiln at a rate controlled by the slope and rotational speed of the kiln. Inside the kiln, raw materials reach temperatures of up to 1650°C. Heating releases H₂O and CO₂ and causes reactions between the solids. The dry process uses more energy in grinding, but less in the heating process in the kiln. At 1480°C, a series of chemical reactions cause the materials to fuse and create cement clinker pellets. Clinker is poured from the lower end of the kiln and transferred to various types of coolers to lower the clinker to handling temperatures (Bye, 1999). Cooled clinker is combined with gypsum and ground into a fine gray powder that passes through a 75 µm sieve. The result of this process is a fine gray powder called Portland cement (Taylor, 1997).

2.1.1 Cement Chemistry and Nomenclature

Cement is such a complex material that in practice, all of the elements are described as oxides. Table 1 indicates the shorthand notation for each of the elements.

Cement notation formula	Traditional formula	Name	Mass %	
С	CaO	Calcium oxide	61-67%	
S	SiO ₂	Silica	19-23%	
A	Al ₂ O ₃	Aluminum oxide	2.5-6%	
F	Fe ₂ O ₃	Iron oxide	0-6%	
Ī	SO ₃	Sulfur trioxide	1.5-4.5%	
Н	H ₂ O	Water		
Ē	CO ₂	Carbon dioxide		

 Table 1. Cement composition abbreviations

Using this nomenclature, the main components of Portland cement are C₃S (tri-calcium silicate, also called alite), C₂S (di-calcium silicate, also called belite), C₃A (tri-calcium aluminate), and C₄AF (tetra-calcium aluminoferrite, also called ferrite) (MacLaren and White, 2003). The composition of these different components varies depending on the type of Portland cement (Type I, II, III, IV, or V). C₃S is responsible for the early strength of concrete and composes 45 to 75% of the total mass. C₂S contributes to later age strength and hydrates and hardens slowly, occupying 7 to 32% of the total mass. C₃A releases a large amount of heat during the first few days of cure and slightly contributes to early strength development. C₄AF hydrates rapidly but contributes little to the strength and is responsible for the gray color of hydrated cement (Taylor, 1997).

2.1.2 Hydration Products

The reaction between cement and water produces "hydration products." During the reaction of C₃S and C₂S with water two important products are formed: C-S-H (calcium silicate hydrate) and CH (calcium hydroxide). C-S-H provides the main source of concrete's strength, and has a variable ratio between SiO₂ and CaO. It forms a gel with limited local crystalline domains, but no long range order (Grutzeck, 1999). CH is the only hydration product with a well-defined stoichiometry and crystal structure. When C₃A and C₄AF react with gypsum, they form two important groups of products: AFt (alumina ferric oxide trisulfate) and AFm (alumina

ferric oxide monosulfate). AFt has the general formula $[Ca_3(Al,Fe)(OH)_6 \cdot 12 H_2O]_2 \cdot X_3 \cdot nH_2O$ where X represents a doubly charged anion or, sometimes, two singly charged anions (Taylor, 1997). Ettringite is the most common and most important member of the AFt phase, in which sulfate is the X. AFm has the general formula $3CaO \cdot (Al,Fe)_2O_3 \cdot CaSO_4 \cdot nH_2O$ and is also known as monosulfate.

2.1.3 Modeling of C-S-H

The most abundant reaction product, and main binding phase in cement is the C-S-H gel. It governs fundamental properties such as strength, ductility, fracture behavior, and durability. It has poor crystallinity and is highly variable in chemical composition, nanostructure, and morphology. For this reason, it has been extremely challenging to characterize at the nanoscale and an ongoing debate surrounding its exact nature continues. Therefore, numerous models for C-S-H paste exist.

Powers and Brownyard were the first to systematically investigate cement paste in the late 1940s. Their model did not distinguish between the different solid phases in cement paste, but referred to them collectively as "cement gel." This model can be described as "Volumetric phase distribution in a hardening cement paste," in which the water is divided into three types: chemically bound, physically bound, and free water (Brouwers, 2004; Brouwers, 2005). Chemically bound water is non evaporable below 105°C and is directly incorporated in the structure of the hydration products, physically bound water is adsorbed on the surfaces of the hydration products, and free water is contained in the capillary and gel pores of the hydrated cement paste.

Brunauer et al. (1958) considered the gel particles described in the Powers-Brownyard model consisted of two to three layers of C-S-H that could roll into fibers. He found that the specific surface area was approximately 200m²g⁻¹ as measured by water sorption. Lower values measured by nitrogen were attributed to the failure of nitrogen molecules in entering all the pore space (Brunauer et al., 1958). Feldman and Sereda described the gel as a three-dimensional assembly of C-S-H layers with pores of dimensions equal or greater than interlayer spaces. This simplified model is shown in Figure 1. They disagreed with Brunauer's measurement of the surface area and claimed that nitrogen gave the correct value (Feldman and Sereda, 1968).



Figure 1. Simplified model for hydrated Portland cement proposed by Feldman and Sereda (1968)

The Jennings and Tennis model considers two forms of C-S-H: high density and low density (Hamlin, 2000; Tennis and Jennings, 2000). Their model suggests surface area measurements using nitrogen are a result of mostly low density C-S-H and assumes high density C-S-H is not accessible by nitrogen, as shown in Figure 2. The main feature of their module is that the C-S-H is made of globules, which pack together to form LD and HD C-S-H structures, and finally these units pack together to form the microstructure of C-S-H.



Figure 2. Jennings model for LD and HD C-S-H formed after drying (Jennings, 2000)

The crystalline calcium silicate hydrate that is considered to be most similar to C-S-H in cement is tobermorite with an interlayer spacing of 1.4 nm (Franceschini et al., 2007). Taylor's model assumes C-S-H gel consists of a mixture of 14 Å tobermorite and jennite domains on the nanometer scale (Taylor, 1993). Results of both Fuji and Kondo (1983) and Cong and

Kirkpatrick (1996) show evidence that C-S-H gel exists as a solid solution between tobermorite and Ca(OH)₂. These models are good at describing synthetic C-S-H phases, while the Taylor model addresses C-S-H obtained through hydration processes of cement. More recently, Pellenq et al. (2009) developed a molecular model of cement paste from the bottom up beginning with tobermorite with an interlayer space of 11 Å. The model was further optimized with Monte Carlo and molecular dynamics simulations and validated against XRD, FTIR, and nanoindentation data. The chemical composition of their model was (CaO)_{1.65}(SiO₂)(H₂O)_{1.75} and is visualized below in Figure 3.



Figure 3. (A) TEM image of clusters of C-S-H (B) the molecular model of C-S-H. Blue and white spheres are oxygen and hydrogen atoms of water molecules, respectively. Green and gray spheres are inter- and intra-layer calcium ions, respectively. Yellow and red sticks are silicon and oxygen atoms in silica tetrahedra (Pellenq et al., 2009)

2.2 Accelerated Testing of Concrete

The hydration process of concrete is a series of complex reactions which occur rapidly at first and slow down over time. The ultimate strength of concrete, therefore, cannot be measured

immediately so standards have been developed to estimate the strength, typically after 28 days. Numerous techniques have been developed to decrease this waiting time, however they have their limits. The 3 main methods accepted by ASTM C684 are: 1) Warm Water Method; 2) Boiling Water Method; and 3) Autogenous Method.

The warm water method consists of curing standard cylinders (200mm long with a diameter of 100 mm) in a 35°C water bath for 24h immediately after molding. The specimens are then demolded and tested in compression. The main limitation of this method is that the strength gain is less than half, as compared to 28 day moist cured concrete at standard conditions, so job site testing may be required (Udoeyo et al., 2010). The boiling water method consists of standard curing of concrete for 24h, followed by a 3.5h cure in boiling water at 100°C, then tested 1h later. This method may produce products of hydration that are slightly different from normal curing conditions. In the autogenous method, specimens are placed in insulated molds made of polyurethane foam immediately after casting and are tested 48h later. No external heat is provided. The strength gain of this method is not high, and is the least accurate method of the three.

Modified techniques for both the warm and boiling water methods have been shown in the literature. Udoeyo et al. (2010) followed a modified boiling method in which they cured in moist conditions for 23h, immersed the samples into boiling water for 3.5h, then tested at 28.5h for compression²⁴. In addition they replaced up to 50% of sand with laterite. The compressive strength increased with the addition of laterite with accelerated samples having between 72 to 84% of the 28 day strength. However, their sample size was relatively small. Naik (1979) also used a modified boiling water method in which samples were moist-cured for 23h then put in 96°C water for 3.5h, beginning at the 23.5h stage. These samples were tested in compression at 28h after being allowed to cool for 1h. Naik (1979) found that there was little to no influence on the strength due to admixtures, aggregates, or type of cement. However, there was some variation in the strength, as 5% of the test results were in error of 15 to 20% when compared to the actual 28 day strength.

The standard boiling water technique, ASTM C 684, was validated by Resheidat and Ghanma (1997) on blended cements manufactured in Jordan. Their results were compared to others using linear regression models, which indicated good correlation between accelerated and 28 day samples. High values of coefficients of variation were found for both normal and

accelerated samples, but was expected since the samples were not prepared in the laboratory. Tantawi and Gharaibeh (2006) made cubes that were placed in an oven ramped up to 93°C in 1h then kept at this temperature for a total of 6h. Then the samples were demolded and allowed to cool for 30 minutes, then tested in compression. The water to cement ratio was varied from 0.45 to 0.6 and two cement doses, 300 and 350 kg m⁻³, were used. Good accuracy in prediction of the 28 day strength was found using the accelerated technique.

Meyer compared 2 data sets from two different locations and time periods in Wellington and Auckland, New Zealand. A straight-line fit and a dynamic linear model were used to evaluate the data sets, which both indicated smaller residual variances for the warm water method than the hot water method. This work also suggested that the methods could be improved by the incorporation of cement chemistry into a master equation and that for super-high strength concrete a linear model is not appropriate (Meyer, 1997). While accelerated testing of concrete usually is performed to determine if the concrete has met compressive strength requirements, there are many more considerations for accelerated testing of polymers. The chemistry and structure-properties of epoxy are completely different than concrete, and will be discussed below.

2.3 What is Epoxy?

Epoxy resins are a class of thermosetting polymers that have a broad range of applications depending on the chemical makeup and curing conditions of the epoxy system. Most epoxy resins are produced by a reaction between epichlorohydrin and bisphenol A, in which two glycidyl groups, called oxirane or epoxy groups, are attached to the ends of bisphenol A. The molecular weight of this resulting molecule depends on the ratio of epichlorohydrin and bisphenol A. In the ring opening reaction, the active epoxide groups react with a curing agent or hardener to form a highly cross-linked, three-dimensional structure. Amine curing agents are the most commonly used and the structure and number of amino groups is what determines the rate of cross-linking and final properties. The reaction between the epoxide group of the epoxy resin and a primary amine is shown below in Figure 4.



Figure 4. Reaction between an epoxide and primary amine

While epoxy resins have many applications, this work focuses on their use in construction materials, specifically fiber-reinforced polymer (FRP) repair materials. FRP composites are increasingly becoming the materials of choice for the repair of damaged concrete structures. These high performance materials, using epoxy as the matrix, have unique properties that make them especially attractive for use in civil applications due to their quick cure time, good mechanical strength, and easy processing. Prediction of the lifetime and performance of the repairs using these materials requires accelerated testing which can include variables such as temperature, humidity, aqueous solutions, or UV exposure; each of these will be further discussed.

2.3.1 Effect of Temperature

The physical properties of epoxies are highly sensitive to the effect of temperature. Increasing the temperature typically produces a decrease in elastic modulus, reduction in tensile strength, and an increase in ductility. As the temperature increases past the glass transition temperature (Tg), almost all of the properties related to its processing and performance are drastically affected (Bicerano, 2002). The Tg is the most important transition and relaxation phenomenon observed for amorphous polymers. It is a reversible structural change between a hard and relatively brittle state and a flexible, rubbery state. At lower temperatures, in the glassy state, conformational changes are severely restricted, but as the temperature increases past the Tg. motion of side groups begins, followed by large segments, until the entire chain can flow.

Free volume theory can be used to explain the physical changes that happen during a glass transition process. At the beginning of the glass transition, a part of the solid polymer turns into a liquid, and the free volume, or the sum of the holes in a polymer due to atomic packing irregularities, increases. The increase in free volume corresponds to changes in the interatomic and intermolecular spacing within the polymer. In general, as the viscosity decreases, the free volume increases. With a decrease in viscosity, or increase in the mobility of polymer chains, there is a change in the heat capacity. The heat capacity in the liquid phase above the Tg is greater than in the solid state below the Tg. This property can be measured by numerous

techniques including differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA).

In DSC, the instrument monitors heat flow, or the energy release on heating, between a sample and reference. As the heat capacity changes during the transition, there is also a change in heat flow. DMA works by applying a sinusoidal deformation (either a controlled stress or strain) to a sample of a known geometry. The storage modulus, E', is the ratio of the stress and strain components in-phase with each other; the loss modulus, E'', is the ratio of the stress and strain components 90° out-of-phase with each other; and the loss tangent is the ratio of the loss and storage moduli. The glass transition is observed as a drop in the storage modulus and as peaks in the loss modulus and loss tangent. Finally, TMA applies a static force and reports dimensional changes. Coefficients of thermal expansion can be easily measured with TMA when the sample carries a zero or negligible load and the material is allowed to freely expand or contract. TMA is significantly more sensitive than DSC for measuring the Tg of cross-linked materials. This difference in measurement is manifested by the variables inherent in the instrument. Since DSC measures heat capacity, the heating rate is a critical parameter, while in TMA, the sample thickness is a critical component. Therefore, correlation of the Tg using the two instruments is not possible because both methods have their own considerations.

The glass transition temperature of epoxies can vary greatly depending on the curing agent. Table 2 shows the change in the glass transition temperature for diglycidyl ether of bisphenol A (DGEBA) epoxy cured with different curing agents. There is a significant dependence of the Tg on the molecular weight of a polymer system. A linear polymer has higher mobility at the chain ends than the center of the molecule because the chain ends are only bonded to one repeat unit, while the inner repeat units are bonded on both sides. Decreasing the molecular weight of this system results in an increase in the concentration of chain ends, and therefore the average mobility of all the repeats units is increased, resulting in a decrease in Tg (Mark, 2004). This relationship has been shown in the Fox-Flory equation in Equation 1 where K is an empirical parameter and M is the molecular weight. As shown by this equation, Tg is a maximum at infinite molecular weight.

$$Tg = Tg_{\infty} - \frac{K}{M}$$
 Equation 1

Curing Agent	Tg (°C)
DETDA	217
DDM	190
DDS	189
TETA	139
Jeffamine-130	65
Jeffamine-230	47
Jeffamine-800	0

Table 2. Change in Tg of DGEBA cured with different curing agents

Throughout this report, DGEBA, or EPON 826, and Jeffamine 230, or poly (oxypropylene) diamine (POPDA) were used. EPON 826 has an epoxy equivalent weight of 178 to 186 g/equiv as reported by the manufacturer. Their chemical structures are found below in Figure 5.



Figure 5. DGEBA and Jeffamine D230 chemical structures

2.3.2 Effects of Water

Epoxy resins can easily absorb water up to 7% of their weight, due to moisture from humid environments (Musto et al., 2000; Mijović and Lin, 1985). This is due to the creation of polar hydroxyl groups from the epoxide ring opening reaction, and tertiary amines during the reaction which forms its cross-linked structure. Water can form hydrogen bonds with other water molecules or polar groups in the polymer. It acts as a plasticizing agent, reducing the intermolecular forces which hold the macromolecule together.

Soles and Yee (2000) investigated sub-Tg moisture transport in epoxy resins. Although direct experimental observation remains to be performed to verify some details, they suggested that water moves through the epoxy through a network of nanopores. Polar sites, such as amine

functional groups, regulate transport of water molecules through the nanopores depending on the orientation of the resin. Figure 6 demonstrates how polar sites can either block or allow moisture to traverse the epoxy resin.



Figure 6. Transport of water through nanopore network in epoxy, proposed by Soles and Yee (2000)

A study by Choi and Douglas (2010) directly examined some anomalous behavior in which the Tg of some epoxy systems increased with exposure to water at certain temperatures. The three potential mechanisms for this phenomena are summarized as 1) post curing induced by the elevated temperature of the water; 2) different states of hydrogen bonding water molecules, one of which induced secondary cross-linking; and 3) the effect of the biphasic structure of epoxy. Choi quantitatively evaluated changes in Tg using DSC, and measured reaction progress, or conversion of the epoxide group through near-infrared IR, and determined that plasticization by water occurred simultaneously as an increase in cross-link density. Samples exposed at 30 and 40°C showed an increase in plasticization as the amount of water increased while samples at 50 and 60°C showed a change in Tg that was independent of the amount of water.

2.4 Accelerated Testing of Epoxies

2.4.1 Change in Properties

The inability to generate precise service life for polymer systems exposed in the field has been a challenge for over a century. Typical field exposures can vary tremendously and involve many years at an exposure site such as Arizona, where it is hot and dry, or Florida, where it is hot and humid. However, this data is usually not repeatable or reproducible, since the weather never repeats itself, and the exposure times make it difficult to conduct tests within the timeframe of materials development or qualification cycles. Thus, accelerated testing is generally performed in an attempt to either predict long-term performance or at least provide a relative ranking of materials. This accelerated testing usually involves elevated temperatures, corrosive solutions, UV exposure, or other degradation techniques (Gu et al., 2009).

Laboratory weathering experiments are an attempt to simulate and accelerate real world degradation conditions. Generally these tests involve exposure to temperatures above those experienced in the field and immersion in water. However, if the exposure temperature is close to or exceeds the glass transition temperature of the polymer (Tg), the mechanism of degradation may be different than under the field condition. Immersion in water can also change the Tg, further complicating the testing. This can make it difficult to compare results obtained from accelerated testing to those from the field.

Numerous studies have shown a decrease in the Tg with exposure to elevated temperature and/or water. Ellis and Karasz (1984) measured the Tg for a number of epoxy systems, and found that the reduction in the Tg for stoichiometric compositions could be matched with a compositional model for the Tg depression (Ellis and Karasz, 1984). Notably, they found that for epoxy-rich samples that were exposed to water at 90°C, the Tg was depressed by moisture absorption during exposure and increased after drying. Amine-rich samples showed a greater depression in the Tg than was predicted in the model. In a follow-up article, they went on to claim that there is no evidence for tightly bound water and that it is unlikely that water disrupts the hydrogen bond network in the epoxy resin (Jelinski et al., 1985).

In contrast, Zhou and Lucas claimed two types of bound water can exist in epoxy resins (Zhou and Lucas, 1999a). Type I bound water acts as a plasticizer, causing a decrease in Tg and Type II bound water promotes secondary cross linking with hydrophilic groups and limits Tg depression. In their epoxy system they found an initial depression of the Tg that was fully recoverable upon drying. This same phenomena was also reported by Bockenheimer et al. in a series of papers which examined a high and low cross-linked system under thermal and hydrothermal aging (Bockenheimer et al., 2004a and 2004b). Under hydrothermal conditions reversible phase separation occurred for both systems as well as the appearance of a new, second

Tg. In a follow up article, Fata and Possart (2006) found that the primary Tg of the thermallyaged epoxy initially decreases then remains constant and a substantially lower, secondary Tg is formed that increased with time, as can be seen in Figure 7. This secondary Tg vanishes upon heating above the primary Tg. Reheating this system does not recover the primary Tg, and is explained by irreversible plasticization due to bonded water (Bockenheimer et al., 2004b). Unfortunately DMA experiments were not performed to verify these conclusions, and it is possible that the heating process was not to a high enough temperature or a long enough time to remove the water.



Figure 7. DSC measurement of a highly cross-linked epoxy during hydrothermal exposure aging at 60°C (Bockenheimer et al., 2004b)

Fredj et al. (2010) also found the development of two phases with exposure to water, as evidenced by two peaks in the DMA (dynamic mechanical analysis) tan δ curve in Figure 8. The primary Tg slightly increased over time and the secondary Tg decreased. This was explained by high and low cross-linking zones. They also found a decrease in the Young's modulus which remained constant after the saturation limit was reached.

Papanicolaou et al. (2006) characterized the mechanical and viscoelastic properties of a DGEBA / DETA (diglycidylether of bisphenol / diethylenetriamine) system using 3-point bend DMA, in combination with differential scanning calorimetry (DSC). As expected, there was a decrease in flexural strength and modulus with increased time and temperature of exposure



Figure 8. Evolution of tan (δ) as a function of temperature for an epoxy with and without water (Fredj et al., 2010)

(Papanicolaou et al., 2006). The samples' Tg increased and tan δ peak decreased with increased exposure and time, and was explained by the secondary network theory proposed by Zhou and Lucas (1999b). A decrease in the shear strength of epoxies aged at 85°C and 85% relative humidity was found by Lin et al. (2006), who explained their results through the common belief that adsorbed moisture attacks the cross-links. However, as shown in their Fourier transform infrared spectroscopy (FTIR) data the epoxy was not fully cured before exposure.

Other studies have performed accelerated testing of epoxies in different solutions. Yang et al. (2008) investigated a commercial epoxy system during exposure to water, salt, and alkali environments. As expected, exposure led to a decrease in the tensile strength, modulus, and tan delta peak height with increased exposure. A slight depression in the Tg was found initially after which there was insignificant change. Alkali environments showed the most reduction in properties. A different study exposed a blended epoxy system to dichloromethane, aviation fuel, propylene glycol, hydraulic fluid, DI water, urea, and simulated seawater at 65°C (Doyle and Pethrick, 2009). The blended epoxy system showed virtually no change in shear strength when exposed to propylene glycol and hydraulic fluid. Epoxy systems exposed to other solutions showed a reduction in properties over time, with the highest degradation due to dichloromethane. Cyclic exposure is another method of accelerated testing of materials and is often coupled with UV exposure. Recently, Singh et al. found that alternating 3-hour cycles of UV radiation and water vapor condensation at 50°C degraded the flexural strength of epoxy up to 81% and induced the removal of surface layers (Singh et al., 2010). Exposure to a constant relative humidity of 80% at 50°C resulted in a 47% reduction in the flexural strength, but interestingly, increased the flexural modulus, while the cyclic exposure decreased the modulus. Shi et al. (2010) exposed Epon 828 to alternating cycles of UV at 55°C and water spray at 25°C with varying times. Besides a depression of the Tg with increasing relative humidity, higher indentation recovery using AFM was found at higher relative humidities. They explained this result by relaxation of the plasticized network. Rezig et al. (2006) found a loss in the thickness and an increase in surface roughness after exposure to UV at 50°C, with higher degradation occurring at a higher relative humidity, as shown in Figure 9. This degradation was inhomogeneous. The formation of nanoscale pits, which deepened and enlarged with time, was observed with confocal microscopy.



Figure 9. 2D and 3D AFM images of samples exposed to different environmental conditions: (a) lab UV/75%RH/50°C, (b) lab UV/9%RH/50°C, and (c) outdoor in Gaithersburg, MD (Rezig et al., 2006)
Other changes in properties have been measured on commercial epoxy systems as well. Hu et al. (2009) found that after cyclic exposure to radiation and condensation a decrease in the coating resistance was found after 28 days. Small blisters and microcracks were formed on the surface which grew over time. In addition the adhesion strength between the epoxy and steel plates decreased over 50% with exposure. Lim and Lee (2000) found that after exposure to boiling water their epoxy system showed a lower contact angle, surface potential, and surface resistivity. They explained these findings by the formation of carboxyl groups which cause rapid deterioration of electrical properties. In summary, most research found a change in the glass transition temperature and a decrease in properties with exposure to temperatures up to 100°C, with and without water or other liquids. A summary of the literature in this area can found below in Table 3 in which the type of epoxy, exposure conditions, exposure time, and property changes can be found.

2.4.2 Degradation Mechanisms of Epoxies

In the literature many mechanisms are suggested to explain results of accelerated degradation experiments. One of the most common explanations for the degradation in properties is the plasticization of the epoxy network. Water increases the free volume and reduces the polymer-polymer chain secondary bonding, resulting in a decrease in Tg.

Doyle and Pethrick (2009) found that for epoxy exposed to water-based solvents there was a depression in the Tg. This indicates reduced cohesive forces between polar chains and an increase in polymer motion. For non-polar solvents, plasticization was coupled with swelling of the resin and was the main suggested mechanism for the change in bond strength. Bockenheimer et al. (2004) also cite water as the source of plasticization of the epoxy network in which the water molecules interrupt the physical cross-links by interacting with the polar groups of the epoxy.

Another research group examining epoxies determined that a splitting of the tan δ peak correlated to a formation of a biphasic structure. The lower temperature tan δ peak was due to the water-plasticized fraction of the specimen, while the higher temperature peak was due to the dried fraction of the specimen, which reflects the amount of cross-linking (Yang et al., 2008; Xian and Karbhari, 2007). They also mention the competing effects of cure progression and plasticization in the early periods of exposure, followed by hydrolysis at longer periods of

Materials	Exposure conditions	Exposure Time	Property Changes
DGEBA/mPDA, TGDDM/DDS, Fiberite 934:TGDDM/DDS (Zhou and Lucas, 1999a)	Water at 45, 60, 75, and 90C	1530 hr	Initial decrease in Tg, then increase. Tg fully recoverable upon drying
DGEBA/DETA (Bockenheimer et al., 2004a)	40C and 60C in air	112 days	Decrease of Tg, recoverable on drying
DGEBA/DETA (Bockenheimer et al., 2004b)	Water at 40C and 60C	79 days	Increase in Tg for low cross-linked epoxy, the high cross-linked epoxy shows a new second Tg with aging and reversible phase separation.
DGEBA/TETA (Papanicolaou et al., 2006)	in water at 60 and 80C	1536 hr	Increase in Tg with exposure, decrease in tan d
Amino amide-epoxy and polyamide-epoxy with 25% filler (Fredj et al., 2010)	DI water and Saline at RT	200 days	Increase in Tg1 decrease in Tg2, 35- 40% decrease in modulus
DGEBA/DDA (Fata and Possart, 2006)	Exposure of epoxy to air and water at 60C	100 days	New secondary glass transition and reversible phase separation
Epoxy/Ni-Au composite Lin et al. (2006)	85C 85%RH	550 hr	50% loss of shear strength
Sikadur 30: aromatic hydrocarbon and aliphatic amine (Yang et al., 2008)	Exposure of epoxy to water, alkali, NaCl, 23C or 60C	2 years	E loss of 30-60%,tensile loss of 40- 70%
Blend of epoxies amine curing agents (Doyle and Pethrick, 2009)	Dichloromethane, aviation fuel, propylene glycol, hydraulic fluid, DI water, urea, simulated seawater at 65C	730 days	Aqueous based system showed a 30% decrease in strength, propylene glycol and hydraulic fluid virtually no change
Epon 862/Epikure 3274 (Singh et al., 2010)	50C 80% RH, cycles of UV and condensation at 50C	4098 hr	Decrease in flexural strength up to 47% in moisture, 81% in UV /condensation
Epon 828/Epikure 3115 (Shi et al., 2010)	Various wet and dry cycles at 25C	56 hr	Higher indentation recovery at higher RH
Dow DER 332/bisaminomethyl cyclohexane (Rezig et al., 2006)	UV radiation at 50C with 9% or 75% RH	140 days	Up to 38% loss in thickness under chamber, 18% outdoor, RMS increase up to 0.7 µm
Commercial 2-part epoxy varnish (Hu et al., 2009)	UV radiation at 60C for 8h then condensation at 50C for 4h	35 days	Decrease in coating resistance after 28 days
DGEBA/MNA with BDMA accelerator (Lim and Lee, 2000)	Boiling water	1000 hr	Decrease in contact angle, surface potential, surface resistivity

Table 3. Summary of changes in properties for accelerated testing of epoxy systems

exposure. Frigione et al. (2006) also mentions the concept of plasticization competing with postcure cross-linking at early periods of exposure. The lowering of the Tg with the absorption of moisture allows the polymer chains to become mobile, which allows a limited displacement of chain segments which promote post curing. This could explain higher values of Tg for longer periods of time and higher exposure temperatures accompanied with an initial increase and then decrease in ductility over time.

In general, while many authors cite plasticization as a mechanism for the degradation in properties, they do not confirm that the effect is reversible. Thus, the claims of plasticization as a mechanism are somewhat tenuous and overall require further investigation.

Another commonly cited explanation for a decrease in properties is centered around the idea that multiple types of bound water can exist in the epoxy network. NMR and FTIR have been used on epoxy resins to determine that water can be bound to the epoxy resin with a mobility between solid and free water (Zhou and Lucas, 1999a; Antoon and Koenig, 1981). In a series of papers, Zhou and Lucas (1999a, b) questioned the polymer-diluent model's ability to accurately predict the glass transition temperature of epoxy systems because the depression of the Tg of epoxies is not a simple matter of the amount of water uptake of the material. They suggested that the Tg is influenced by a dual mechanism process. Type I bound water causes a depression of the Tg due to interruption of interchain bonds and Type II bound water offsets that drop through secondary cross-linking resulting from a water-resin interaction. Type I bound water forms single hydrogen bonds while Type II forms multiple hydrogen bonds and has a higher activation energy, making it harder to remove from the resin. Papanicolaou et al. (2006) used the previous model to explain their findings. Exposure of their epoxy to DI water at elevated temperatures resulted in no variation in E', but an increase in the Tg, while the strength was decreased with exposure.

Li et al. (2010) used FTIR to analyze water absorbed into 6 different epoxies and fit the hydroxyl stretching region with four different components. These regions corresponded to 2 water molecules without a hydrogen bond, one hydrogen bond, and double hydrogen bonds (loose or tight). 2D correlation analysis suggested that diffusion was accomplished by water molecules with loose double hydrogen bonds and the impeding step originated from the rearrangement of local chains to open additional polar sites and the energy required by water molecules to dissociate from the epoxy network.

Wu and Siesler (2003) used 2D ATR-FTIR to investigate the diffusion of water in epoxy networks at room temperature. The basic concept of 2D IR experiments are somewhat similar to 2D NMR experiments, but since vibrational relaxation rates are many orders of magnitude faster than spin relaxations, the double Fourier transformation technique developed for 2D NMR experiments is not really applicable. In 2D IR experiments an external perturbation, such as a change in concentration, is applied to the sample which selectively induces time-dependent reorientations of electric dipole transition moments associated with the individual modes of vibration in the system (Noda, 1989). Individual dipole transition moments respond differently to the external perturbation and have unique reorientations rates which can be used to identify highly overlapped IR bands. Wu and Siesler (2003) fit the hydroxyl stretching region with 3 components: weak water-water hydrogen bonds, strong water-water hydrogen bonds, and waterepoxy hydrogen bonds as shown in the shaded regions in Figure 10. They explained a positive shift in the OH stretching band as an indication of interactions between water molecules and the carbonyl oxygen in the epoxy matrix, as a result of water diffusion into the epoxy network. Over time the epoxy structure limits the movement of water molecules and forces the water molecules to form clusters with other water molecules.



Figure 10. Asynchronous 2D correlation IR spectra of water in epoxy in the spectral range 2800– 3700 cm⁻¹ (Wu and Siesler, 2003)

2D FTIR spectroscopy was also used by Musto (2003) on epoxies exposed to thermal degradation at 200° C. He found the disappearance of hydroxyl, CH₂, and CH groups with increasing exposure. The oxygen attack led to the formation of two groups, amide and aldehyde/ketone groups.

Oxidation is another mechanism suggested for degradation of epoxy resins. Monney et al. (1998) exposed an epoxy system to UV radiation at 42°C in air and confirmed the existence of a thin photo-oxidation layer that evolved at a constant rate. This was monitored by ATR-IR which indicated the loss of CH and CH₂ groups which form radicals which aid in the production of carbonyl groups, particularly ketone and ester groups. Hong (1995) performed thermal degradation of epoxy films on various metal substrates and also found the formation of carbonyl groups and the degradation of CH₂ groups using IR spectroscopy. He also found evidence for cleavage of nitrogen-phenyl bonds in the epoxy backbone. XPS fitting of the C1s spectra indicated carboxyl species were produced and that the degradation occurred more rapidly on the copper substrate than the steel or aluminum. Lim and Lee (2000) also found the presence of carboxyl groups after exposure to boiling water. After exposure they found an increase in the Ols peak height and changes in the Cls peak, along with a decrease in contact angle, indicating a change in the hydrophilic property of the surface. Meiser et al. (2010) also found that exposure in air at 60° and 120°C with moisture created alkyl radicals which produced carbonyl groups, amide groups, and chain scissions. Chain scission was indicated by a decrease in the stretching band of ether groups at 1034 cm⁻¹ as shown in Figure 11. In this image, the solid lines are on the surface and the dashed lines are at 350 µm below the surface. Malajati et al. (2011) found that water exposure resulted in the oxidation of CH₂ groups which leads to the formation of carboxylic acids, while the combination of water and UV light caused hydrolysis. Similar short network fragment products were found in both works.

Hydrolysis is an irreversible process that results in chain scission in epoxies reported in the literature as a result of exposure to water. After 6 day of exposure to DI water at 90°C, Xiao et al. (1997) found that the intercross-linking chain segment containing nitrogen was cut or leeched out during the aging process. This XPS result was confirmed by FTIR results which found the absence of a characteristic peak of the DDA curing agent. They suggested that water interacted with the tertiary amine groups in the resin to form N-H and –OH bonds in the polymer



Figure 11. ATR-IR spectra of various stoichiometries of epoxy and amine curing agent after 25 days of aging at 120°C on the surface and a depth of 350 µm (Meiser et al., 2010)

chain. Fata and Possart also examined a DDA cured system and discovered evidence of both plasticization and hydrolysis. They found that thermal aging at 60°C did not cause any chemical modifications, but a new phase was formed that was reversible upon heating above the Tg. Hydrothermal aging also produced a new phase, but simultaneously, hydrolysis cleaved cross-links specific to DDA-cured epoxy. The hydrolysis cleaved only imino-ether-like cross-links, but amine-like or ether-like cross-links were unaffected (Fata and Possart, 2006). This mechanism is depicted below in Figure 12, with the corresponding wavelengths for the functional groups that are identified using FTIR spectroscopy as shown in Figure 13.



Figure 12. Hydrolysis degradation mechanism of DDA-cured epoxy (Fata and Possart, 2006)



Figure 13. FTIR of the DDA-cured epoxy system at 60°C up to 101 days (Fata and Possart, 2006)

Jana and Zhong (2007) examined the effect of both water and UV radiation and also suggested hydrolysis as the dominant mechanism. UV radiation degraded the polymer network more severely than water alone and, as with the other studies, an increase in carbonyl groups was observed due to hydrolysis and photooxidation of alkyl, phenyl, and aromatic ester linkage units.

A different mechanism was suggested by Hu et al. (2009) who exposed their commercial epoxy to UV and water. They hypothesized that the water and oxygen exposure created soluble degradation products from the epoxy which penetrated into the network along with water to form osmotic cells. The cycling of the UV and water caused osmotic pressure effects which lead to the formation of blisters which in turn ruptured, which correspond to a deterioration of properties.

Table 4 gives a brief summary of the degradation mechanisms for epoxy systems. Essentially, at lower exposure temperatures in the presence of water plasticization is proposed as the dominant mechanism, with the caveat that true plasticization, which requires reversibility, is generally not demonstrated in these studies. At higher temperatures and with UV exposure oxidation and hydrolysis are cited as the primary degradation mechanism.

Materials	Exposure conditions	Exposure Time	Mechanism
Blend of resins and amine cure agents cured on aluminum (Doyle and Pethrick, 2009)	Dichloromethane, aviation fuel, propylene glycol, hydraulic fluid, DI water, urea, simulated seawater at 65C	730 days	Plasticization/Swelling
DGEBA/DETA (Bockenheimer et al., 2004)	Water at 40C and 60C	79 days	Plasticization
4,4'-isopropylidenephenol- epichlorohydrin with an aliphatic amine hardener (Xian and Karbhari, 2007)	DI water at 23, 40, 60 C	24 months	Plasticization competing with post curing in early stages, followed by hydrolysis
Sikadur 30: aromatic hydrocarbon and aliphatic amine (Yang et al., 2008)	Exposure of epoxy to water, alkali, NaCl at 23 or 60C	2 years	Post cure vs plasticization
Sika S50, M16, M20 (Frigione et al., 2006)	DI water at RT	28 days	Plasticization and water-substrate interaction vs cross-linking
DGEBA/mPDA, TGDDM/DDS, Fiberite 934:TGDDM/DDS (Zhou and Lucas, 1999a)	Water at 45, 60, 75, and 90C	1530 hr	Type I bound water forms a single hydrogen bond with epoxy, Type II bound water forms multiple hydrogen bonds.
DGEBA/mPDA, TGDDM/DDS, Fiberite 934:TGDDM/DDS (Zhou and Lucas, 1999b)	Water at 45, 60, 75, and 90C	1530 hr	Type I bound water plasticizes the network, Type II bound water forms a secondary cross-link.
DGEBA/TETA (Papanicolaou et al., 2006)	in water at 60 and 80C	1536 hr	Single or double hydrogen bonds, Type I plasticizes, Type II forms secondary cross-link
Novolac epoxy resin (Wu and Siesler, 2003)	DI water at RT	16 min	Carbonyl and hydroxyl groups form H- bonds with water at low concentrations, but at high concentrations water forms clusters
DGEBA, TGAP, TGDDM, DDS, DDM (Li et al., 2010)	20C and 75C in DI water	13 hr	Loose double bound water molecules diffuse through the network
TGDDM/DDS (Musto, 2003)	200C in air	1,000 min	2 competitive pathways forming amide or aldehyde and/or ketone. Molecular breakdown with disappearance of hydroxyl, CH2, and CH groups.
DGEBA/MTHPA (Monney et al., 1998)	UV and 42C	250, 500, and 1000 hr	Oxidation of matrix and formation of carbonyl groups.
Magnobond 6388- 3:TGDDM/amidoamine (Hong, 1995)	Cu, Al, and steel at 150C	1, 45, and 90h	Nitrogen - phenyl groups broken and carbonyl and amides formed
DGEBA/MNA with BDMA accelerator (Lim and Lee, 2000)	Boiling water	1000h	Oxidation of matrix and formation of carbonyl groups.
DGEBA/DETA (Meiser et al., 2010)	90%RH, 60C 120C	300 days	Oxidation, hyperperoxide decomposition and Cope elimination, resulting in chain scission.
Phenoxy resin (Malajati et al., 2011)	UV and salt water cycles	100h	Water cause oxidation of CH2 groups with formation of carboxylic acids. UV and water caused hydrolysis of phenyl formates.
DGEBA/DDA (Xiao et al., 1997)	DI water at 90C	6 days	Chain scission through hydrolysis
DGEBA/DDA (Fata and Possart, 2006)	Exposure of epoxy to air and water at 60C	100 days	Plasticization and Hydrolysis cleaves imino-ether cross-links
Epon 828/Epikure and reactive graphite nanofibers (Jana and Zhong, 2007)	water at 60C and UV	30 days	Hydrolysis
Commercial 2 part epoxy varnish (Hu et al., 2009)	UV radiation at 60C for 8h then condensation at 50C for 4h	35 days	Soluble degradation products penetrate the matrix with water, which forms osmotic cells.

Table 4. Summary of mechanisms of degradation for accelerated testing of epoxy systems

2.5 Accelerated Testing of FRPs

2.5.1 Change in Properties

The presence of the fiber in a composite can have a strong effect on the aging behavior of the system compared to neat epoxies. Ramirez et al. (2008) exposed their carbon fiber epoxy composite to salt water and DI water at 40° and 60°C and found a decrease in Tg up to 19°C, a 50% decrease in the flexural strength, 25% decrease in the transverse strength, and an 18% decrease in the modulus. They claimed that since carbon fibers do not absorb moisture, absorption took place at the interface through wicking and possibly through cracks. Since concrete was not part of the study, they only examined fiber-matrix interactions. Miyano et al. (2005) results confirmed the irreversible loss in properties with exposure in their CFRP-epoxy system. However, they found that the vinylester CFRP systems could regain their flexural strength upon re drying. Adams and Singh (1996) found all but one of their epoxy composites had a recoverable loss in shear modulus and interlaminar shear stress. The one composite that was not recoverable did not exhibit degradation in thermal conditioning, but only with exposure to steam in the form of delamination along the fibers. This set of composites was not post-cured, unlike the other systems, so it was, most likely, more easily plasticized. Unfortunately, chemical analysis was not performed in the study. Another study by Zhang et al. (1997) showed reversible property loss of flexural strength, modulus, and interlaminar shear strength after exposure to boiling water at 100°C for 2 days, then drying at 105°C for 1 day.

When exposed to other solutions, such as salts or alkali, FRP composites showed similar reduction in properties. Chen et al. (2007) exposed two FRP systems (E-glass / vinylester and carbon / epoxy) to various salt solutions under cyclic exposure at different temperatures and found reductions in tensile strength and interlaminar shear stress. The solution containing 2:20:2 of NaOH, KOH, and Ca(OH_{J2} showed the most degradation of all the solutions although the epoxy-CFRP samples showed better resistance to the environmental conditions. Micelli and Nanni (2004) examined FRP rods consisting of carbon fibers and epoxy/vinylester matrices under cyclic environments including alkaline solution, elevated temperatures, and UV irradiation. Alkali aging resulted in up to 40% loss in shear strength, but almost no loss after environmental cycles of freeze-thaw, high relative humidity, high temperature, or UV radiation. The samples lost minimal tensile strength in alkali aging and environmental cycles. The authors recognized a major limitation of the work being the absence of stress during the accelerated

aging processes. Murthy et al. (2010) exposed vinyl ester and epoxy systems to artificial seawater at room temperature for several weeks. The flexural, tensile, and interlaminar shear strength all decreased with increased exposure with the epoxy system exhibiting more degradation than the vinyl ester based composites.

Some studies showed little to no change in properties after environmental exposure. The epoxy CFRP composites of Lee and Peppas (1993) exhibited no change in Tg with exposure to water at various temperatures. At 80°C the interfacial shear strength of the DGEBA system was strongly reduced, while the TGDDM system was not significantly degraded in any of the exposure systems. Ray (2006) found the effect of changing temperature and humidity had little impact degrading the ILSS and shear strength of his GFRP epoxy/polyester composites. No chemical analysis was performed so it is difficult to assess if the samples were truly degraded at 50° and 60°C.

Some studies showed that exposure to accelerated aging conditions had no effect on longitudinal properties, but the transverse directions were significantly degraded. Kumar et al. (2002) performed cyclic exposure of condensation and UV light on a commercial CFRP, with continuous oriented fibers, known as IM7/997 for a period of 1,000 hours. They found no effect on the modulus or Poisson's ratio, but a large reduction in the transverse tensile strength. No real changes were found in the longitudinal properties, but the authors warned that over longer periods the accelerated conditions would lead to so much matrix erosion that even the longitudinal properties would be affected. Based on the principles of the rules of mixtures for composite materials, the modulus of the composite will be higher than the modulus of the matrix in the longitudinal direction, so no decrease in the transverse tensile strength or modulus is expected. For composites tested in the longitudinal direction the total load sustained by the composite, F_e, is equal to the loads carried by the matrix phase, F_m, and the fiber phase F_f as shown below in Equation 2 (Callister and Rethwisch, 2011).

$$F_c = F_m + F_f$$
 Equation 2

Hulatt et al. (2002) also found no real changes in longitudinal properties of epoxy GFRP and CFRPs exposed to wet/dry cycles and salt solutions. Also UV radiation and salt solution produced no adverse effects on the ultimate failure stress while water and 60°C exposure produced some degradation of the composites. However, there was a relatively large amount of error reported in this work, with a coefficient of variance above 10% for many samples. Boualem and Sereir (2011) performed a predictive study on the mechanical degradation properties of a graphite epoxy under hygrothermal aging using a quadratic failure criterion in stress space. They found that at early moisture diffusion times hygrothermal stresses reach their maximum values and longitudinal direction properties are unaffected, while in the transverse direction the properties are significantly reduced.

2.5.2 Change in Properties of FRPs with Concrete

Similar trends can be found in the literature regarding accelerated degradation of epoxy FRPs bonded to concrete. Benzarti et al. (2011) examined CFRP and unidirectional carbon fiber sheets with four different epoxies bonded to concrete under conditions of 40°C and 95% RH, and found a decrease in pull-off strength with exposure, seen in Figure 14. This decrease was not consistent with data from shear tests, which did not show any change and was explained by the evolution of the interfacial load transfer which counterbalanced the effect of joint weakening. The aged specimens showed greater strain levels in the free edge region, and over time, the load was progressively redistributed over a larger length of the lap joint. However, the concrete substrates underwent a surface treatment and were either sandblasted or diamond ground, which could lead to a more complex interface. They also found a drop in the Tg for one type of epoxy, which became more severe over time, while another epoxy system did not exhibit any loss. Some samples of concrete also underwent carbonation treatment. These samples showed higher initial strength and less degradation with exposure than untreated samples.

A different study by Mufti et al. (2007), examined GFRPs made of E-glass and vinylesters used in repair conditions in Canada for 5 to 8 years They were exposed to freeze thaw conditions, wet / dry cycles, deicing salts, saltwater, and thermal loading. The researchers found no reduction of the Tg of the matrix or cracking of the concrete in any of the samples, which is inconsistent with results from simulated or accelerated laboratory studies. However, the thermal range of the field conditions did not exceed 35°C, which is typically well below the glass transition temperature of most commercial epoxy systems. Lyons et al. (2002) also found minimal degradation on their FRP-composite with various exposures up to 40 days. Using modified double cantilever beam samples to determine the Mode I strain energy release rate indicated the only statistically significant degradation of toughness was observed at 100°C and 95% RH. However, they used masonry bricks and did not perform a chemical analysis of the



Figure 14. Change in pull-off strength of bonded interfaces of concrete composites after 628 days (Benzarti et al., 2011)

epoxy. In contrast, Leveque et al. (2005) found their composite had a Tg that increased up to 100 hours of exposure then decreased afterwards after thermal exposure at 210°C.

Toutanji and Gomez (1997) examined FRPs bonded to type II Portland cement under cyclic environmental conditions, but with salt solution. They used three different amine cured epoxy systems with two different carbon fibers and two different glass fibers. They found that even with the harsh environments of wet/dry cycling, the beams exhibited an increase in load capacity (compared to samples without FRP) when the FRPs were bonded to the tension side of the concrete beams. However, the ultimate load decreased as compared to the non-exposed samples (up to 33%). The change in properties was attributed to the degradation of the epoxy since the fibers did not break at specimen failure and debonded at the fiber-concrete interface.

Other studies exhibited a similar reduction in properties. Two different studies (Au and Buyukozturk, 2006; Tuakta and Buyukozturk, 2011) on commercial epoxy CFRP systems found a sharp reduction in fracture toughness with exposure to DI water at 23°C and 50°C. Peel fracture experiments exhibited a greater loss than shear fracture experiments but both methods

demonstrated a separation at the epoxy/concrete interface as compared to dry samples which failed in a concrete delamination mode. Interestingly, they found that after a certain time, the bond strength approached a value after which no significant degradation occurred and that after drying the composite could not regain its original strength after wet-dry cycles.

A series of studies by El-Hawary et al. (2000; 1998) in Kuwait examined the effect of sea water on epoxy repaired concrete comparing field use to laboratory results. No real loss in tensile or bond strength was found over the course of 18 months of exposure. Interestingly, the buildup of sea shells was reported to increase the strength of samples exposed directly to the sea water. A major limitation of the work was the small population size of only 2 samples per group. Mourad et al. (2010) also found no significant changes in tensile strength or modulus in glass/epoxy composites after 1 year of exposure to seawater at 23°C or 65°C while glass/polyurethane composites exhibited degradation at the fiber/matrix interface. Silva (2007) also found little to no loss in properties for samples exposed to various environments. His samples were commercial GFRP epoxy composites that were exposed to salt fog, humidity cycles, and UV degradation. No change in tensile modulus was found for water immersion at room temperature and UV exposure, and a change of less than 10% loss was observed for temperature and salt fog cycles. No change was found in the tensile strength under room temperature water, and less than 12% loss for all other conditions after 10,000 hours of exposure. A series of papers by Silva and Biscaia (2010) in simulated tide water, and salt fogging indicated the bending load capacity of GFRP composites on concrete was improved after exposure. There was no degradation for samples immersed in DI water, and samples in moisture or salt fog cycles showed an initial decrease after 6,000 hours that increased by 10,000 hours. Slip was affected by artificial aging and decreased for all conditions with the bond visibly more degraded by the salt fog process. Finite element analysis was performed and was in good agreement with the experimental data. The 2D and 3D models matched the experiment with the exception of the maximum bond stress and slip at the interface, where the 3D model gave better representation.

Karbhari et al. (1997) performed peel tests on 2 different epoxy FRPs on cement mortar to determine interfacial fracture energies. In addition to finding that exposure of the composites

Materials	Exposure conditions	Exposure Time	Property Changes
T700 and AS4 carbon fiber, MAS epoxy, VE D411, VE D8084, VE H922L (Ramirez et al., 2008)	Salt water, DI water 40°C and 60°C	1200 hours	Decrease in Tg, 50% decrease in flexural strength, 18% decrease in modulus
CFRP with DGEBA and amine hardeners (Benzarti et al., 2011)	40°C 95% RH	20 months	Changes in Tg dependent on epoxy type, strength of all epoxies decrease by factor of 2 or 3. composite pull-off tests result in decrease, nothing for shear
GFRP (Mufti et al., 2007)	-35 to 35°C. outdoor conditions in Canada	5 to 8 years	No Change in Tg or degradation
TGDDM/DDS, DGEBA/DDA and CFRP (Micelli and Nanni, 2004)	Water at 50,70,90, and 100°C	1200 hours	Minimal effect on Tg. Large decrease in interfacial shear strength.
Commercial Poly-amide cured epoxy with glass fiber tows on concrete masonry bricks (Lyons et al., 2002)	RT, 60°C 95% RH, 100°C 95% RH	163 days	35% decrease in fracture toughness only for 100°C 95%RH
Carbon fiber / epoxy composite (Leveque et al., 2005)	180 and 210°C	2 months	Tg increased till around 100 hours of aging then decreased.
E-glass - vinylester and CFRP – epoxy (Chen et al., 2007)	NaOH, KOH, Ca(OH)2, NaCl, Na2SO4 , RT, 40C, 60°C, cyclic	120 days	Reduction in tensile strength varying from 8- 50% difference, 8-30% reduction in interlaminar shear strength
CFRP, epoxy-vinylester modified resin (Micelli and Nanni, 2004)	Alkaline solution at 22°C and 60°C, 200 cycles -18 to 4°C then 600 cycles 16 to 49°C with UV, then 160 cycles each of RH of 60-100% at 16°C followed by 27°C then 38°C	up to 200 cycles	Alkali aging resulted in 30-40% loss tensile, transverse loss 0-90% dependent on T and material, environment cycles average 0-5% change on tensile and transverse
GRFP/CFRP epoxy composite (Murthy et al., 2010)	Seawater	450 days	Decrease in ILSS, flexural, and tensile strength
Type II cement, 3 different amine cured epoxies, 2 carbon and 2 glass FRPs (Toutanji and Gomez, 1997)	35 g/l salt at 35°C 90% RH 4h wet 2h dry	75 days	5 to 30% reduction in flexural strength
Commercial epoxy and concrete (Tuakta and Buyukozturk, 2011)	23C and 50°C in DI water and cyclic exposure	8 weeks	Up to 70% decrease in fracture toughness
CFRP with amine cured epoxy (Au and Buyukozturk, 2006)	23 and 50°C with 50% and 100% RH	8 weeks	Up to 60% shear fracture toughness loss at 50°C in water
Epikote 828 and T300 carbon fibers (Miyano et al., 2005)	150°C in air, 95°C in water, 1 cycle wet then dry. Testing performed at 25, 50, 80, 100, and 120°C	2 or 120 hours	Irreversible loss in strength upon drying as compared to vinylesters
Ciba-Geigy 913, 914, 924 epoxies and E-glass, TS carbon, XAS carbon fibers (Adams and Singh, 1996)	Steam and 100°C over silica gel and 100°C	756 hours	Shear loss and ILSS factor up to 2x recoverable upon drying, except for 913 composites
Vicotex 1452 with amide curing agent and T300 CFRP (Zhang et al., 1997)	Boiling water at 100°C and DI water at 70°C 100% RH	2 days exposed, 1000 hours for RH	30-40% reduction in strength, 50-50% reduction in ILSS, reversible after drying.
DGEBA based resin and polyester resin with E-glass fibers (Ray, 2006)	50°C 60%RH to 50°C 95%RH and 50°C 60% RH to 70°C 60% RH	38 hours	Little change in ILLS and shear strength

Table 5. Summary of changes in properties for accelerated testing of FRP systems

Type I and V cement with 3 different commercial Kuwaiti epoxies (El-Hawary et al., 1998)	Open air, room temp, 60C, 80°C	18 months	No apparent difference in strengths with time or temperature
Type I and V cement with 3 different commercial Kuwaiti epoxies (El-Hawary et al., 1998)	Open air, room temp, 60C, 80°C	18 months	No change in tensile strength, 25% decrease in bond strength after 18 months.
Unidirectional glass / epoxy (Mourad et al., 2010)	Sea water at 23 and 65°C	1 year	No change in tensile properties
SEH 51/Tyfo GFRP with Tyfo S Epoxy (Silva, 2007)	Salt fog cycles with variation from 20% to 90% RH and UV cycles. GFRP jacketed cylinders exposed to 50 g NaCl/l at 18°C and salt fog cycles	10,000 hours	Little degradation under various conditions
IM7 carbon fiber 997 epoxy (Nakamura et al., 2006)	UV at 60°C and 50°C 100% RH with cyclic exposure	1000 hours	Slight increase in modulus for low amplitude fatigue samples. Uniaxial and flexural strength decreased ~25% with UV and condensation
SEH 51/Tyfo GFRP with Tyfo S Epoxy (Silva and Biscaia, 2010)	Tide Simulation (5% NaCl for 3 days then 4 days dry), salt fog cycles (8 hours salt fog at 35°C 98% RH 16 hours dry), immersion	10,000 hours	Salt water immersion improved properties, however plasticization of interface.
SEH 51/Tyfo GFRP with Tyfo S Epoxy (Silva and Biscaia, 2008)	50g/l salinity at 35°C and -10°C for 12 hours then 10°C for 12 hours	10,000 hours	Increase in load capacity with salt fog and immersion cycles reduced capacity with freeze thaw cycles GFRP, reduced pullout all GFRP, CFRP reduced capacity and pull out under all conditions
Commercial epoxy and mortar with E-glass or carbon fibers (Karbhari et al., 1997)	s-15.5°C for 24 hours, 20°C for 24 hours	60 days	Energy decrease in sea water and water. Increase in energies at -15C and under freeze thaw conditions
IM7/997 carbon fiber epoxy composite (Kumar et al., 2002)	UV at 60°C and condensation at 50°C with cyclic exposure	1000 hours	Very small variations in elastic moduli and Poisson's ratio. 29% reduction of transverse tensile strength. No effect on longitudinal properties
Carbon or glass fiber/epoxy prepreg (Hulatt et al., 2002)	22, 45, and 60°C in air, water/salt wet/dry cycles, and UV exposure	2000 hours	No effect on longitudinal modulus for all conditions. Strength decreased only for 0/90 composites in water.
Graphite/epoxy (Boualem and Sereir, 2011)			Longitudinal direction strength remains constant, but in transverse direction properties are significantly reduced

Table 5 (continued)

to ambient water temperatures depressed the Tg, they also found that exposure of the composites to -15.5° C and freeze-thaw cycles of -15.5° C to 20° C actually increased the G_{IC} and G_{IIC} values for measurements up to 60 days. Exposure to DI water and synthetic sea water at room temperature resulted in a slight decrease which was more pronounced in the G_{IIC} values. G_{IIC} values are primarily dependent on the properties of the epoxy while G_{IC} values are primarily dependent on the interface. It also appeared that the carbon fiber systems exhibited less change in properties than the glass fiber systems.

A summary of the aforementioned findings can be found in Table 5. The specific materials, exposure conditions, exposure times, and changes in properties are organized for easy reading. The changes in properties are more complicated than neat epoxy. Overall, a decrease or little to no change in properties is found with environmental exposure.

2.5.3 Degradation Mechanisms of FRPs

Several degradation mechanisms for FRPs are discussed in the literature, with water absorption being the most common. A recent paper by Benzarti et al. (2011) examined four different epoxy-CFRPs with concrete exposed at 40°C and 95% relative humidity and found a decrease in pull-off strength and a drop in the Tg over time. Pull-off tests indicated a change in the failure mode from a substrate failure to cohesive failure within the polymer joint. These changes with accelerated aging supported their claim that water absorption was the mechanism for degradation. Karbhari et al. (1997) also found the same change in failure mode and claimed plasticization of the matrix, but gave more insight. After the water has penetrated into the resin through capillary flow through microcracks and voids, debonding stresses across the fiber-resin interface can occur due to resin swelling and osmotic pressure.

While water exposure typically causes a degradation in properties, Silva and Biscaia (2010) reported that exposure of their GFRP-concrete system to salt water caused improvement in the properties of the concrete, but a higher plasticization of the interface. After 10,000 hours of exposure to environmental conditions, the interface was strongly degraded, with minor slippage between the GFRP and concrete.

The same water absorption mechanism is also cited for FRP systems without concrete. Khan et al. (2010) found a reduction in ILSS and considered microcracking as a possible mechanism for degradation, but found no change in moisture content after reaching saturation. As a result, they concluded plasticization was responsible for the loss in properties. Lee and Peppas (1993) examined the diffusive and mechanical behavior of TGDDM and DGEBA resin based epoxy / carbon composites and found a weakening of the interfacial bond strength could be caused by hygrothermally induced interfacial stresses. Ray (2006) explained his variation and lack of degradation of the ILSS of his GFRP composites as a result of water absorption and reducing internal stresses.

In addition to water absorption, Zhang et al. (1997) reported resin swelling during exposure of their CFRP to 70°C and 100% relative humidity, along with a change in failure mode from brittle fracture to yielding and ductile failure. Specimens immersed in boiling water examined under SEM showed that bare fibers and voids in the matrix were evident, implying the boiling water leached the resin out and destroyed the interface. They suggested that boiling water was not an appropriate accelerated aging process.

Mourad et al. (2010) claimed a dual mechanism of stress relaxation-swelling-mechanical adhesion and breakdown of chemical bonds between the fibers and matrix at the interface, due to seawater exposure of their glass/epoxy composites. They also found no change in the modulus and an increase in the ductility which they explained by plasticization and improved mechanical adhesion between fiber and matrix which was explained by hydrolysis causing swelling of the resin. While SEM images were taken, no chemical characterization of the composite was performed, so the exact degradation of certain groups was not evident. Tuakta and Buyukozturk (2011) acknowledged that reversible degradation of their composite would undergo plasticization and swelling while irreversible degradation would involve hydrolysis or microcracking. They found irreversible degradation of their epoxy CFRP-concrete composite under cyclic moisture and temperature cycles, and as a result claimed hydrolysis of their system. As with the previous study, they did not include chemical characterization to verify their suggested mechanism, nor did they include SEM images.

Park et al. (2008) suggest the three dominant deterioration mechanisms at the matrixfiber interface were osmotic cracking, interfacial debonding, and delamination, which caused micro cracks and pore development as a result of artificial aging in simulated concrete environments. The decrease in ILSS was accompanied by an increase in pore volume and failure typically at the fiber, rather than matrix. However, they used a commercial vinyl ester resin and found the resin did not undergo significant chemical reactions with the hydroxyl ions.Au and Buyukozturk (2006) found that after exposure of CFRP epoxy-concrete composites to 100% RH



Figure 15. FTIR spectra of IM7/997 specimens after 500 hours of UV or condensation (Kumar et al., 2002)

the mode of failure changed from delamination to interface separation. They suggested an interfacial toughening and weakening mechanism as a result of water absorption by the epoxy, and admitted the validity of this claim requires further testing.

UV studies on epoxy GFRPs by Lee and Lee (1999) indicated that degradation developed from the formation of new polar groups on the surface and penetration of the inner layer by reoriented oxygen groups. XPS confirmed the oxidation of the polymer and the formation of carbonyl groups. Exposure of a commercial CFRP to UV and moisture by Kumar et al. (2002) resulted in continuous weight loss and various morphological and chemical changes. Exposure of UV radiation alone caused the formation of microcracks in the epoxy due to increased cross-linking from photo-oxidation reactions. No morphological changes were evident from moisture alone. However the combined exposure resulted in severe degradation in the form of matrix erosion, void formation, and fiber-matrix debonding. The authors suggested a mechanism to explain this observation. Exposure to UV resulted in the creation of a thin layer of chemically modified epoxy, and the following treatment with moisture leached away soluble degradation products, which exposed a fresh layer that could once again be attacked by UV radiation. In addition, absorbed moisture in the epoxy matrix could enhance the photo-oxidation reactions due to the increased availability of H⁺ and OH⁻ ions. FTIR data indicated reductions in the peak

attributed to C-N stretching vibrations, demonstrating the presence of chain scission reactions as shown in Figure 15. The synergistic manner in which UV radiation and moisture attacked the composite led to the most degradation and widest variety of mechanisms of all the literature.

In summary, as with the neat epoxy degradation mechanisms, plasticization is the most commonly cited mechanism, although there is no evidence of reversibility, and thus the claims of

Materials	Exposure conditions	Exposure Time	Mechanism
CFRP with DGEBA and amine hardeners (Benzarti et al., 2011)	40°C 95% RH	20 months	Plasticization
Commercial epoxy and mortar with E- glass or carbon fibers (Karbhari et al., 1997)	15.5°C for 24 hours, 20°C for 24 hours	60 days	Plasticization of resin and debonding stresses due to resin swelling and osmotic pressure
Epoxy prepreg CFRP (Khan et al., 2010)	70°C 85%RH	60 days	Plasticization
TGDDM/DDS, DGEBA/DDA and CFRP (Lee and Peppas, 1993)	Water at 50,70,90, and 100°C	1200 hours	Plasticization and Hygrothermally induced stresses
DGEBA based resin and polyester resin with E-glass fibers (Ray, 2006)	50°C 60% RH to 50°C 95% RH and 50°C 60% RH to 70°C 60% RH	38 hours	Plasticization and reducing internal stresses
SEH 51/Tyfo GFRP with Tyfo S Epoxy (Silva and Biscaia, 2010)	DI water at 40°C with 12 hours at 20% RH then 12 hours at 90% RH, 8 hours salt fog at 35°C 98% RH then 16 hours drying, DI water at 22°C	10,000 hours	Plasticization of interface
Vicotex 1452 with amide curing agent and T300 CFRP (Zhang et al., 1997)	DI water at 100°C and 100% RH at 70°C	2 days immersio n, 1000 hours for RH	Resin swelling and plasticization. Boiling water attacked fiber- matrix adhesion and produced voids.
Unidirectional glass / epoxy (Mourad et al., 2010)	Sea water at 23 and 65°C	1 year	Stress relaxation, resin swelling, hydrolysis and plasticization
Commercial epoxy and concrete (Tuakta and Buyukozturk, 2011)	23°C and 50°C in DI water and cyclic exposure	8 weeks	Hydrolysis or microcracking rather than swelling stress and plasticization
Commercial vinyl ester and GFRP (Park et al., 2008)	Immersion in alkali solution 20°C	120 days	Matrix osmotic cracking, interfacial debonding, delamination
CFRP with amine cured epoxy (Au and Buyukozturk, 2006)	23 and 50°C with 50% and 100% RH	8 weeks	Interfacial toughening and interface weakening mechanism
Bisphenol A type epoxy and glass fiber (Lee and Lee, 1999)	UV	50 hours	Oxidation and formation of carboxyl groups
IM7/997 carbon fiber epoxy composite (Kumar et al., 2002)	Cyclic exposure of UV at 60°C and condensation at 50°C	1000 hours	UV creates thin layer of soluble degradation products which are leached away by condensation

Table 6. Summary of mechanisms of degradation for accelerated testing of FRP systems

plasticization need further study. However, hydrothermally induced stresses and resin swelling are also mentioned as mechanisms for the FRP composites. Table 6 gives a brief overview of the mechanisms along with exposure conditions and exposure times for the various FRP systems.

2.5.4 <u>Summary of Accelerated Testing of Epoxy and FRP Systems</u>

Under typical accelerated conditions a loss of mechanical properties of epoxy systems is usually observed. From room temperature to 90°C in water, the most commonly claimed mechanism of degradation is plasticization which causes an increase in polymer chain mobility and a change in the Tg. Exposure to other liquids, such as saltwater or alkali solutions, results in similar changes. Exposure to UV radiation from 40° to 150°C results in a reduction in properties attributable to oxidation. A combination of water and UV radiation at increased relative humidity and/or temperatures causes degradation by hydrolysis. FRP systems also undergo a loss of properties under accelerated aging conditions, typically due to the degradation of the epoxy matrix. As with neat epoxy systems, plasticization is claimed to occur with exposure to water from room temperature to 60°C. There is a loss in shear, tensile, and flexural strength and a decrease in fracture toughness. However, some studies have found no change in tensile properties with exposure to sea water, DI water, or air at the same temperatures. These studies explain this unexpected result by a stress relaxation-swelling-mechanical adhesion mechanism. In addition, under various conditions of UV, water or air, from room temperature to 45°C, no change in longitudinal modulus has been reported. This makes sense because of the orientation of the fibers in the FRP system. Combination of UV and water from 50 to 60°C results in a combination of oxidation and hydrolysis of the FRP and a reduction in the tensile strength. Table 7 provides an overall summary of the findings from the literature. Since the conditions for accelerated aging testing sometimes overlap in the literature it is difficult to attribute mechanisms precisely to specific testing conditions. However, the overall trends are clear: exposure to water and temperatures higher than room temperature result in a decrease in mechanical properties. When exposure temperatures are close to or exceed the glass transition temperature of the polymer plasticization occurs, so note must be taken of the Tg of the polymer, and rigorous control of the testing conditions must be observed before testing begins.

While the literature has addressed the changes in properties for epoxy and FRP-concrete systems with environmental exposure, there is still much work to be performed regarding

chemical interactions between epoxy and concrete. There are numerous theories regarding why epoxy performs so well as a repair material, but the fundamental epoxy-concrete bond has still not fully been explored. This report will provide insight into the issues of this important interaction considering both civil and engineering standpoints.

Material	Exposure Conditions	Exposure Time	Property Change	Mechanism
Epoxy	water/air 40-90°C	up to 2 years	decrease in Tg, strength, and modulus	Water absorption
	60-100°C/UV at 42°C	up to 300 days	decrease in contact angle, surface potential and resistivity	Oxidation
	UV at 60°C/UV at 60°C and water	up to 35 days	decrease in flexural strength	Hydrolysis
FRP	water from 40-100°C	up to 20 months	decrease in Tg, strength, toughness	Water absorption
	UV at 60°C/Condensation at 50°C	50 hours	decrease in flexural strength	Oxidation
	UV at 60°C/Condensation at 50°C	1,000 hours	decrease in tensile strength	Hydrolysis
	23 to 80°C with and without sea water	up to 18 months	no significant change in te strength	nsile or shear
	22-60°C in air, water/salt wet/dry cycles, and UV at 60°C	up to 2,000 hours	no significant change in longitudinal properties	

Table 7 Summary	v of prop	erty changes	and mech	anisms for	epoxy and	d FRP sys	tems
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3 Nature of the Concrete-Epoxy Interface

3.1 Motivation

Epoxies are an important class of structural adhesives. An adhesive is a substance used to join the surfaces of two solid surfaces, referred to as adherends. Intimate molecular contact between the adhesive and adherend is an important factor, but is not the only criteria for effective bonding. The forces across the interface must also be sufficiently strong to hold them together under an applied load. While epoxy systems are frequently employed as adhesives in the engineering field, little is known regarding their interfacial bonding with concrete at the nanoscale. For the general description of adhesion between various types of materials, several different mechanisms have been proposed: mechanical interlocking, diffusion, electrostatic, and adsorption theory (Kinloch, 1980). From the civil engineering standpoint, mechanical interlocking is a sufficient theory to explain adhesion between FRP materials and concrete. Numerous research has shown the effect of surface preparation on the mode of failure (Kim et al., 2010), fracture energy (Karbhari et al., 1997), or bond strength (Beushausen, 2010; Ghafari and Naderi, 2011). However, from a chemistry standpoint this theory is inadequate in describing intermolecular forces and atomic interactions that describe physical properties and mechanisms of degradation.

3.1.1 Theories of Adhesion

Mechanical interlocking involves the flow of the adhesive into the pores, holes, and crevices of the surface of the substrate, and after curing, locks mechanically to the surface. Numerous articles by other authors on concrete surfaces have shown that a rough surface preparation leads to higher bond strength (Karbhari et al., 1997; Garbacz et al., 2005; Ye et al., 1998). However, these increases can also be attributed to other factors such as efficient removal of weak surface layers, improved interfacial contact, and the enhancement of energy dissipative mechanisms in the adhesive (Kinloch, 1987). Wake (1982) suggested the effects of mechanical interlocking and surface force components could be multiplied to give a result for the measured joint strength.

Diffusion theory suggests that when an adhesive contains an adherent solvent, the adhesive can diffuse into the substrate with an interchange of molecules. This theory requires

that both the adhesive and adherend are polymers and has found limited application when the polymer is below its Tg.

According to the electrostatic theory of adhesion, upon contact of adhesive to substrate, electrons are transferred across the interface to balance their respective Fermi levels. This will result in the formation of a double layer of electrical charge at the interface. This theory is regarded as a dominant factor in biological and particle adhesion, but for an insulating polymer like epoxy, will not play a large role.

Adsorption is the adhesion of atoms or molecules of gas, liquids, or dissolved solids to a surface. It differs from absorption, which only deals with liquids. The exact nature of the bonding depends on the interacting species, but the process is generally classified as physisorption or chemisorption. Physisorption is caused by weak intermolecular forces and does not involve a significant change in the electron orbitals of the species involved. Chemisorption is due to valence forces in which new types of ionic or covalent bonds are formed. Typical binding energies for physisorption range from 10-100 meV, while chemisorption ranges from 1-10 eV.

3.1.2 Hydrogen Bonding

The hydrogen bond is a type of dipole-dipole interaction in which a hydrogen atom of one molecule is attracted to an electronegative atom of the same (intramolecular) or different (intermolecular) molecule. For the classical view on hydrogen bonding, we can turn to the directional interaction of water molecules. The large difference in electronegativity between the H and O atoms makes the O-H bonds of the water molecule characteristically polar, with the H atom having a partial atomic charge of +0.4 and -0.8 for the O atom. Neighboring water molecules orient themselves so that the local dipoles $O^{\delta-}H^{\delta+}$ point at $O^{\delta-}$ as shown in Figure 16. The classical view can be extended to analogous interactions of X-H^{...}A formed by strong polar groups $X^{\delta-}H^{\delta+}$ interacting with $A^{\delta-}$, where X or A may be O, N, or F (Steiner, 2002).

The hydrogen bond really is a complex interaction made up electrostatic, van der Waals, and covalent bonding interactions. The electrostatic contribution is directional and the van der Waals is isotropic. The strength of the hydrogen bond lies between that of van der Waals and covalent bonds and may vary, depending on the specific interactions, from 0.2 to 40 kcal per mole. IR and NMR spectroscopy have both become standard methods to investigate hydrogen bonds in the solid state, however, if there are many symmetry independent bonded groups, band overlap normally prevents detailed analysis.



Figure 16. Hydrogen bonding between water molecules

Although not much is known about the epoxy-cement interface, prior work on the metalepoxy interface provides some insight (Schmidt and Bell, 1986). When a metal surface is exposed to water, the oxide surface of the metal forms hydroxyl groups which are available to the epoxy for hydrogen bonding. The strength of the bond depends on the concentration of hydroxyl groups on the surface. Pretreatment of the metal surface can be used to remove oxide layers and change the hydroxyl concentration, or to create a rougher surface which also improves bonding. Three mechanisms are proposed as to why water has a detrimental effect on this bond: one, water displaces epoxy, which forms hydrogen bonds with the oxide layer; two, a hydration layer forms which acts as a weak boundary layer, resulting in a decrease in adhesion strength; three, the metal corrodes, leading to delamination of the epoxy. Clearly only the first mechanism is applicable to the ceramic-polymer interface when epoxy is bonded to concrete. Thus, a strong hypothesis is that epoxy bonds to cement via hydrogen bonding, and that water can displace these hydrogen bonds leading to a weakening of the adhesion strength.

The objective of this chapter was to determine if hydrogen bonding interactions are responsible for the strong adhesion between concrete and epoxy. Small molecule epoxy analogs were adsorbed to cement paste particles to isolate specific functional groups that may interact. ATR-FTIR was used to examine the very surface of the molecules and solid state ¹H, ¹³C, ²⁹Si MAS NMR was used to investigate bulk properties of the composites.

3.2 Experimental Procedure

Small molecule analogs of the larger cross-linked epoxy system were used in order to isolate specific bonds that may form between cement and different components of the epoxy network. The chosen epoxy analogs were: Bisphenol A (BPA, 99% purity),



Figure 17. Chemical structures of Bisphenol A, glycidyl phenyl ether, and n-ethyldiethanolamine n-ethyldiethanolamine (EDA, 98% purity), and glycidyl phenyl ether (GPE, 99% purity). These small molecules were purchased from Sigma Aldrich and used without further purification. The chemical structures of these molecules are shown in Figure 17.

Composite samples were prepared by curing cement paste (without sand or other aggregates) with a water-to-cement ratio of 0.375 for 3 weeks followed by 1 week immersion in lime solution. Then the cured cement paste was dried, ground, and sieved to a particle size of 38 μ m or smaller. Next, various mass loadings of the epoxy analogs were dissolved in 2 mL of acetone and stirred for 15 minutes. The solution was then poured into a flask with 0.5 g of the cement paste particles, mixed for 15 minutes, and dried in an oven overnight at 60°C to evaporate the solvent.

3.2.1 FTIR Theory and Technique

Fourier Transform Infrared (FTIR) spectroscopy is a useful tool for polymer characterization. In the transmission technique, IR radiation is guided through an interferometer that splits the beams in two, where one beam travels a different optical distance. The beams are recombined and passed through the sample, which then travels to a detector. The measurement acquired is made in the time domain, which is then Fourier transformed to the frequency domain to give a spectrum. Although the sample is irradiated with a whole range of IR frequencies, absorption only occurs at specific frequencies that match the vibrational frequencies of the molecule.

Another IR sampling technique is Attenuated Total Reflectance (ATR). Instead of the IR beam passing through the sample, the beam is passed through an ATR crystal that is in contact with the sample. The beam forms an evanescent wave that extends into the sample, only when the crystal is made of an optical material with a higher refractive index than the sample. The intensity of the evanescent wave decays exponentially with distance from the interface. The penetration depth (dp) into the sample is typically 0.5 to 2 μ m, or the near surface, but depends on many factors as shown in Equation 3.

$$dp = \frac{\lambda}{2\pi n_{IRE} \sqrt{\sin^2 \theta - \left(\frac{n_S}{n_{IRE}}\right)^2}}$$
Equation 3

where λ is the wavelength, n_{IRE} is the refractive index of the crystal, and n_s is the refractive index of the sample. An additional important experimental consideration is the contact pressure between the sample and crystal.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy collects the scattered radiation from the bulk of powder samples, typically in a KBr matrix. The limitation of this technique is that there is no linear relation between the band intensity and concentration, so quantitative analysis is very complicated.

In this section of work, the ATR technique was used to quantitatively analyze the bonding between the epoxy analogs and concrete. FTIR samples were analyzed using a hemispherical ZnSe crystal with a multi angle attachment on a Magna-IR E.S.P. System 760 Spectrometer with 128 sample and reference scans at 4 cm⁻¹ resolution from 600 to 4000 cm⁻¹. The spectra were ATR corrected using OMNIC 6.1 software. Solid powder samples were placed in firm contact with the ZnSe crystal by placing the powder on a metal plate which was then raised by turning a screw until the powder was touching the crystal and further pressure could not be applied by hand. Liquid samples were pipetted onto the crystal and no further pressure was required.

3.2.2 NMR Theory and Technique

Nuclear Magnetic Resonance (NMR) spectroscopy is a nondestructive technique and was first successfully used on cementitious materials in the early 1980s (Lippmaa et al., 1982; Wieker et al., 1982). It is based on analysis of the interaction between an oscillating radio frequency and a collection of atomic nuclei in the presence of a strong magnetic field.

In NMR, experiments are not performed on the electrons of atoms, but on the nuclei. Nuclei with an odd numbered mass, such as ¹H and ¹³C, have a spin. The number of orientations for the specific nucleus is determined from quantum mechanics where a nucleus of spin *l* has 2l + 1 orientations. In the case of ¹H and ¹³C, when an external magnetic field is applied, the two energy levels split. The initial populations of the energy levels are described by the Boltzmann distribution, where the fractional number of particles Ni/N, occupying a set of states i, possessing energy E_i is:

$$\frac{N_{i}}{N} = \frac{g_{i}e^{-E_{i}/(k_{B}T)}}{Z(T)} \frac{N_{i}}{N} = \frac{g_{i}e^{-E_{i}/(k_{B}T)}}{Z(T)} \frac{N_{i}}{N} = \frac{g_{i}e^{-E_{i}/(k_{B}T)}}{Z(T)}$$
Equation 4

 K_B is the Boltzmann constant, T is temperature, g_i is the number of levels having energy E_i , and Z(T) is the partition function. The lower energy levels will contain slightly more nuclei than the higher level as a result. The frequency of radiation required to excite these nuclei into the higher level is determined by the difference in energy between the energy levels. This precise resonant frequency is dependent on the magnetic field experienced by the nucleus, and can be affected by electron shielding, which is dependent on the chemical environment. Typically the proton reference frequency is measured relative to the frequency of tetramethylsilane (TMS) for ease in comparing data. The chemical shift is defined as nuclear shielding divided by applied magnetic field and is expressed as $\delta = (v-v_0)/v_0$, where TMS is set to v_0 . The location of the chemical shift is so small that it is common to multiply the value by 10^6 and then express its value in parts per million (ppm).

While NMR can yield useful data for liquid samples, it is more challenging to perform on solids. A broadening of the resonances of NMR spectra for solid state samples occurs because most atoms can only undergo restricted vibrations and rotations at room temperature, each in a slightly different electronic environment, which can make interpretation almost impossible. Magic Angle Spinning (MAS) was first used successfully in 1958 by Professor Edward Andrew, which allowed him to obtain high resolution spectra of solid state samples. In MAS, the sample is spun at a high frequency (between 5 and 60 kHz for commercial probes) at the magic angle of 54.74° with respect to the direction of the magnetic field. Dipolar and quadrupolar interactions along with chemical shift anisotropy can be averaged out using MAS to yield spectra with much sharper signals (Hennel and Klinowski, 2005).

In one-dimensional NMR, the signal is recorded as a function of one time variable, and then Fourier transformed to produce a spectrum that is a function of one frequency variable. In two-dimensional NMR, the signal is recorded as a function of two time variables, t₁ and t₂, and then Fourier transformed twice to give a spectrum that is a function of two frequency variables.

For a 1D experiment, right after the pulse sequence, data are acquired. A 2D experiment involves a few more steps. In the first part of this experiment, called the preparation time, the sample is excited by 1 or more pulses. The group of pulses may be purely radio frequency, or

may include magnetic gradient pulses. When a pulse is applied, the magnetic moment of the nuclei rotates away from alignment of the external magnetic field, along the +z direction, down towards the x-y plane. This resulting magnetization is allowed to evolve for the first time period, t₁. Then another pulse or series of pulses is applied, called the mixing time, in which magnetization is transferred from the first nucleus to the second one. Finally, the signal is recorded as a function of the second time variable, t₂.

1D NMR experiments were conducted at two locations: College de France in Paris, France and Sandia National Labs in Albuquerque, New Mexico. The instrument in Paris recorded ¹H spectra using an Advance III Bruker spectrometer operating at ω L=700 MHz. Magic angle spinning (MAS) was applied with a spin speed of 60 kHz, with a 5 s repetition delay. ¹³C NMR experiments were performed with an Advance III 300 Bruker spectrometer operating at ω L=75.4 MHz. Proton to carbon cross-polarization magic angle spinning (CP-MAS) sequence was applied with pulse lengths of 5 µs, 1 ms contact time and a recycle delay of 10 to 20 s. For ²⁹Si experiments samples were packed into a 7 mm rotor and relaxation delay of 60 s was used.

The other instrument recorded ¹H NMR spectra using an Advance III 600 Bruker spectrometer operating at ω L=600 MHz (¹H) using a 2.5 mm rotor. Magic angle spinning (MAS) was applied with pulse lengths of 2.5 µs and a recycle delay of 5 s with a spin speed of 30 kHz. Spectral deconvolutions were performed using DMFIT software.

2D homonuclear ¹H NMR experiments were conducted using the instrument in Paris. Spin diffusion (Massiot et al., 2002) (2D NOESY) and double quantum (Feike et al., 1996) (BABA or back to back) experiments were performed to determine the specific interaction/proximities between functional groups. The Nuclear Overhauser Effect (NOE) is a phenomenon in which transfer of nuclear spin polarization from one nuclear spin population to another occurs through cross-polarization. NOESY experiments make use of NOE to establish correlations of nuclei that are spatially close. Double quantum experiments make use of strongly dipolar-coupled networks instead of fighting the dipolar interactions (Schnell and Spiess, 2001).

Interpretation of data for both types of experiments is similar. For diffusion experiments, both the x- and y-axis correspond to the chemical shift and the intensity of the peaks are presented in a third dimension, such as contour lines or different colors. In this plot, diagonal peaks have the same coordinate, while cross peaks have a different value for each coordinate and are found on the off-diagonal. Diagonal peaks correspond to the peaks in the 1D experiment,

while cross-peaks indicate coupling between pairs of nuclei. In the case of double-quantum experiments, the chemical shift is doubled in the second dimension. Auto correlation appears at $2*\delta i$ while correlations between signals at $\delta 1$ and $\delta 2$ ppm respectively show a cross peak at $\delta 1+\delta 2$.

3.3 Results and Discussion

3.3.1 <u>FTIR</u>

Figure 18 shows an FTIR-ATR spectrum of cured cement paste at an incident angle of 42°. This spectra has been run through the ATR correction algorithm to compensate for variation in sampling depth. The band at 874 and 1420 cm⁻¹ corresponds to C-O from CaCO₃, the peak at 960 cm⁻¹ corresponds to SiO₄ in calcium–silicate-hydrate, the peak at 1654 cm⁻¹corresponds to OH in water molecules, and the broad peak from 3000 to 3700 cm⁻¹ is the hydroxyl region. For the neat, cured cement paste the hydroxyl band was deconvoluted into 2 peaks, one at 3642 cm⁻¹ corresponding to Ca(OH)₂ and one at 3410 cm⁻¹ corresponding to calcium–silicate-hydrate. These assignments are in good agreement with the literature (Ghosh and Handoo, 1980; Chollet and Horgnies, 2011; Delgado et al., 1996). A summary of these characteristic IR absorption bands is shown in Table 8.

ATR spectra of the small molecules at room temperature are shown in Figure 19 where GPE and EDA are liquids, and BPA is a solid powder. Both the BPA and EDA show a broad, asymmetric band attributed to the vo-H of self-hydrogen bonded hydroxyl groups. The width of this band is related to the different lengths of formed hydrogen bonds which adsorb at slightly different frequencies. For BPA, the peak of this band is located at 3315 cm⁻¹ and for EDA it is located at 3320 cm⁻¹.

Figure 20 shows the hydroxyl region of ATR spectra taken at 45° after applying the small molecules to the cement paste particles. All the samples have been corrected, using OMNIC software, for CO₂ and H₂O, and then ATR corrected to account for the variation in penetration depth with wavelength and incident angle. While there is much noise due to residual water vapor in the chamber, major shifts in the OH band may still be observed. Cement paste before treatment had its broad band located at 3398 cm⁻¹, and after treatment with GPE the position did not change. After treatment with BPA and EDA a shift to lower wavenumbers for the broad peak



Figure 18. ATR IR spectrum of cured cement paste

Table 8. Assignment of observed peaks for cured cement paste (Ghosh and Handoo	, 1980;
Mojumdar and Raki, 2005; Gao et al., 1999)	

Peak Position	IR Assignment
(Wavenumber, cm ⁻¹)	
874	Asymmetric stretching vibration of CO from CaCO ₃
960	SiO4 from C-S-H
1110	Stretching vibration of S-O in [SO ₄] ⁻²
1420	Asymmetric stretching vibration of CO from CaCO ₃
1654	Bending mode of OH from H ₂ O
3413	Symmetric and asymmetric stretching vibration of OH
	from C-S-H
3643	OH in Ca(OH) ₂



Figure 19. ATR spectra of the neat small molecule epoxy analogs and cement paste



Figure 20. ATR spectra of the hydroxyl region of cement samples after treatment took place. The BPA sample shifted to 3321 cm⁻¹ and the EDA sample shifted to 3359 cm⁻¹. Most likely this is simply spectra overlaying of the hydroxyl groups of the small molecules with the OH region of the cement paste. IR work on BPA by other authors has demonstrated an increase in the v_{O-H} band after hydrogen bonding with another molecule (Slootmaekers and Desseyn, 1991). These results are counterintuitive, since the hypothesis envisioned the cement paste as being able to hydrogen bond with the various small molecules containing hydroxyl groups.

Additional loadings of BPA on the cement paste were performed to determine if a gradual shift in the vo-H band could be observed. However, increasing the amount of BPA did not yield any increase in the wavenumber of the overall peak shown in Figure 21. In addition, no overall change in the shape of the band was observed. Using the DRIFT-IR technique also gave the same results.



Figure 21. ATR IR spectra of (a) neat cement paste, (b) cement paste + 30% BPA, (c) cement paste + 20% BPA, (d) cement paste + 10% BPA, and (e) cement paste + 7% BPA

Since additional hydroxyl groups were contributed by the small molecules, simple observation of the IR spectra does not yield enough information about the nature of the interaction because of the overlapping bands. Peak subtraction was performed to investigate if the data contained more information than initially assumed. This process has been proven in other systems to show interactions with water and different states of hydrogen bonding (Li et al., 2010; Ngono et al., 1999). First, samples were ATR corrected using 1.5 as the index of refraction of the sample and 2.4 for the ZnSe crystal. Next, the composite sample spectrum had the small molecule contribution subtracted in OMNIC software with the formula I=A-k*B where A is the composite sample, B is the neat small molecule, and k is a constant. The constant was determined by normalizing to the V_{CH3} stretch located from 2,975 to 2,965 cm⁻¹. Unfortunately,



Figure 22. Subtracted ATR spectra of 10%, 20%, and 30% BPA added to cement paste peak subtraction yielded no new results, as shown in Figure 22. The results of the peak subtraction were spectra similar to the neat cement paste with no significant change in the location of the Vo-H band.

3.3.2 <u>NMR</u>

Before probing epoxy-cement interactions using solid state NMR, epoxy-silica nanoparticles and epoxy-laponite systems were investigated. These two systems were examined because they have a more well-defined structure than cement. Silica nanoparticles (Aerosil 380) were 7 nm in diameter. Laponite exists as platelets made up of three sheets containing a middle sheet of magnesium ions in an octahedral coordination with oxygen atoms and hydroxyl groups and two outer sheets composed of tetrahedral silica sheets (Cummins, 2007). The platelets have an average diameter of 25 nm and a thickness of 0.92 nm, with these finite dimensions being responsible for the occurrence of silanol groups on the edges. During the manufacturing process, some magnesium ions are substituted with lithium ions resulting in a negative charge, which is balanced by interlayer sodium cations. This synthetic clay has a negative face charge and a rim charge that may be negative or positive depending on the pH¹⁰⁵. Laponite's chemical structure has been reported by the manufacturer as Na^{+0.7}[SisMg5.5Lio.3]O₂₀(OH)₄]^{0.7-}. Compared to other clays, laponite has a relatively high edge to surface ratio of 0.07 (Jaber and Lambert, 2010).

Liquid NMR on the small molecules was performed to identify the resonances of the functional groups before interaction with the two nanoparticle systems. For these experiments the small molecules were dissolved in ¹³C enriched acetone. The same procedure for the

adsorption of the small molecules to the cement powder was followed for the two types of composites with a 10 mM/g concentration. Initial solid state ¹H and ¹³C experiments indicated no apparent interactions between the silica nanoparticles and small molecules, so the more complex laponite system was investigated more thoroughly. Figure 23 shows the ¹³C NMR spectra of the EDA composites and Figure 27 shows the ¹³C NMR spectra of BPA and silica and laponite nanoparticles. In all the ¹³C NMR spectra the resonance at 30 ppm is due to unevaporated acetone.



Figure 23. ¹³C NMR spectra of EDA composites

Solid state ¹H NMR spectra of the pure laponite samples showed 2 resonances at 0.5 and 4 ppm, assigned to silanol groups and interlayer water, respectively. Figure 24 shows the ¹H spectra of laponite, liquid BPA, and laponite-BPA composite. For the liquid BPA the resonance at 1.5 ppm (peak 1) was assigned to the methyl group, the 6.6 and 7 ppm signals (peak 3 and 4) to aromatic hydrogen atoms, and the resonance at 5 ppm to the hydroxyl groups. The solid BPA resonances were located in slightly different chemical shift positions. Signals at 0.7 ppm, from

6.6 to 7.1 ppm and at 8.5 ppm were assigned to the methyl groups, the aromatic hydrogen atoms and the hydroxyl groups respectively. The small shoulder at 4.8 ppm may be due to nonhydrogen bonded hydroxyl groups, as BPA has been shown to have, but has only been demonstrated using FTIR (Fei et al., 2004). While there may be some slight changes in the chemical shift peaks between BPA and the laponite composite, no strong change in the hydroxyl group chemical shift was observed.



Figure 24. ¹H MAS NMR spectra of BPA – laponite composites

Although the EDA small molecule also has hydroxyl groups, the composite did not exhibit a downfield shift in its ¹H NMR spectra as seen in Figure 25. The GPE composite did not show any significant changes in the ¹H NMR spectra either, but that was expected since the small molecule did not have any groups that could contribute to hydrogen bonding with the cement. Figure 26 shows the ¹H NMR spectra of the GPE composites.

Since laponite has no carbon atoms in its chemical makeup, it gave no peaks in ¹³C NMR spectra, so interpretation was straightforward. Figure 27 shows the ¹³C spectra of the various BPA composites. For identification, the various carbon peaks for the solid BPA have been indicated on the spectra corresponding to the molecule.



Figure 25. ¹H NMR spectra of EDA – laponite composites



Figure 26. ¹H NMR spectra of GPE – laponite composites


Figure 27. ¹³C MAS NMR spectra of BPA composites

Wu et al. investigated blends of phenolic resins and poly (hydroxyl ether) of bisphenol A and found as the quantity of phenoxy increased, intermolecular hydrogen bonds increased, as indicated by a downfield shift of the OH substituted carbon in the phenoxy at 66 ppm (Wu et al., 2000). For the bisphenol A composites investigated in this work, the carbon resonance that would correspond to a group that could hydrogen bond would be peak 1 at 154 ppm, corresponding to the carbon of the phenol group. This downfield shift was not observed for either the aerosol or laponite composites. In fact, no significant changes in the spectra for any of the laponite-small molecule systems was observed in ¹³C spectra.

Although concrete does not have as well defined a chemical structure as laponite, it yielded more interesting NMR results. Previous work on cement has focused mainly on calcium

silicate hydrate, C-S-H, since it is the main hydration product of cement and is the major phase responsible for the mechanical properties of concrete. The C-S-H structure of hydrated cement is still not fully resolved because it is nearly an amorphous material. However a large body of work has been performed on synthetic C-S-H systems where the CaO to SiO₂ ratio has been varied, usually between 0.7 and 2.0. These model systems closely resemble the minerals tobermorite and jennite. The C-S-H structure is made up of distorted Ca-O sheets with silicate tetrahedral chains on each side. These layers stack along the [001] direction and calcium and water molecules are contained in the interlayer space. In jennite, half of the oxygen atoms from the Ca-O sheet are shared with OH- groups, where in tobermorite all of the oxygen atoms are shared with the silicate chains. Figure 28 shows an image depicting the structure of jennite according to Churakov (2008).



Figure 28. The structure of jennite. Ca and Si sites are shown as polyhedra, interlayer Ca sites are shown as large gray spheres, and water molecules are represented by spheres with black lines (Churakov, 2008)

The role of water in hydrated cement paste is very complex and controversial. Besides water vapor held in the pores, it has been suggested that water can exist as capillary water, adsorbed water, and interlayer water (Pelleng et al., 2008). Capillary water is defined as water molecules held in voids larger than 5 nm, while adsorbed water is held by hydrogen bonds and is physically bound. Chemically bound water is located in between the calcium silicate lamellae and is directly incorporated into the structure of the cement hydration products (Wang et al., 1998). More specifically, work performed by Cong and Kirkpatrick (1996) on crystalline calcium silicate hydrates confirmed the presence of hydrogen bonding groups Si-OH and Ca-OH using ²⁹Si and ¹⁷O MAS NMR. A more recent study has demonstrated a covalently bonded polymer-C-S-H meso-composite using alkoxysilanes that interact with the silicate chains as evidenced by a new T¹ resonance in the ²⁹Si spectra. This is an important distinction, because previous theories suggested polymers became bound in the interlayer space. To confirm the formation of covalent bonds between the polymer and C-S-H, ²⁹Si CP MAS NMR experiments were performed on composites prepared in D₂O. For the neat C-S-H sample, no resonances were able to be distinguished, while for the composites, a resonance in the Q¹ region was found, indicating polarization transfer from protons to inorganic Q¹ silicates. Since all of the protons are located in the polymer, it was concluded that the polymer chains are spatially close to silicate tetrahedral and that the silanes are incorporated into C-S-H silicate chains.

The current study examines the interaction of small molecules with hydrated cement paste. As with the laponite studies, the neat cement paste gave no carbon signals without direct excitation, so only ¹H MAS solid state experiments were performed. The ¹H spectrum of hydrated cement paste gave 2 broad resonances assigned to the hydroxyls of Ca(OH)₂ at 1.2 ppm and the interlayer water of calcium silicate hydrate at 5.4 ppm. These resonance assignments are in good agreement with work by other authors (Rottstegge et al., 2006; Korb, 2009). Figure 29 shows the ¹H MAS NMR spectra for the cement paste and its various small molecule composites. No narrow signal from any of the organic components is found, indicating the small molecules have been immobilized in the inorganic matrix. Results by other authors on white cement and phenol suggests that ds-phenol exists in Portland cement in two forms, unbound and bound to the cement matrix (Janusa et al., 1993). The unbound environment is assumed to be liquid like and exist in cement pore water in ionized form. The bound environment demonstrates



Figure 29. ¹H Solid State MAS NMR spectra of cement paste composites reduced motion of the organic inside the cement, and implies binding of the phenol through its hydroxyl groups.

As with the FTIR data, no significant differences in the spectra, compared to the neat molecules, could be observed. The only exception was the BPA treated sample which shows a small shoulder from 8 to 10 ppm. For the sample treated with BPA the methyl resonances were located at 2.4 ppm, the phenyl ring resonances were located at 7.1 ppm, and the hydroxyl resonances were located at 9.1 ppm. Although the hydroxyl resonance is small, it is a downfield shift from the solid bisphenol A OH resonance at 8.7 ppm. To determine if this small shoulder was meaningful, further BPA loadings were prepared. Figure 30 shows the ¹H spectra of the BPA loadings from 7 to 30%.



Figure 30. ¹H Solid State MAS NMR spectra of additional BPA loadings

For the 20% BPA loading, two new small peaks are found at 9.7 and 10.9 ppm. The presence of two peaks is puzzling, however this strong downfield shift is typically indicative of a strong hydrogen bond. Since the C-S-H gel may have both silanols and interlayer water, this may provide two different chemical environments for the BPA hydroxyls to interact with. At the 30% BPA loading there is the emergence of two additional small peaks at 14.8 and 17.7 ppm (not shown). These two peaks were also found on a different instrument with the same BPA loading.

However, these peaks may be a result of contamination or impurities, as proton resonances this high are usually only due to P-OH groups.

¹H MAS NMR experiments were conducted at a different location on a different instrument, on similar samples. The spectra of these BPA-cement paste composites is shown in Figure 31. The 5% and 15% BPA loadings show a very small peak at 10.4 ppm. However, comparison to the solid BPA is difficult due to the lack of detection of the hydroxyl resonance. This may be due to a slower spinning speed used in the experiment (30 kHz). In any case, the detection of the small peak suggests some kind of interaction between the hydroxyls of the BPA exists. Unfortunately, further experimentation with other loadings of BPA on the cement paste did not produce these resonances above 10 ppm or new resonances that were visible at all.



Figure 31. ¹H Solid State MAS NMR spectra of various BPA loadings on cement paste



Figure 32. 2D ¹H NMR spin diffusion and double quantum results for cement + GPE



Figure 33. 2D ¹H NMR spin diffusion and double quantum results for cement + EDA



Figure 34. 2D ¹H NMR spin diffusion and double quantum results for cement + BPA

3.3.3 <u>2D NMR</u>

Both spin diffusion experiments and double quantum experiments were performed to further characterize the specific interactions taking place between the small molecules and cement paste. For the spin diffusion experiments, typically a mixing time of 40 ms was used. Figure 32, Figure 33, and Figure 34 show the 2D spin diffusion and double quantum results for GPE, EDA, and BPA cement composites respectively. The loading of small molecules on the cement paste was 7% by weight.

Figure 32 indicates the absence of interaction between specific GPE protons and cement paste. Since off diagonal peaks indicate interactions between specific groups and only diagonal peaks are present, we can assume that there are no interactions between GPE hydrogen groups and the cement paste. The resonances for the various groups have been approximated. The phenyl ring was assigned to the signal 7 ppm, the ether linkage at 4 ppm, and the epoxide hydrogen atoms at 2 ppm. The diffusion experiment did not indicate any interaction between the organic and inorganic, only the organic molecule groups in spatial proximity with itself. The double quantum experiment gave an autocorrelation resonance around 1 ppm, indicating the cement paste Ca(OH)₂ group interacting with itself.

In Figure 33 the resonances for EDA at 1, 3 and 4 ppm were assigned to the CH₂, methyl and hydroxyl groups, respectively. The diffusion experiment did not indicate any interaction between the organic and inorganic components, only the organic molecule groups exhibits a spatial proximity with itself. As with the previous double quantum experiment, the same intramolecular interaction was found.

In Figure 34 the BPA resonances at 1 and 7 ppm were assigned to methyl groups and phenyl rings respectively. For both the diffusion and double quantum experiment two sets of peaks were found, most likely corresponding to dipolar coupling between the methyl group and phenyl ring. However, since the cement paste also has a peak located around 1ppm due to Ca(OH)₂ there may be a possibility of an organic-inorganic interaction. Therefore, further experiments on different loadings of BPA were performed.

For the 2D spin diffusion experiments with 20 and 30% BPA, shown in Figure 35, the same correlation between the 1 ppm and 7 ppm appeared, as evidenced in the red circles within the larger blue region. However, for the Cement + 20% BPA, there is an additional interaction at 10 ppm (seen as a blue dot in the top left corner, and as a region of ellipsoidal shapes in the bottom right corner) with the broad peak from 6 to 8 ppm and 1 ppm. This may indicate the hydroxyl group interacting with the phenyl ring, methyl group, or cement paste. While this interaction is not as strong as the BPA methyl-phenyl ring interaction, this is to be expected due to the relatively weak strength of hydrogen bonds. In addition, spin diffusion experiments only give spatial information, and not necessarily a chemical interaction. Unfortunately, the resolution is not sufficient to determine if the interactions are intramolecular or intermolecular.



Figure 35. 2D ¹H NMR spin diffusion experiments for 20 and 30% BPA.

²⁹Si experiments were performed to see if any interactions between cement silanols and bisphenol A took place. Ideally, HETCOR ¹H -> ²⁹Si experiments should allow determination of the presence of possible cross-peaks between Si-OH signals and ¹H resonances of BPA. Unfortunately, no ¹H -> ²⁹Si CP MAS spectra could be recorded with a reasonable S/N ratio, probably due to an averaging of the ¹H - ²⁹Si dipolar coupling induced by the mobility of the BPA molecules.

Figure 36 shows the cement paste before and after treatment. Original Portland cement contains Q⁰ sites in the calcium silicate phase, which are unreacted material without a network of

Si-O-Si bonds in the silicates (Rottstegge et al., 2006). Q^1 sites are present in the form of linked silicate tetrahedral endgroups and Q^2 sites are present in the middle of silicate chains (Hanna et al., 1995). The ²⁹Si spectra of the cement paste contains the Q^0 site located at -72 ppm, the Q^1 site at -80 ppm, and the Q^2 site at -85 ppm. No significant change in the chemical shift of these peaks was found after treatment with BPA. A slight increase in the Q^2/Q^1 ratio from 0.4 to 0.8 was found, indicating a change in the degree in the silicate polymerization. The broadness of the Q^2 peak demonstrates the presence of a variety of different silicate chain lengths, and the peak at -86.7 on the shoulder of the Q^2 peak is attributed to the different local environment, such as bridging and paired groups (Beaudoin et al., 2009). The small peaks between -100 and -110 for the cement + BPA curve are most likely noise.



Figure 36. ²⁹Si NMR spectra of cement paste before and after treatment with BPA.

3.4 Summary and Conclusions

The first part of this work investigated the nature of the epoxy-concrete bond. The initial hypothesis was that hydrogen bonding takes places at the interface, so small molecule analogs of the epoxy molecule were adsorbed onto cement paste particles to create a more simple system to

analyze. ATR-FTIR experiments on the surface of these composites did not show any change in the hydroxyl area (3,000 cm⁻¹ to 3,700 cm⁻¹) or other significant changes giving evidence of a hydrogen bond. Solid state NMR experiments showed a weak interaction between BPA and cement paste and small change in the chemical shift of the OH group. A few select samples with 20 and 30% BPA showed new peaks with chemical shift values above 10 ppm, however these results were not reproducible. 2D NMR experiments also suggested a small interaction, but the functional groups undergoing the interaction could not be directly determined. Most likely, for these small molecules and this specific type of Portland cement with a 0.38 water-to-cement ratio, weak hydrogen bonding exists that is difficult to detect on the specific composites made.

One of the main limitations of the investigation of hydrogen bonding in this research was only using a water-to-cement ratio of 0.38. Perhaps using at 0.4 or 0.5 water-to-cement ratio would increase the number of cement hydrates so there would be a greater number of sites available for interaction on the cement paste surface. Also, the cured cement particle was ground down to 38 μ m or less, so perhaps even smaller particle sizes down to 1 μ m or less would give a stronger signal due to the larger surface area. In addition, Type I/II Portland cement was used while other authors have used white cement, due to the lower iron content which reduces the interference of paramagnetic relaxation (Janusa et al., 1993). Another consideration for NMR experiments could be to use D₂O rather than H₂O. Due to the smaller magnetic moment of deuterons, the broadening of the spectra would be much less, so that much better resolution may be acquired.

4 Epoxy Degradation by Environmental Exposure

4.1 Background

While use of FRPs for repair and strengthening of bridges and other infrastructure is routinely performed, accurate prediction of the long term mechanical properties of these materials in the field is quite difficult. While accelerated testing on FRP materials typically involves elevated temperatures, exposure to aqueous solutions, and increased stress levels, these methods typically do not take into account the degradation mechanisms experienced by the materials. A number of investigations have determined that environmental exposure of FRPs leads to a significant loss of properties as discussed in Chapter 2. In all cases, a significant loss in bond strength was observed, or the failure mode changed from cohesive in the concrete to adhesive at the interface with exposure (Jana and Zhong, 2007). In some cases, a loss in properties is explained by chain cleavage due to water hydrolyzing cross-links (Fata and Possart, 2006).

Aiello et al. (2002) examined the mechanical properties of epoxy and concrete beams after environmental exposure to air from 40-50°C and water immersion at 23°C. They determined the mechanical properties of the epoxy were almost completely recovered after the service conditions were returned to room temperature. They concluded that the effect of an increase of temperature on bond strength is only due to the viscoelastic properties of the adhesive, and the presence of water induces a reduction in bond strength and a higher weakness at the interface.

Ellis and Karasz (1984) discussed the importance of sample handling and preparation during DSC to determine the Tg of epoxy under various conditions. From their data they implied that the ice melting endotherms observed were due to the presence of free water produced by the diluent's diffusion out of the sample during thermal analysis. They also suggested that the free water is distributed in minute cracks in the sample, which allow a high surface area for contact, for the re adsorption process to occur. This is in agreement with their previous research, which suggested that the free volume approach can be used to explain the effect of water on Tg and that water acts as a plasticizer in epoxy systems.

Two different approaches have been used for explaining property loss by plasticization in epoxy systems. The first is the disruption of interchain hydrogen bonds by water molecules, which plasticizes the polymer (Zhou and Lucas, 1999a; Adamson, 1980). Alternatively, under wet conditions, water can reach the interfacial region and break the hydrogen bonds between the epoxy and substrate since water is a strong hydrogen bonding agent. This will result in displacing the epoxy from the substrate and create a weak water layer at the interface (Schmidt and Bell, 1986). As discussed in Chapter 2, water molecules can also be found clustered together into sub micro-scale cavities within the epoxy matrix (Pethrick et al., 1996). In this study, accelerated aging conditions are used to investigate a loss in properties and change in degradation mechanism.

4.2 Experimental Procedure

Two different epoxy systems were investigated in this work. The model epoxy system consisted of a diglycidyl ether of bisphenol A (DGEBA, EPON 826) and poly(oxypropylene) diamine (POPDA, Jeffamine D-230) purchased from Momentive and Huntsman, respectively. The other commercial system investigated (Sikadur 300) had an unknown chemical composition, due to the proprietary nature of the chemicals. The mass ratio of DGEBA to POPDA for the model epoxy system was 100 to 32.9, to reach stoichiometric equivalence between functional groups, while the commercial system components were mixed by weight based upon the manufacturers' information. The two liquid components were mixed vigorously for 5 minutes to ensure even mixing. The mixed material was then degassed for 30 minutes under vacuum to remove air bubbles, and transferred into dogbone molds made from Silastic T-2, a commercial PDMS mold system, using a pipette. The dimensions of the dogbones are 2.5" long, 0.375" wide, and 0.125" thick, corresponding to ASTM D638 Type V dogbones. After 1 week of curing at room temperature, samples were demolded and placed in controlled water baths with constant temperatures from 30-90°C.

Samples immersed in water from 30-60°C were kept at the UF Coastal Engineering Labs, and samples from 70-90°C were kept at the State Materials Office Labs. Samples were also exposed to UV aging with and without water at 60°C using a Q-Sun Xenon Model XE-3 weatherometer maintaining 0.68 W/m² and a relative humidity of 45%. Every 2 weeks samples were removed from the environmental chambers and tested for mechanical properties and weighed for water absorption.

Five dogbones per experimental condition were tested for mechanical properties to get an accurate population size. Samples were tested in tension using a universal testing machine

according to ASTM D3039 using a strain rate of 5 mm/min and a 1,000 lb load cell until failure. All mechanical data was analyzed using IBM SPSS using an ANOVA test. A general linear model was used, with repeated measures, with a 95% confidence level. Within-subjects variables were temperature, or UV exposure and the between-subjects factor was time; the covariate was the unexposed set of epoxy samples.

In order to evaluate the mechanisms of accelerated degradation experienced by the epoxy dogbones, Fourier transform infrared spectrometry was used (FTIR; Nicolet Magna 760, Thermo Electron Cooperation), in the diffuse reflectance infrared Fourier transform (DRIFT) mode and ATR mode. The DRIFT and ATR spectra were recorded over the range of 650-4000 cm⁻¹ with a KBr beam splitter and an MCTA detector using 64 scans at a resolution of 4 cm⁻¹. For the DRIFT sample preparation, slices of the aged epoxy were taken after mechanical testing then combined with KBr powder in a proportion of 1:100. After the epoxy and KBr powder were milled for 30 seconds, spectra were acquired. Sample preparation for ATR samples involved cutting a middle section, close to the fracture surface of the sample, using a razor blade and clamping the part of the sample that was directly exposed to the UV radiation to the ATR crystal. The ATR spectra were taken using a hemispherical ZnSe crystal at an incident angle of 45°.

4.3 Results and Discussion

4.3.1 <u>Change in Mechanical Properties of the Model Epoxy System during Hygrothermal</u> <u>Exposure</u>

Over the course of eight weeks of exposure to water the model epoxy system exhibited a gradual color change from colorless to orange which can be seen in Figure 37. With increasing temperatures, this effect was more evident. This is most likely due to oxidation of the ether and nitrogen groups (Monney et al., 1998; Noskov, 1975). The samples exposed to UV radiation also underwent a color change, which was accompanied by a loss in mass and an increase in surface roughness. The tensile test results after 8 weeks are summarized in Table 9 and the full list of data is shown in Appendix A along with examples of load-displacement curves in Appendix B.

After 8 weeks of exposure, up to 33% of the modulus and 38% of the peak tensile strength was lost. The strain at failure increased up to 5.1% from 3.5%. The loss in physical properties for epoxy systems experiencing hygrothermal exposure has been reported by other

authors and is typically attributed to the formation of hydrogen bonds between the epoxy hydroxyl groups and adsorbed water (Apicella et al., 1984).



Figure 37. Change in color of epoxy dogbones after exposure to water at various temperatures and UV radiation

 Table 9. Summary of changes in properties for the model epoxy system after hygrothermal exposure

Exposure	t	$\mathbf{F}(\mathbf{C}\mathbf{D}_{\mathbf{r}})$	Г	- (MD -)	_	- (0/)	_	A (0/)
(()	(weeks)	E (GPa)	$\mathbf{E}_{\mathbf{S}}$	σ (MPa)	$\sigma_{\rm s}$	£ (%)	Es	A (%)
Control	8	2.45	0.08	74.5	4.8	3.5	0.4	0
30	8	2.13	0.16	64.1	2.1	4.6	0.8	1.14
40	8	1.93	0.07	65.5	4.8	4.7	0.7	1.34
50	8	1.91	0.15	67.6	6.2	5.1	0.9	1.35
60	8	1.77	0.14	56.5	6.2	4.7	0.4	0.82
70	8	1.65	0.07	49	3.5	4.5	0.7	4.36
80	8	1.67	0.19	49	3.5	4.3	0.2	7.47
90	8	1.62	0.17	46.2	4.1	4.2	0.5	6.22

Note : t = time; E = modulus; E_s= standard deviation of E; σ = peak stress; σ _s = standard deviation of σ ; ϵ = strain at failure; ϵ _s = standard deviation of ϵ ; A = percent change in cross sectional area after exposure but prior to mechanical testing.

It is possible to predict the mechanical properties of cross-linked polymer systems by using rubber elasticity theory. A required assumption is that there is no volume change on deformation and that affine deformation occurs (Sperling, 2006). The average length of a chain in the strained state can be determined by

$$r^2 = \frac{1}{3}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2)r_i^2$$
 Equation 5

where α represents the fractional change in dimension of each of the three directions. For most polymers, r_i^2/r_0^2 is equal to approximately 1. The stress may be predicted by the equation of state for rubber elasticity:

$$\sigma = \frac{\rho RT}{M_c} \frac{r_i^2}{r_0^2} (\alpha - \frac{1}{\alpha^2})$$
 Equation 6

In this equation n represents the concentration of active network chain segments, R is the gas constant, and T is temperature. When a polymer becomes swollen this results in a decrease in the network chain segment concentration, and therefore a decrease in stress. A swollen polymer is also predicted to exhibit a decrease in modulus, due to a decrease in cross-link density, v_e .

$$E = 3v_e RT$$
 Equation 7

Figure 38 shows the changes in the modulus for samples exposed to water at temperatures from 30 to 90°C over the period of 8 weeks; note that only one error bar for a set of samples is present for ease of visibility. From the graph it appears that after 4 to 6 weeks, the value of the modulus remains constant. The increase in sample mass confirmed saturation of the sample around 4 weeks and will be discussed later in the chapter. While some additional decrease or increase may be found after the initial 4 weeks, these changes are not statistically significant. Results of the statistical analysis are shown in Appendix E. As predicted by rubber elasticity theory, with higher exposure temperatures, lower values for the modulus were found, and the relationship between modulus and temperature was shown to be statistically significant. Samples exposed to 30°C showed the least degradation, while those at 90°C showed the most.

The same basic trend was found for peak stress, shown in Figure 39. However, the loss in strength was more noticeable for samples tested above the Tg of the epoxy. The Tg of this system is 45°C after 1 week of cure in ambient conditions, as measured by DSC. Samples



Figure 38. Change in modulus for the model epoxy system with hygrothermal exposure



Figure 39. Change in peak stress for the model epoxy system with hygrothermal exposure

exposed to water from 60 to 90°C decreased in peak stress much more than those below 50°C. Once again, after about 4 weeks the loss in properties remains constant; however, there was no statistically significant difference in the stress values with any of the variables.

Samples exposed to water demonstrated a greater strain at failure than the control sample as shown in Figure 40. While the difference in strain as a function of temperature was statistically significant, the change in strain over time was not. For all the exposed samples the strain throughout the exposure time was higher than the control group, as a result of chain swelling due to water absorption. The increase in the cross sectional area was found to increase up to 7% at 8 weeks of exposure, which indicates an interruption of inter chain hydrogen bonding rather than simply occupying the free volume (Adamson, 1980).



Figure 40. Change in strain for the model epoxy system with hygrothermal exposure

4.3.2 <u>Change in Mechanical Properties of the Model Epoxy System during UV and Water</u> <u>Exposure</u>

UV exposure was conducted on the model epoxy system with and without the presence of water at 60°C. The change in the tensile modulus after exposure is shown in Figure 41 and the control and water exposure at 60°C are also provided for comparison. While some loss in properties occurred, it seems the UV exposure was not as detrimental to the modulus as water exposure alone. Initial degradation up to 2 weeks was not as severe with UV alone. This suggests that at short time periods water's effect on the tensile modulus is more dominant than UV exposure. However, the only statistically significant relationship was the change in modulus as a function of the time. The details of the mechanical properties may be found in Appendix C.

The peak stress of samples exposed to UV exposure showed a gradual decrease over time. At short periods, up to 4 weeks, samples exposed to UV radiation showed little degradation, possibly due to additional curing of the epoxide group. However at longer periods, UV radiation resulted in more degradation than UV and water or water alone. Unfortunately, none of the variables were statistically significant.



Figure 41. Change in modulus with UV and water exposure for the model epoxy system



Figure 42. Change in peak stress with UV and water exposure for the model epoxy system



Figure 43. Change in strain with UV and water exposure for the model epoxy system

Figure 43 shows the change in strain during UV exposure. Note error bars have been omitted. Over time, the strain decreased with UV exposure. It is puzzling that at early time periods, up to 4 weeks, the strain is higher for UV samples than UV with water. The combined effects of UV degradation and absorption of water makes a clear explanation difficult. Once again, none of the variables were statistically significant.

4.3.3 Change in Mechanical Properties of the Commercial Epoxy System

The commercial epoxy system (Sikadur 300) showed a similar trend as the model epoxy system in regards to change in modulus and peak strength with exposure to water at various temperatures. In addition, the same gradual color change from colorless to orange was seen. The full list of data for the Sikadur 300 epoxy system is shown in Appendix D. Figure 44 shows the change in modulus with water exposure for the Sikadur 300 epoxy system.

As with the model epoxy system, the tensile modulus decreased with higher temperatures; note error bars have been removed for ease in visibility. After 4 weeks the modulus seemed not to undergo any further change. A lower modulus was seen for samples exposed above 30°C. The effect of temperature on the modulus was statistically significant, while time was not.







Figure 45. Change in peak stress with hygrothermal exposure for Sikadur 300



Figure 46. Change in strain with hygrothermal exposure for Sikadur 300

The same pattern follows for the peak strength. With higher exposure temperature, a lower peak strength was found. After 4 to 6 weeks, the decrease in strength remained constant. As with the modulus, the effect of temperature on the peak stress was statistically significant, while time was not.

Unlike the model epoxy system, there was no significant change in the strain to failure with exposure. The chemical explanation for the lack of change in strain with exposure is not known, due to the proprietary chemical nature of the epoxy systems. There was no statistical significance for any of the variables for the change in strain for the commercial system.

4.3.4 Diffusion of Water into the Model Epoxy System

Water diffusion in epoxy resins has frequently been described by Fick's second law (Pethrick et al., 1996). This mathematical expression is described in Equation , where C represents concentration of the diffusing substance as a function of time t and position x, and D is the diffusion coefficient.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$
 Equation 8

The total amount of substance diffusing into the epoxy resin, M_t , as a function of time across the thickness, h, is given by the integral of the solution of Equation . This equation assumes the diffusion occurs only in one dimension. M_{max} is the maximum amount of the diffusing substance at infinite time.

$$\frac{M_{t}}{M_{max}} = 1 - \frac{8}{\pi^{2}} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^{2}} \times \exp\left[-D(2n+1)^{2} \frac{\pi^{2} t}{h^{2}}\right]$$
Equation 9

This curve can be divided into two parts, when Dt/h^2 is greater than 0.05 and less than 0.05. If $Dt/h^2 > 0.05$ Equation can be rewritten as

$$\frac{M_t}{M_{max}} = 1 - \frac{8}{\pi^2} \exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right]$$
Equation 10

If $Dt/h^2 < 0.05$ Equation can be rewritten as

$$\frac{M_{t}}{M_{max}} = \frac{4}{h\sqrt{\pi}}\sqrt{Dt}$$
 Equation 11

Figure 47 shows the diffusion behavior of the model epoxy system at various temperatures with exposure up to 8 weeks, where % weight gain is plotted against $t^{1/2}$. Water uptake in the epoxy appears to follow behavior predicted by Fick's law where in the initial stage the sorption curve is linear, and above the linear region the sorption approaches saturation. The diffusion coefficient can be calculated from the slope of the linear region of a plot of water uptake (M_t) vs. time ($t^{1/2}$), shown in Figure 48. Samples were typically saturated within 3 weeks. Water uptake was obtained from the average weight gain of two samples during exposure, where M_{0i} is the initial mass and M_{ti} is the mass of the sample at time *i*.

$$M_t = \frac{M_{ti} - M_{0i}}{M_{0i}} \times 100$$
 Equation 12

From these linear fits, the diffusion coefficients were calculated using Equation 13 where m is the slope of the fit. M_{sat} corresponds to the point at which the epoxy samples were saturated with water, or no significant change was shown in the weight gain.







Figure 48. Fitting of the linear region of the various samples

$$m = \frac{4M_{sat}}{h\sqrt{\pi}}\sqrt{D}$$
 Equation 13

The diffusion coefficients for the different water temperatures are summarized in Table 10. It is clear that at higher temperatures, the diffusion coefficients increase, which corresponds with findings from other authors (Nunez et al., 1999; Al-Harthi et al. 2007). However, the sample dimensions used in this study are not flat sheets, but dogbone shaped with a more complex geometry so the calculated diffusion coefficients are higher than the true diffusion coefficients. It is important to note that this study only investigates a short time period of 8 weeks, so it is assumed that primarily stage 1 diffusion occurs.

Assuming Fickian behavior of water diffusing into the epoxy, an Arrhenius equation can be used to calculate the diffusion activation energy, Ea, where D_0 is a pre-exponential factor, R is the gas constant, and T is absolute temperature.

$$D = D_0 e^{-\left(\frac{E_0}{RT}\right)}$$
 Equation 14

Fitting ln D against 1,000/T gives a slope E_a/R , by which the activation energy can be determined. This plot is shown in Figure 49. The calculated activation energy for the model epoxy system was 27.29 ± 2.89 kJ/mol. This activation energy is in agreement to those calculated by other authors for similar epoxy systems (Yang et al., 2008; Apicella et al., 1984; Barral et al., 1995).

Table 10. Diffusion coefficients at different water temperatures for the model epoxy system

T (°C)	D (10 ⁻⁹ m ² /s)
30	20.36
40	34.76
50	39.71
60	41.45
70	68.92
80	97.85
90	126.36



Figure 49. Calculation of Ea/R for the model epoxy system

4.3.5 IR Characterization of Degradation

DRIFT and ATR IR experiments were performed on the model epoxy system to determine the mechanism of property loss for the cured epoxy after various environmental exposure conditions. Table 11 indicates IR assignment of the various absorption peaks. These assignments are in good agreement with those found by other authors (Jana and Zhong, 2007; Nikolic et al., 2010; Mertzel and Koenig, 1986).

Figure 50 shows the IR spectra of the samples exposed to water for 8 weeks from 30 to 90°C. While there is much overlap for the exposed samples, it appears that there is an increase in the hydroxyl region from 3100 to 3700 cm⁻¹ relative to the aromatic ring stretch at 1510 cm⁻¹, typically used as an internal standard. In addition there is the appearance of the OH bending vibration of water at 1625 cm⁻¹. To estimate the amount of absorbed water for each exposure condition, the area under these peaks was obtained and normalized to the area under the phenyl ring. While these normalized values cannot be used to determine absolute concentrations, they can be used for relative comparisons. This process has been demonstrated by other authors on epoxy systems (Musto et al., 2000; Choi and Douglas, 2010). These values are shown in

Peak Position (Wavenumber, cm ⁻¹)	IR Assignment						
829	In plane deformation of phenyl-H						
917	Epoxy bending						
1,033	IR Assignment In plane deformation of phenyl-H Epoxy bending C-O-C stretching O-C-C stretching C-C-O-C stretching Twisting mode of CH ₂ units C-H in plane deformation in aliphatic units Aromatic ring stretching O-H bending vibration C-H and CH ₂ stretching Phenyl-H stretching						
1,097	O-C-C stretching						
1249, 1182	C-C-O-C stretching						
1297	Twisting mode of CH ₂ units						
1456, 1362	C-H in plane deformation in aliphatic units						
1609-1582-1510	Aromatic ring stretching						
1650	O-H bending vibration						
2960-2930-2870	C-H and CH ₂ stretching						
3050	Phenyl-H stretching						
3300	N-H stretching						
3440	Hydroxyl stretching						

Table 11. IR peak assignment of the absorption bands in the model epoxy system (Jana and
Zhong, 2007; Nikolic et al., 2010; Mertzel and Koenig, 1986)



Figure 50. DRIFT IR spectra of the model epoxy system.(a) unexposed epoxy sample after 8 weeks and (b) exposed samples after 8 weeks. Spectra have been normalized to the aromatic ring stretch at 1510 cm⁻¹.

Temperature	1510 cm ⁻¹	3434 cm ⁻¹	1625 cm ⁻¹	H2O /	OH /	Total Water /				
(°C)	Area	Area	Area	Phenyl	Phenyl	Phenyl				
control	1.994	28.146	4.794	2.404	14.115	16.519				
30	0.809	29.728	3.795	4.689	36.728	41.416				
40	0.509	25.674	3.347	6.583	50.489	57.072				
50	0.575	21.261	2.997	5.209	36.956	42.165				
60	0.721	45.929	5.364	7.440	63.702	71.141				
70	0.388	24.437	2.882	7.432	63.013	70.445				
80	0.535	23.899	3.042	5.690	44.695	50.384				
90	0.496	28.722	3.560	7.174	57.884	65.057				

 Table 12. Area comparisons of water absorption peaks relative to the phenyl ring for exposure at various water temperatures

Table 12. While the normalized areas indicate that the epoxy network has adsorbed a large amount of water, unfortunately, there is no trend as a function of exposure temperature. This is most likely due to sample handling and preparation.

The bending mode of water in epoxy occurs at a lower wavenumber than the band of liquid water at 1648 cm⁻¹. Typically, the formation of hydrogen bonds affects the vibrational spectra of the groups involved by decreasing the frequency of stretching modes and increasing

the frequency of bending modes (Mertzel and Koenig, 1986). For water absorption in epoxies, it has been proposed by other authors that since the wavenumber of the water held in the epoxy resin is between the wavenumber of free water and liquid water, it is hydrogen bonded to the epoxy, and this interaction is reversible (Bockenheimer et al., 2004b; Ngono et al., 1999). The increase in both of these regions suggests that hygrothermal aging induces hydroxyl groups into the epoxy chains as water diffuses into the network. Using rubber elasticity theory, with swelling of the polymer network by hydrogen bonding of water with the epoxy, a decrease in strength and elasticity is predicted, which was confirmed by the mechanical testing.

Figure 51 shows the IR spectra of the samples exposed to UV and water for 8 weeks at 60°C. Spectra have been CO_2/H_2O , ATR, and baseline corrected for ease of comparison. It seems that after UV exposure there is an increase in OH groups around 3,300 cm⁻¹ and C=O groups at 1650 cm⁻¹ and 1725 cm⁻¹. These changes have been reported by other authors as indicative of the oxidation mechanism (Gu et al., 2009; Jana and Zhong, 2007; Musto et al., 2001; Delor-Jestin et al., 2006). In addition, for the samples exposed to both UV radiation and water immersion at



Figure 51. ATR IR spectra of samples after 8 weeks of exposure to (a) UV and water, (b) UV only and, (c) unexposed

60°C, a decrease in ether groups was found at 1085 cm⁻¹ for the trans ether link and 1232 cm⁻¹ for the aromatic ether ink, and can be seen in Figure 52. A comparison of the relative areas of the OH, CO, and C=O to the phenyl group is shown in Table 13. The results of the table show a large increase in C=O groups and a small decrease in C-O groups with exposure to UV only. With UV and water exposure, there is a large increase in OH groups, and a large decrease in C-O groups.

The formation of carbonyl groups may result from oxygen attack of ether groups or methylene groups linking two phenyl groups in the DGEBA epoxy resin (Hong, 1995). Since the sample exposed to UV only did not show a large increase in the OH area, it can be assumed that solely oxidation took place. In the presence of both UV radiation and water, it is generally believed that hydrolysis of the ester linkages occurs, with the formation of a hydroxyl and carbonyl (Lin et al., 2006). This process decreases the effective average cross-link molecular weight, and absorbed moisture can attack the cross linked chains and cause chain scission.



Figure 52. ATR IR spectra of samples after 8 weeks of exposure to (a) UV only (b) unexposed and (c) UV and water

	1510	3434	1085	1232	1725			
	cm ⁻¹	OH /	С=О /	Total				
Exposure	Area	Area	Area	Area	Area	Phenyl	Phenyl	Ester/Phenyl
control	1.948	9.426	2.914	4.585	0.048	4.839	0.025	3.850
UV	1.018	3.550	0.636	2.708	0.463	3.489	0.455	3.286
UV+water	1.102	9.603	0.287	2.015	0.081	8.715	0.074	2.089

Table 13. Area comparisons of various absorption peaks relative to the phenyl ring for exposureto UV radiation with and without water

4.4 Summary and Conclusions

This part of the research focused on accelerated aging of two epoxy systems, including a model DGEBA-POPDA system, and a commercial system. Mechanical testing was performed along with IR spectroscopy and diffusion modeling to determine the change in properties and mechanisms of degradation. A decrease in tensile strength and modulus and an increase in strain to failure was found with higher temperatures. An increase in hydroxyl and H₂O regions in the IR spectra was found after 8 weeks exposure. With UV and UV with water exposure, the modulus did not decrease as much as with water alone. However, the peak stress was significantly decreased with the UV radiation, reducing the peak stress by an even greater amount than 90°C in water. The strain after UV exposure decreased less than the control after 8 weeks, reducing the ductility of the samples which is typical of UV degradation. However, the data from UV degraded samples was not statistically significant. IR data provided evidence of the oxidative degradation mechanism for samples exposed to UV radiation alone, while evidence of hydrolysis was found for samples exposed to UV and water.

While the goal of this part of the study was to examine how properties changed with time, the epoxy lost its strength by 4 weeks and then no further degradation occurred. However, the lack of further change may be due to the relatively short testing duration (8 weeks). To get a true correlation between lab and field conditions, longer testing periods are essential, along with a greater variation in temperatures. Also, varying the type of curing agent may be interesting to examine other evidence for degradation mechanisms.

Based on the results from Chapters 3 and 4, as well as the literature review in Chapter 2, we propose the following set of conditioning protocols for testing of FRP-concrete bond:

- 1. Exposure to water immersion at temperatures that are 15°C above and below the Tg for 1, 2, and 8 weeks
- 2. Exposure to UV and water since this condition changed the epoxy mechanism of degradation from oxidation to hydrolysis

5 Small Beam Testing

5.1 Testing Conditions

Based on the recommendations in Chapter 5, exposure conditions and exposure times in Table 14 were defined for FRP-concrete bond testing. Five composite systems and two different concrete strengths were selected for the study. Three specimens per exposure condition were tested. A three-point bending test was utilized to test FRP-concrete bond durability (Gartner 2007).

Exposure Condition	Temp. (°C)	Exposure Times (weeks)	Number of specimens
Immersed in water	30	1, 2, 8	105
Immersed in water	60	1, 2, 8	105
RH=100%	60	1, 2, 8	90
UV & RH=100%	60	1, 2, 8	15

Table 14. Summary of conditioning protocols

The test matrix for FRP reinforced concrete samples presented in Table 15 was created for the purpose of the durability study. It should be noted, however, that tests on the combined effect of UV and moisture at 60°C were not performed due to unexpected circumstances. Concrete strength for all samples was 10,000 psi except for Composite D and Composite F which were tested for concrete strengths of 4,000 psi and 10,000 psi. Therefore designations such "D04" and "D10" signify the corresponding concrete compressive strength.

FRP Reinforcement	System		Immersion + 30°C		Immersion + 60°C		Immersion + UV + 60°C		100%RH					
	Fiber Weight (kg/m ²)	Material	Material Expos time (week		sure ne Exposur eks) (wee		re time eks)		Exposure time (weeks)		ne	Exposure time (weeks)		e
			1	2	8	1	2	8	1	2	8	1	2	8
1 in wide bonded CFRP fabric	0.644	Composite A	3	3	3	3	3	3	3	3	3	3	3	3
1 in wide bonded CFRP fabric	0.618	Composite B	3	3	3	3	3	3	3	3	3	3	3	3
1 in wide bonded CFRP fabric	0.600	Composite C	3	3	3	3	3	3	3	3	3	3	3	3
1 in wide bonded CFRP fabric	0.644	Composite D04	3	3	3	3	3	3	3	3	3	3	3	3
1 in wide bonded CFRP fabric	0.644	Composite D10	3	3	3	3	3	3	3	3	3	3	3	3
1 in wide laminate	N/A	Composite E	3	3	3	3	3	3	3		3	3	3	3
NSM CFRP tape	N/A	Composite F04				3		3				3		3
NSM CFRP tape	N/A	Composite F10	3	3	3	3	3	3				3	3	3

Table 15. Test matrix

5.2 Durability Test Specimen Design and Fabrication

5.2.1 Specimen Design

All the concrete specimens had a square cross section measuring 4 in. x 4 in. and were 14 in. long. This specimen size was deemed adequate to capture the bond behavior in bending at a small scale. The size was also chosen to match the previous work conducted at the University of Florida by Gartner et al. (2011). The amount of FRP reinforcement was picked to enable the debonding failure of the FRP instead of a concrete shear failure. If too much reinforcement is applied to the specimen the bond strength cannot be fully utilized and the specimen is likely to fail in shear by reaching the ultimate shear capacity of concrete. Adequate cross sectional area of surface bonded FRP was determined based on the available experimental data (Gartner et al. 2011). FRP strips measuring 1 in. in width and 8 in. in length were deemed appropriate to
achieve a desired failure mode of the test specimen. In addition, to better simulate the behavior of FRP in flexural applications, by promoting Mode II loading condition, a 2 in. deep notch was provided at the specimen midspan to simulate cracked concrete (as shown in Figure 53). Furthermore, the notch allows testing beam specimens in a three-point bending test instead of a four-point bending test because the notch presence eliminates the need for a constant moment region and reduces the possibility of a shear failure.



Figure 53. Three-point bending test setup

5.2.2 Three-point Bending Test Bond Strength Index

One of the most important details worth discussion is how the physical value that is obtained from the three-point bending test relates to the actual bond strength. First, it should be regarded that bond strength is usually defined in terms of loading condition. Namely, the most commonly observed loading conditions are Mode I, Mode II, and a mixture of the two. Mode I or the peel mode starts at the ends of the laminates and propagates towards the midspan (Figure 54). Peeling occurs as a result of the end offset of FRP reinforcement from the supports, which allows for the ends of FRP reinforcement to be exposed somewhere along the span. If boundary conditions in FRP reinforcement at the ends (free end boundary condition) are examined it can be easily concluded that there is zero curvature at the location. To satisfy the boundary conditions, and due to the existence of bending stresses in concrete, FRP laminate needs to bend in the direction opposite to the direction of beam bending, which will cause Mode I loading at the location (Sebastian 2001).

Mode II, on the other hand, is observed in the vicinity of vertical flexural cracks. According to Sebastian (2001), when concrete's tensile capacity is reached, flexural cracks open, which loads the FRP in direct shear (Figure 54).

Mixed mode (Figure 54) happens as a result of inclined cracks along the span and is a

function of phase angle ψ (mode mixity parameter - $\psi = \tan^{-1} \frac{K_{II}}{K_{I}}$) which is dependent on crack

inclination angle (Sebastian 2001).

With the newly developed anchoring techniques, Mode I loading may be neglected. Therefore, Mode II crack development is considered the most critical in flexural FRP applications.



Figure 54. Loading modes in interfacial region

The purpose of the three-point bending test, described previously, is to directly simulate Mode II loading condition which is deemed representative of the FRP-reinforced beam behavior when subjected to bending. The quantity recorded from these tests is the ultimate load that caused failure of the test specimen. Even though the specimen failure load is not representative of the actual bond stress that caused FRP to debond, it provides a way to indirectly express the bond strength in flexural applications. The ultimate exposed specimen failure load normalized to averaged control specimen failure load will be referred to as bond strength index (BSI). Bond strength index, as defined here, is representative of both peel mode and Mode II loading conditions, with Mode II being more dominant. It should be noted that in this study terms such as bond capacity, bond strength, and bond degradation, when used in relation to three-point bending test, refer to bond strength index, and not the actual debonding stress.

5.2.3 CFRP Composites

All composite materials used in this study are commercially available from U.S. manufacturers. In the following paragraphs, CFRP composite systems that were used to reinforce the concrete beam specimens, and corresponding adhesives are described.

Composite A is a custom, unidirectional carbon fabric orientated in the 0° direction that, combined with Adhesive A, forms a wet-layup composite system that is used in infrastructure applications (Table 16).

Composite B is a high strength unidirectional carbon fiber fabric that is field laminated by epoxy to form a carbon-fiber-reinforced polymer (CFRP). Properties are specified in Table 16.

Composite C consists of Composite C Primer, Composite C Putty, Adhesive C (Composite C Saturant), and dry fabric constructed of high strength carbon fibers (Table 16):

- Composite C Primer is a low viscosity, 100% solids, polyamine cured epoxy. Being the first component of the system applied to the concrete surface, Primer is used to penetrate the pores of concrete substrate and to provide a high bond base coat for the Composite C system. According to the manufacturer's product data sheet, Primer should be mixed following these ratios: a) 3 parts of component A to 1 part of component B by volume; or b) 100.0 parts of component A to 30.0 parts of component B by weight.
- Composite C putty is a 100% solid, non-sag paste epoxy material that is applied as a second layer of Composite C system. The purpose of putty is to level the uneven surfaces before the application of Composite C fibers. Additionally, Putty improves adhesion of subsequent coatings on substrates. Putty shall be mixed according to the following ratios:
 a) 3 parts of component A to 1 part of component B by volume; or b) 100.0 parts of component A to 30.0 parts of component B by weight.
- Finally, fibers, when saturated with Adhesive C, form a high strength carbon fiberreinforced polymer (CFRP). This material, as stated by the manufacturer, can provide additional strength to concrete, masonry, steel and wood structural elements.

Composite D consists of Composite A system carbon fiber fabric and Adhesive D (Table 16).

Composite E is a pultruded carbon fiber-reinforced polymer (CFRP) laminate. Composite E is bonded onto the structure as external reinforcement using Adhesive E (Table 16).

Composite F is a 0.63 in. wide CFRP tape used for structural strengthening with fibers in 0/90 direction. The technique used to apply the reinforcement to a structural member is known as Near Surface Mounted (NSM) strengthening. Composite F is used in combination with Adhesive F.

Composite System	Fabric weight (g/m ²)	Thickness (in)	Ultimate Tensile Strength (psi)	Modulus of Elasticity (10 ⁶ psi)
Composite A	644	0.04	143,000	13.90
Composite B	618	0.04	123,200	10.24
Composite C	600	0.04-0.06	550,000	33.00
Composite D	644	0.04	n/a	n/a
Composite E	n/a	0.047	449,000	23.90
Composite F	n/a	0.079	300,000	18.00

Table 16. Properties of composite systems (information provided by manufacturers)

5.2.4 Epoxy Adhesives

Adhesive A is a two-component epoxy matrix material for bonding applications. It is a material used in structural applications to provide a wet-layup composite system for strengthening structural members. Adhesive A provides a long working time, with no offensive odor. Adhesive A is mixed according to the following ratios: a) 100.0 parts of component A to 42.0 parts of component B by volume; or b) 100.0 parts of component A to 34.5 parts of component B by weight. The recommended minimum cure time is 72 hours at 70 F. The preceding description of the material is provided by the manufacturer.

Table 17. Adhesive A mechanical properties 72 hours post cure at $140^{\circ}F(60^{\circ}C)$ – as reported by the manufacturer

Property	ASTM Method	Typical Test Value
Tg	D4065	180° F (82° C)
Tensile Strength	D638 Type 1	10,500 psi
Tensile Modulus	D638 Type 1	461,000 psi
Elongation Percent	D638 Type 1	5.0 %
Compressive Strength	D695	12,500 psi
Compressive Modulus	D695	465,000,000 psi

Adhesive B is a two-component, 100% solids epoxy that is used as an impregnating resin with Composite B CFRP fabric, and as a seal coat and impregnating resin for horizontal and vertical applications. The recommended minimum cure time is 14 days at normal ambient conditions (73°F and 50% R. H.).

reported by the manufacturer				
Property	ASTM Method	Typical Test Value		
Tg	D4065	46		
Tensile Strength	D638	8,000 psi		
Tensile Modulus	D638	250,000 psi		
Elongation Percent	D638	3.0 %		
Compressive Strength	D695	N/A		
Compressive Modulus	D695	N/A		

Table 18. Adhesive B mechanical properties (14 day cure at 73°F (23°C) and 50% R.H.) – as reported by the manufacturer

Adhesive C is a 100% solids, low viscosity epoxy material that is used to saturate the fibers of Composite C to form a carbon fiber reinforcing laminate (CFRP). Physical properties of Adhesive C are provided in Table 19.

Table 19. Adhesive C mechanical properties (based on cured samples at $72^{\circ}F$ ($20^{\circ}C$) and 40% R.H.) – as reported by the manufacturer

Property	ASTM Method	Typical Test Value
Tg	D4065	163°F (71°C)
Tensile Strength	D638	8,000 psi
Tensile Modulus	D638	440,000 psi
Elongation Percent	D638	3.5%
Compressive Strength (28 day)	D695	12,500 psi
Compressive Modulus (7 day)	D695	380,000 psi

Adhesive D is a two-part epoxy with a known chemical composition, comprised of diglycidyl ether of bisphenol A (DGEBA) and poly(oxypropylene) diamine (POPDA). The mix ratio of DGEBA to POPDA was 100 to 32.9.

Adhesive E is a 2-component, 100% solids, structural epoxy paste adhesive. This adhesive conforms to the current ASTM C881 and AASHTO M-235 specifications. The epoxy is used as an adhesive for bonding external reinforcement to concrete, masonry, steel, wood, stone, etc., structural bonding of composite laminates, and structural bonding of steel laminates to

Property	ASTM Method	Typical Test Value
Tg	D4065	N/A
Tensile Strength (7 day)	D638	3,600 psi
Tensile Modulus (7 day)	D638	650,000 psi
Elongation Percent (7 day)	D638	1.0%
Compressive Strength (28 day)	D695	8,600 psi
Compressive Modulus (7 day)	D695	390,000 psi

Table 20. Adhesive E mechanical properties (at 73°F (23°C) and 50% R.H.) – as reported by the manufacturer

Table 21. Adhesive F mechanical properties at 77°F (25°C), cured 7 days – as reported by manufacturer

Property	ASTM Method	Typical Test Value
Tg	D4065	N/A
Tensile Strength (7 day)	D638	4,000 psi
Tensile Modulus (7 day)	D638	N/A
Elongation Percent (7 day)	D638	1.0%
Compressive Strength (28 day)	D695	12,500 psi
Compressive Modulus (7 day)	D695	450,000 psi

concrete. Epoxy components should be mixed by volume or weight following the ratio A:B=3:1. The pot life is approximately 70 hours at 73°F. The recommended minimum curing time is 72 hours at normal ambient conditions (73°F and 50% R.H.).

Adhesive F is a two-component 100% solids non-sag epoxy adhesive. Aside from being used as an adhesive for Composite F, Adhesive F can be used for anchoring fasteners and dowels into concrete. The epoxy is packaged in 15.8 oz. biaxial cartridges that proportion epoxy components in a A:B=2:1 ratio, by volume.

5.2.5 Specimen Fabrication

Concrete beams used to conduct the experiment were fabricated at the FDOT State Materials Office (SMO) located in Gainesville, FL. Two concrete mixture designs were created by Dr. Harvey DeFord. Target design strengths were 10,000 psi and 4,000 psi. Low water–to-cementitious material ratio (w/cm) of 0.353 was maintained for the 10,000 psi mixture in order to achieve a high compressive strength, whereas w/cm=0.56 was used for the 4,000 psi mixture. The 360 specimens were constructed from 12 batches of concrete as presented in Table 25.

The concrete mixtures were composed of: fine aggregate GA-397, coarse aggregate 87-090 (#89), Portland Cement Type I/II and admixtures - air entrainer (Darex AEA), plasticizer and water reducer (Adva Cast 600 and WRDA 60). No pozzolans were included in the mix design. Refer to Table 22 and Table 23 for the specific mix proportions.

MATERIAL	SOURCE	WT. PER YD3 (LB)	SPECIFIC GRAVITY	VOL. PER YD3 (CF)	WT. PER BATCH (LB)
CEMENT	Cemex	840.0	3.15	4.27	155.6
WATER	Local	296.5	1.00	4.75	54.9
FINE AGG.	GA-397	1230.2	2.642	7.46	227.8
COARSE AGG.	87-090	1429.9	2.413	9.49	264.8
AIR ENTRAINER	Darex AEA	1.26 oz	1.02	0.001	6.9 ml
ADMIXTURE	WRDA 60	25.20 oz	1.15	0.026	138.0 ml
ADMIXTURE	Adva Cast 600	25.20 oz	1.08	0.026	138.0 ml
AIR (DESIGN)	Local	0.01330		0.972	
TOTAL		3796.75		27.00	

Table 22. Example 10,000 psi mix proportions

Table 23. Example 4,000 psi mix proportions

MATERIAL	SOURCE	WT. PER YD ³ (LB)	SPECIFIC GRAVITY	VOL. PER YD ³ (CF)	WT. PER BATCH (LB)
CEMENT	Cemex	536.0	3.15	2.73	99.3
WATER	Local	300.2	1.00	4.81	55.6
FINE AGG.	GA-397	1438.6	2.642	8.72	266.4
COARSE AGG.	87-090	1367.5	2.413	9.08	253.2
AIR ENTRAINER	Darex AEA	0.18 oz	1.02	0.000	1.0 ml
ADMIXTURE	WRDA 60	36.52 oz	1.15	0.038	200.0 ml
ADMIXTURE	Adva Cast 600	0.00 oz	1.08	0.000	
AIR (DESIGN)	Local	0.02217		1.620	
TOTAL		3642.42		26.99	

Sand was dried in the oven for 24 hours to minimize the absorbed moisture. On the other hand, coarse aggregate was soaked in water for at least 48 hours in order to be saturated at the time of mixing. Coarse aggregate moisture content was determined as per ASTM C566, prior to mixing the concrete, to adjust the batch quantities accordingly. Beam production procedures are presented in Table 24.



Figure 55. Fine aggregate, coarse aggregate, and cement (left to right)



Figure 56. Darex AEA, Adva Cast 600, and WRDA 60 (left to right)

Table 24. Beam production procedures

Step Description

1 Steel forms were coated with form release oil to facilitate beam removal and form cleaning and disassembling



2 Concrete was mixed in portable mixer by adding a "butter batch" (composed of 10% of the designed mixture) first, which ensured that the mixer surface is coated before adding the actual mix materials. This secured the mixer surface from mix materials adhering to it. Materials were added to the mixer in the following order: coarse aggregate, sand and cementitious material. Water was added gradually so that it gets dispersed uniformly. Admixtures were added into the mixer to improve the workability. Concrete was first mixed for 3 minutes, allowed to sit for 3 minutes, and then mixed for additional 2 minutes.



- 3 Slump was measured as per ASTM C143 to ensure that the proper consistency of the mix was reached. The design slump range was between 3 and 5 in.
- 4 Concrete air content was measured for each batch according to ASTM C231 and recorded in the data sheet.
- 5 Concrete was poured half-way into the forms and vibrated for 30 seconds on a vibrating table.



6 Forms were filled all the way and vibrated for additional 30 seconds.

7 Excessive concrete from the top was removed and the beam surface was flattened

8 Filled forms were covered with plastic cover in order to preserve the concrete moisture.

Six cylinders per batch were constructed.



After filling the forms, concrete was allowed to harden for 24 hours before removal from the forms. Beams were then marked (production date and batch number) and placed in the moist room to cure at 20°C and 100% relative humidity for 28 days.

Concrete compressive strength was measured as per ASTM C39 at 7 and 28 days by the FDOT SMO staff. Cylinders measured 4 in. in diameter and were 8 in. high. Modulus of elasticity and Poisson's ratio were acquired as well, according to ASTM C469. Table 25 summarizes the collected data. For each mix, six cylinders from one of the batches were used to measure the 7-day and 28-day compressive strengths, whereas another three cylinders from a different batch were used to determine the concrete elastic constants. Three spare cylinders per mix remained unused.

Date	Mixture Designation	No. of beams	MOE (psi)	Poisson's Ratio	28-day compressive strength
7/30/12	Mix #1-10k – A	30	n/a	n/a	9,537
7/30/12	Mix #1-10k – B	30	5,200,000	0.29	n/a
8/2/12	Mix #2 – 10k – A	30	5,250,000	0.27	n/a
8/2/12	Mix #2 – 10k – B	30	n/a	n/a	9,650
8/7/12	Mix #3 – 10k – A	30	n/a	n/a	1,0430
8/7/12	Mix #3 – 10k – B	30	5,400,000	0.27	n/a
8/9/12	Mix #4 -10k – A	30	n/a	n/a	7630
8/9/12	Mix #4 -10k – B	30	5,350,000	0.27	n/a
8/13/12	Mix #5 -10k – A	25	n/a	n/a	10,130
8/13/12	Mix #1 – 4k – A	35	3,800,000	0.27	4,550
8/16/12	Mix $#2 - 4k - A$	30	n/a	n/a	3,770
8/16/12	Mix $#2 - 4k - B$	30	3,850,000	0.24	4,320

Table 25. Concrete mechanical properties

After curing, the specimens were notched at midspan to half of the depth. The notch at the midspan of each beam is provided to ensure that debonding initiates at midspan so that the bond length is known.

NSM specimens (Figure 57 right) required an additional cut through the beam soffit along the full length of the beam. A diamond saw specifically designed for high strength concrete was used. After cutting, the groove was cleaned with a stream of water. Before FRP application, the groove was also air blasted. Groove preparation conformed to NCHRP Report 514 Section 4.4.4. To achieve the optimum adhesion between the concrete surface and epoxy layer reinforced with surface-bonded FRP (Figure 57 left), the FRP placement area was sandblasted (Figure 57). Coal slag abrasive with a mesh size of 20-40 was used as a blasting medium. Beams constructed from 10,000-psi concrete were sandblasted until the aggregate was revealed, producing a surface roughness corresponding to ICRI surface profile chip (SPC) No. 3. The same procedure was followed for the 4,000-psi beams. However, the achieved surface roughness corresponded to ICRI surface profile chip No. 5. Beams were then air blasted to remove the remaining sand and debris from the surface. Additionally, the surface was wiped off with acetone to eliminate any additional dust, laitance, grease, etc.

Concrete beams were then repaired by applying FRP following the procedures described in Table 26, Table 27, Table 28, and Table 29.



Figure 57. Specimen cross-section: surface bonded (left) and NSM (right)



Figure 58. Specimen sandblasting

Table 26. Procedure for application of Composite systems A, B and D

Step Description

1. CFRP fabric was cut in 8x1 in. strips Figure



Cutting CFRP fabric



8x1 in. CFRP fabric strips

2. Epoxy was mixed by weight in proportions prescribed by manufacturer for up to 3 minutes



(a) Epoxy component A

(b) Epoxy component B



(c) Epoxy mixing

- 3. Prime coat of epoxy was applied to the FRP placement area by a nap roller and allowed about a minute to soak in
- 4. FRP fabric was fully saturated with epoxy

Saturated FRP was placed on to beams in a designated area, followed by pushing the FRP longitudinally against the concrete surface (from the centerline to the outer edges) in order to push out entrapped air bubbles



5.

Step Description

Figure

No.

Additional layer of epoxy was applied with a nap roller in order to fully encapsulate the fibers



Table 27. Procedure for application of Composite C system

Step Description

No.

1. Prime coat was mixed according to the manufacturer's manual and applied to the concrete surface with a nap roller

2. Putty was mixed according to the manufacturer's instructions and applied (wet-on-wet) over the prime coat with a spatula

3. Saturant Part A was pre-mixed with a drill and a mixing paddle for 3 minutes, as specified by manufacturer





Step Description

No.

4. Composite C Saturant was mixed following the manufacturer's recommendations

5. Fibers were saturated using a nap roller

- 6. Saturated fibers were placed onto the beam specimen in a designated area; followed by pushing the fibers against the surface from the centerline to the outer edges in order to eliminate entrapped air bubbles
- 7. A second layer of Saturant was applied in order to fully encapsulate fibers.

Figure



Table 28. Procedure for applications of Composite E system

Step Des	scription
----------	-----------

No.

- 1. CFRP laminate was wiped with acetone
- 2. The epoxy was mixed by weight, as defined by manufacturer
- 3. Epoxy was applied to concrete surface with a spatula to a nominal thickness of 1/16 in., as recommended by manufacturer
- n/a

Figure

n/a



(a) Applying epoxy to achieve a rooftopline shape



(b) Laminate with the epoxy on

4. Epoxy was applied onto the laminate to form a rooftop-like shape

Step Description

No.

5. Laminate was placed onto the concrete surface

6. Laminate was pressed into the epoxy resin to eliminate the entrapped air and excessive epoxy

7. Excess adhesive was removed, and the beam was allowed a minimum of 7 days to cure in standard laboratory conditions (recommended by manufacturer to reach the adhesive's design strength)

Figure



Table 29. Procedure for application of Composite F system

Figure

Step Description

No.

1. CFRP tape was wiped with acetone



2. The epoxy was poured into the bucket



 Epoxy was mixed for 1-2 minutes until a consistent color of the mixture was attained



Step Description

Figure



4. One layer of epoxy was placed into the NSM channel to the maximum of 1/3 depth of cut (with a spatula)



(a) Filling up the channel with epoxy



(b) Cross-sectional view



5. CFRP tape was placed ensuring proper centering within the channel

Step Description

No.

Figure

6. Channel was completely filled with epoxy

7. Excess epoxy is removed so that epoxy is in level with the beam surface





(a) Removing excessive epoxy



(b) Final product

Following the recommended curing time, prepared beams were placed in an exposure tank system located at the University of Florida Coastal Lab (Figure 59). A maximum of 12 beams per tank were placed to enable for proper water circulation. Water level was adjusted so that the entire area of bonded FRP was submerged. Water temperature was measured and recorded 3 to 5 times a week to ensure a proper quality control. Water temperature fluctuation within the limits of $\pm 1^{\circ}$ C was considered acceptable.

Exposure to RH=100% was accomplished by lowering the water level in the tanks and placing the beams above the water level. Humidity and temperature were constantly monitored with a humidity meter.



Figure 59. Exposure of test specimens

5.2.6 Durability Test Procedures

All test results reported in this report were obtained by following the herein described test procedure. After taking the beams out of the exposure tank system they were allowed at least 1-2 hours (but no more than 24 hours) to dry and cool down before testing. At the time of testing the beam's temperature was within standard laboratory conditions temperature of $70^{\circ}F \pm 5^{\circ}F$. The temperature was measured using an infrared thermometer. Each beam was then placed in the testing fixture (Figure 60), making sure that it was properly aligned/centered within the test apparatus.



Figure 60. Concrete beam in test fixture

Data was collected either from the testing machine's internal load cell or externally affixed load cell. Load and cross-head displacement data was recorded using the appropriate software packages provided by the testing machine/load cell manufacturer.

Load was applied at a constant displacement rate of 0.017 in/min until the total specimen failure, identified by either debonding of FRP or concrete shear failure (Figure 61). The load rate was established to result in an increase in average FRP bond stress of between 60 and 120 psi/minute (as described in Harries et al. 2012), which results in failure of the test specimen in less than three minutes.



Figure 61. (a) Debonding failure; (b) shear failure

5.3 Results and Discussion

5.3.1 Small Beam Test Results

Typical load-displacement plots from the three-point bending test are presented in Figure 62. As the specimen is loaded, apparent changes in stiffness are noted on the load-displacement plot. Differences exist in behavior between control and exposed samples, due to effects of moisture and high temperature. Changes in stiffness correspond to the occurrence of microcracking near the interface, formation of macrocracks, and finally debonding of CFRP from the specimen (Wu et al. 2001). As described earlier, failure usually happens along the interface between the epoxy and concrete (adhesive failure) or inside the concrete substrate (cohesive failure). Failure modes were recorded for each test as a percent of adhesive failure (Figure 63). In this study, cohesive failure mode was rarely observed, and mostly in 4,000 psi concrete specimens. A majority of test samples exhibited different degrees of adhesive failure. Specimens reinforced with Composite F system experienced only shear failure. Failure modes of surface-bonded samples will be discussed later in this report.



Figure 62. Representative averaged load-displacement plots for control and exposed samples









Figure 63. Failure modes: a) 0% adhesive; b) 50% adhesive; c) 100% adhesive

Bond strength indices for each exposure condition are presented in Figure 64 for 1, 2, and 8 week exposure periods. Composite systems A, B, D04, and D10 show similar behavior. After initial 7 or 14 days of exposure (depending on the exposure condition) they reached a minimum BSI, and then a partial recovery is noted at 8 weeks. Composite D10, however, showed no recovery after 8 weeks for exposure to immersion at 30°C.

Composite system C, on the other hand, seems to be particularly sensitive to synergistic effects of water and high temperature. While Composite C samples regained their initial loss in strength after 8 weeks for immersion at 30°C, they showed a drop after 8 weeks of additional 17 and 20% for exposure to immersion at 60°C and RH=100% at 60°C, respectively.

A similar behavior was observed in Composite E. However final drop in strength (corresponding to 8 weeks exposure) was associated with a change in failure mode from cohesive/adhesive in the control, to CFRP laminate decohesion or adhesive failure mode between CFRP laminate and epoxy (Figure 65). Specimens exposed to immersion at 30°C did not experience this shift in failure mode.

Composite F specimens generally exhibited shear failure modes, which indicated that the bond strength was not degraded sufficiently to affect the ultimate performance of the NSM reinforcement. This indicates that larger test specimens may be required to study bond in NSM applications. As the shear crack extended through the NSM groove that is filled with epoxy, the loss in specimen capacity may be accredited to loss in epoxy stiffness due to plasticization of epoxy matrix. Since there is not sufficient evidence on performance of its bond, Composite F will not be further discussed in this report.



Figure 64. Bond strength index: (a) immersion in water at 30°C; (b) immersion in water at 60°C; and (c) RH=100% at 60°C



Figure 65. CFRP laminate failure modes: (a) adhesive failure between CFRP laminate and epoxy; (b) CFRP laminate decohesion

5.3.2 Analysis of Small Beam Durability

Data presented in in this report were combined with data from Dolan et al. (2008) and analyzed. This section presents results of the analysis of the combined FDOT and NCHRP durability beam test data.

As the FRP concrete specimens are exposed to water, moisture ingress into the FRPconcrete bond and the constituent materials takes place. For water immersion, Au (2005) determined that this process takes up to 8 weeks to reach equilibrium. In direct shear and peel tests on exposed samples; however, for one of the tested epoxy systems, no further change in bond fracture properties was noted after two weeks of exposure. This was explained by the existence of a moisture concentration threshold above which no further degradation in bond properties occurs for a given epoxy system.

These findings were used in the statistical analysis of the combined data. The time required to reach moisture equilibrium was assumed to be 60 days. In many of the tests in the database, the exposure times may have been shorter or significantly longer than this period. Consequently, some discretion was used in interpreting the data; if bond strength index for a particular exposure condition showed that bond degradation plateaued in less than 60 days, then that amount of time was considered the threshold for that specific exposure condition and composite system.

The NCHRP study on durability of FRP reinforcement was performed from 2005 to 2008 as a collaboration between University of Florida and University of Wyoming under NCHRP project number 12-73. For the purpose of the NCHRP research project, three-point bending test methodology, previously described, was utilized to study effects of different aggressive environments on FRP-concrete bond performance. This section provides a short overview of findings that were reported by Dolan et al. (2008). The data obtained from this report will be referred to as NCHRP data later in this document.

Table 30 shows the NCHRP conditioning times and exposure conditions. Fabrication, conditioning and testing of Group 1 specimens was performed at University of Wyoming, while Group 2 was managed by University of Florida. Tidal-outdoor real time specimens were kept in ambient conditions of the fender system of the SR 206 bridge in Crescent Beach, FL, whereas solar-outdoor real time specimens were placed on the roof of a six-story university building in Laramie, WY.

Exposure Condition	Temp. (°C)	Approximate Exposure Times (months)	Number of specimens	Group
	30	0.25, 0.5, 1, 3, 6, 12, 18	210	1&2
Submargad	40	0.25, 0.5, 1, 3, 6, 12, 18	210	1&2
Submerged	50	0.25, 0.5, 1, 3, 6, 12, 18	210	1&2
	60	0.25, 0.5, 1, 3, 6, 12, 18	300	1&2
100% Relative Humidity	20 and 60	0.5, 1, 2, 3, 6, 12	105	1
75% Relative Humidity	20	0.5, 1, 2, 3, 6, 12	105	1
Wet-dry cycling 2 days submerged/5 days dry	20	2, 4, 6, 11.5	90	1
Chloride solution (submerged)	50	12	15	2
Alkali solution (submerged)	50	12	15	2
Sustained Load + Submerged	50	6	15	2
Ultraviolet Radiation+ 2 weeks submerged/2 weeks dry	Solution - 50 Dry - 20	12	15	2
Fatigue-Repeated load	20	n/a	45	1
Tidal- Outdoor real time	Variable	12, 18	45	2
Solar-Outdoor real time	Variable	18	30	1
Pressurized hygrothermal (pressure vessel)	60	0.1, 0.25, 0.5	45	1
Control (dry ambient)	20	28 days	60	1&2

Table 30. NCHRP exposure conditions

Five hundred Group 1 concrete beams were cast by Rocky Mountain Prestress, in Denver, CO and had a 28-day compressive strength of 9,700 psi. The mixture had a water-to-cementitious material (w/cm) ratio of 0.32, and cementitious material:fine aggregate:coarse aggregate ratio of 1:1.65:1.96 by weight. Additionally, 315 beams were cast in two separate batches (of 105 and 210 specimens, respectively). The measured 28-day concrete strength for these two batches was 6,700 psi and 6,900 psi.

Group 2 concrete beams were cast in 6 batches of 75 beams each at the Florida Department of Transportation State Materials Office (FDOT SMO) in Gainesville, FL. This mixture had a w/cm=0.35 and cementitious material:fine aggregate:coarse aggregate ratio of 1:1.5:1.7 by weight. The measured 28-day compressive strength ranged from 9,250 psi to 10,500 psi.

		1
Composite System	Group 1	Group 2
Composite B	No protective coating, minimum recommended amount of epoxy used	With protective coating
Composite C	N/A	N/A
Composite D	Used Composite C fabric instead Composite A fabric	Used Composite C fabric instead Composite A fabric
Composite E	1 in. wide strip	³ / ₄ in. wide strip

Table 31. Specifics of Group 1 and Group 2 test specimens

Certain anomalies were reported that related to the specifics of test specimens in Group 1 and Group 2 presented in Table 31. Namely, there appeared to be a significant discrepancy in bond strength indices between Group 1 and Group 2 for Composite B system. This was explained by the fact that Group 1 Composite B specimens were subjected to a coverage study where the amount of epoxy was varied, which seemed to adversely affect the durability of the system.

Moreover, all Composite E specimens experienced FRP delamination after exposure for 12 months. The delamination, however, occurred after only 28 days of conditioning in 60°C water. This signifies low resistance of the laminate to aggressive environments and is not representative of the system's bond performance; it rather gives a lower bound value.

Combined NCHRP (consisting of Group 1 and Group 2 data) and FDOT (Group 3) data provide over 900 test results and, to the best of the authors' knowledge, is the largest existing database of its kind. This database covers most, if not all, conditioning environments to which FRP-concrete bond may be exposed in real world applications. Therefore, the database is deemed appropriate for evaluation of durability properties of FRP-concrete bond.

In terms of CFRP bond behavior, and for the purpose of data analyses, three distinguishing types of CFRP composite systems (Figure 66) were identified:

- 1. CFRP Wet-layup without putty (Composite A, Composite B, Composite D)
- 2. CFRP Wet-layup with putty (Composite C)
- 3. CFRP Laminates (Composite E)



Figure 66. (a) Wet-layup without putty; (b) wet-layup with putty; (c) CFRP laminates

Blackburn (2013) showed that Adhesive A, Adhesive B, and Adhesive D have a similar behavior in terms of variation of Tg due to exposure to hygrothermal conditions. Adhesive C Saturant, Adhesive C Putty, and Adhesive E each showed distinguishing behavior in the same study, justifying separation of FRP composite systems into three groups.

Data for each of the three categories was subjected to statistical analysis to examine the influence of different accelerated conditioning environments and exposure times on distribution of data.

5.3.3 Analysis of Data for CFRP Wet-layup Without Putty

Histogram and kernel distribution estimation are both non-parametric ways of representing distribution of data in a given population. A well-known fact is that histogram shape is dependent upon the starting point and width of bins. Therefore, for the same distribution different histograms would be obtained depending on the choice of aforementioned parameters. Moreover, histograms do not provide a smooth transition between the data points.

Kernel density estimation solves the problem of bin location by placing a kernel function at each data point. Then, by utilizing kernel weighting functions a smooth estimate of data distribution is provided.

The estimated density at each point of the given population may be written as:

$$f(x) = \frac{1}{n} \sum_{i=1}^{n} K\left(\frac{x - x_i}{h}\right)$$
 Equation 15

where K is the kernel function; its bandwidth is h; and n is the size of population.

It should be noted that each kernel density function satisfies the following:

$$\int K(t)dt = 1$$
 Equation 16

There are multiple kernel functions that are commonly utilized, such as: triangular, rectangular, cosine, Gaussian, etc. For the purpose of the analyses in this study, a Gaussian weighting function of the following form will be utilized:

$$K(t) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}t^2}$$
 Equation 17

To achieve a smooth and accurate kernel density estimate, an appropriate value of kernel bandwidth needs to be chosen. The choice was made based on Silverman's (1986) "rule of thumb" which recommends the following value:

$$h = 0.9An^{-1/5}$$
 Equation 18

where $A = \min(standard \ deviation, interquartile \ range/1.34)$, and n is the size of the population. Interquartile range (also known as midspread or middle fifty) is the difference between the upper (third) and lower (first) quartile. The chosen bandwidth is known to show all important features in a probability density plot.

To determine the actual distribution of data, histogram and kernel density estimate functions were plotted (Figure 67) for all wet-layup without putty data.

Data is distributed bimodally. By looking at the data closely, it was inferred that data grouped around the first (lower) peak in the histogram corresponds to Group 1 exposure of Composite B system samples that were subjected to the coverage study (varying amounts of applied epoxy) to water immersion at 30°C through 60°C. Interesting fact, though, is that this high degradation in beam specimen ultimate strength for Composite B system was not observed in Groups 2 and 3.



Figure 67. Histogram and density distribution of test data

To show that data are not normally distributed, a Q-Q plot was created (Figure 68). A Q-Q plot is a probability plot that provides a method of comparing two probability distributions by graphical means. That is accomplished by plotting the distribution quantiles against each other. In order to check if the acquired data follows the normal distribution, its quantiles were plotted against the theoretical normal distribution quantiles. In the case where experimental data follows the normal distribution, the points on Q-Q plot lie on the reference line. Based on Figure 68, only one part of the data is normally distributed.

Since a significant discrepancy between Group 1 and Group 2 test results for Composite B FRP system was observed, the two sets of data were separated into two subgroups (one contained only data from Group 1 (Data subset 2) for exposure to water immersion from 30°C through 60°C, and the other group was created from the remaining data (Data subset 1). Then,

the same probability distribution analysis was performed on both data sets. It can be observed from the histogram and probability density distribution for Data subset 1 that it appears to follow the normal distribution (Figure 69).







Figure 69. Histogram and density distribution of test data



Figure 70. Q-Q plot for test data

Furthermore, the Q-Q plot for the data set, excluding specified data points from Group 1 confirms that the data distribution is very close to theoretical normal distribution (Figure 70).

To determine the most appropriate statistical model fit for the presented data, one-sample Kolmogorov-Smirnov and Anderson-Darling statistical tests were utilized. The data population at hand was tested against 50 known statistical models to find the best fit.

One-sample Kolmogorov-Smirnov compares the empirical cumulative distribution function to the theoretical cumulative distribution function (shifted log-logistic and normal in this case). The statistic is computed from the largest absolute difference between the two. The null-hypothesis is that the population sample is drawn from the reference theoretical distribution. The null-hypothesis cannot be rejected if the test statistic is lower than the reference value for chosen significance level α . Even though Kolmogorov-Smirnov is a widely used test, it was shown that the Anderson-Darling test may be a more powerful tool in estimating to goodness of statistical fit (Stephens 1974).

The Anderson-Darling test follows essentially the same procedure as the Kolmogorov-Smirnov test; however, in calculating the statistic, it gives more weight to tails of a distribution. Null-hypothesis and rejection criteria are similar to Kolmogorov-Smirnov.

Based on results from statistical tests on 50 theoretical distributions, it was found that the given population is best represented by a shifted log-logistic distribution (also known as three-parameter log-logistic). The log-logistic model has a very similar distribution as the lognormal
statistical model. The three-parameter log-logistic probability density function is defined as:

$$f(x) = \frac{\frac{\alpha}{\beta} \left(\frac{x-\gamma}{\beta}\right)^{\alpha-1}}{\left(1 + \left(\frac{x-\gamma}{\beta}\right)^{\alpha}\right)^2}$$
Equation 19

where x is a random variable, α is a continuous shape parameter, β is a continuous scale parameter, and γ is a continuous location parameter.

The cumulative distribution function for the three-parameter log-logistic model is:

$$F(x) = \frac{1}{1 + \left(\frac{\beta}{x - \gamma}\right)^{\alpha}}$$
Equation 20

The values of the parameters in Equation 20 that were used to fit the data are presented in Table 32. Normal distribution parameters are included in Table 32 for comparison purposes. It should be noted that μ is mean, and σ is standard deviation of the population.

Shifted log-logistic distribution		Normal distribution	
		para	meters
α 109,410,000		μ	0.879
β 67,993,000		σ	0.109
γ -67,993,000			

Table 32. Statistical models parameters

Kolmogorov-Smirnov and Anderson-Darling tests results for shifted log-logistic and normal distributions are presented Table 33. By comparing the results it may be noted that the shifted log-logistic model provides a somewhat better estimate of the actual distribution of data.

Table 33. Statistical test results

	Shifted log-logistic		Normal	
	Kolmogorov- Anderson-		Kolmogorov-	Anderson-
	Smirnov	Darling	Smirnov	Darling
Sample size	345	345	345	345
Statistic	0.0375	0.498	0.0552	0.8678
Critical value (CV) for Significance level of 0.05	0.0765	2.501	0.0765	2.502
P-value	0.75	N/A	0.281	N/A
Rejection criterion (is Statistic>CV?)	No	No	No	No

Shifted log-logistic data fit along with the corresponding normal distribution is presented in Figure 71. Probability function values on y-axis were both scaled to the match the total area under the function of 1.0. From the figure it is apparent that the models yield a very similar estimate of the data distribution. Cumulative distribution functions for each model show an excellent agreement too (Figure 71). Normal distribution is deemed an acceptable representation of the data spread based on the observations. Furthermore, normal distribution is incorporated in LRFD design specifications and is widely accepted in the civil engineering scientific community. Therefore, for the purpose of this study, normal distribution will be assumed for each set of data.



Figure 71. Statistical fit models for Data subset 1: probability density function (left) and cumulative distribution function (right)

Data subset 1 was further analyzed to compare effects of the lowest and the highest temperature exposure condition (30°C and 60°C) on the bond capacity. Data was, therefore, divided into two series: one containing data for exposure to 30°C only, and the other one composed of data related to specimens exposed at 60°C. Histograms and probability density functions for each data group are presented in Figure 72 and Figure 73. For the comparison purposes, both probability distribution functions are presented in the same plot in Figure 74. On average, specimens exposed to 60°C experienced a higher degradation in bond capacity (Table 34). This is most likely due to change in epoxy degradation mechanisms due to temperatures higher than their glass transition temperature (Tg). The spread of data for 30°C samples is, on the other hand, wider and skewed towards the upper bound of test values. This may be due to the fact that change in bond moisture content occurs more gradually than in the 60°C samples where the rate of water diffusion into the FRP-concrete system is accelerated due to higher temperature. Samples that are tested early in the exposure cycle generally achieve higher capacities too.



Figure 72. Histogram and probability density estimate for samples exposed to 30°C



Figure 73. Histogram and probability density estimate for samples exposed to 60°C



Figure 74. Comparison of probability density estimates for 30°C and 60°C of Data subset 1Table 34. Normal distribution parameters for 30°C and 60°C of Data subset 1TemperatureMeanStandard deviation30°C0.940.1160°C0.870.08

The subset of data corresponding to Group 1 exposure to water immersion at 30°C through 60°C was subjected to the similar analysis as Data subset 1 to determine the appropriateness of normal distribution fit. Histogram and probability density function was plotted in Figure 75. To support the assumption Q-Q plot in Figure 76 was created to show that the majority of data follows theoretical normal distribution.

Based on the Kolmogorov-Smirnov and Anderson-Darling statistical tests it was concluded that normal distribution with the parameters of σ =0.123 and μ =0.567 is a good fit for the data set. Statistical model fit is graphically represented in Figure 77. Normal distribution fit for both data subsets is presented in Figure 78. It should be regarded that the two distributions have similar variances.

To confirm the assumption of equal variances, an F-test and two-tailed Levene's test of equality of variances for a significance level of α =0.05 were performed on the data subsets. The F-test is the simplest statistical test of equality of variances. The F-test statistic is obtained by dividing variances of the two groups of data that are being compared. From the test statistic a P-value is calculated. Normally, null-hypothesis (that the variance between two populations is



Figure 75. Histogram and probability density estimate for Data subset 2



Figure 76. Q-Q plot for Data subset 2

	Normal		
	Kolmogorov- Anderson-		
	Smirnov	Darling	
Sample size	82	82	
Statistic	0.0552	1.9286	
Critical value (CV)			
for Significance	0.1319	2.5018	
level of 0.05			
P-value	0.11	N/A	
Rejection criterion (is Statistic>CV?)	No	No	

Table 35. Statistical tests results for Group 1 data



Figure 77. Normal distribution fit for Data subset 2



Figure 78. Comparison of normal distribution models for two data subsets (wet-layup without putty)

equal) is rejected if the P-value is less than 0.05. The F-test is very sensitive to violations in the normality assumption, and therefore, it may not be the best statistical tool to test equality of variances.

Levene's test is a homogeneity-of-variance test that is not as sensitive to departures from assumption of normality of data. Levene's test compares the absolute departures of each data point from the group's mean to calculate the test's statistic. Levene's test null-hypothesis (that variances across the groups are equal) is rejected when the P-value is less than 0.05.

Equality of variance test results are presented in Table 36. From the presented data, the null-hypothesis that the variances for the two populations are equal cannot be rejected. Therefore, for the purpose of further analysis it will be assumed that Data subset 1 and Data subset 2 come from populations with equal variances.

	Data subset 1	Data subset 2	
Mean	0.879 0.567		
Variance	0.0119 0.0		
No. of samples	345	82	
Degrees of freedom	81 344		
Levene's test P-value	0.872		
F-test P-value	0.137		
Reject criterion (P-value<0.05)	No		

Table 36. Levene's and F-test results

To show that the two subsets, however, do not come from the same population, and consequently cannot be analyzed as a single set of data, one-way ANOVA analysis was applied to the data subsets.

Analysis of Variance (ANOVA) is a statistical test primarily used to compare differences in means of two or more groups of data. That is accomplished by comparing the variation of data within the groups to variation of data between the groups. One-way ANOVA can be formulated as follows:

$$x_{ij} = \mu_i + \epsilon_{ij}$$
 Equation 21

where *i* and *j* represent group and the individual observation respectively, *x* is a specific data point, ϵ_{ij} is unexplained variation (error) within the group *i* and observation *j*, and μ_i is the mean of group *i*. In ANOVA, assumption is made that variances of all groups are equal.

The null hypothesis in ANOVA is that population means are equal. The alternative hypothesis is that at least one mean is different from the rest. The hypothesis can be rejected if a significant P-value limit is not reached, which is usually 0.05. The P-value is calculated from the ANOVA test statistic, F-ratio. The F-ratio is defined as:

$$F - ratio = \frac{Mean of Between Groups SS}{Mean of Within Groups SS}$$
Equation 22

where "SS" stands for "Sum of Squares".

Sum of squares between the groups is calculated as:

Between Groups
$$SS = SSB = \sum_{i=1}^{k} n_i (\bar{x}_i - \bar{x})^2$$
 Equation 23

where k is the total number of groups, n_i is the total number of data points in group i, $\overline{x_i}$ is mean of group i, and \overline{x} is mean of the overall population.

Sum of squares within the groups is determined as follows:

Within Groups
$$SS = SSW = Total SS - SSB$$

= $\sum_{i=1}^{n} (x_i - \bar{x})^2 - SSB$ Equation 24

where x_i is *i*-th data point in a the entire population of size n, \bar{x} is mean of the overall population.

Then, mean of sum of squares between the groups is defined as:

$$Mean of SSB = MSSB = \frac{SSB}{df_b} = \frac{SSB}{k-1}$$
 Equation 25

where df_b is number of degrees of freedom between the groups, and k is the total number of groups.

Similarly, mean of sum of squares within the groups is calculated as:

Mean of SSW = *MSSW* =
$$\frac{SSW}{df_w} = \frac{SSW}{n-1}$$
 Equation 26

where df_w is number of degrees of freedom within the groups and n is the size of the population.

Finally, the F-ratio and corresponding P-value may be calculated. Based on the results from ANOVA presented in

Table 37 it can be concluded with 95% confidence (significance level of 0.05) that Data subset 1 and Data subset 2 do not have equal means. In other words, the two subsets differ, and therefore they will not be grouped together for the purpose of further analyses.

	Data subset 1	Data subset 2		
No. of samples	345	82		
Sum	303.26	46.511		
Mean	0.879	0.567		
Variance	0.0119	0.0152		
	Between groups	Within groups		
Sum of squares	6.44	5.32		
Degrees of freedom	1	425		
Mean square	6.44	0.0125		
F-ratio	514.45			
P-value	0.000			
Rejection criterion (P- value<0.05)	Yes			

Table 37. ANOVA results

5.3.4 CFRP Wet-layup With Putty (Composite C)

Histogram and probability density function for an entire population of data are presented in Figure 79. Again, data is observed to be bimodally distributed, and when looked at as a whole it deviates from theoretical normal distribution (Figure 80.).



Figure 79. Histogram and probability density estimate for wet-layup with putty



Figure 80. Q-Q plot for wet-layup with putty

After looking at the data more closely it was concluded that data grouped around the lower peak (left) on the probability density function in Figure 79 generally corresponds to exposure equal to or longer than 60 days. Furthermore, it was noted that the following exposure conditions did not have as detrimental effect on the bond capacity as the other conditioning protocols:

- Group 1 exposure to water immersion at 20°C
- Group 1 exposure to wet-dry cycles at 40°C
- Group 1 exposure to wet-dry cycles at 60°C
- Group 1 exposure to RH=75% at 20°C
- Group 1 exposure to RH=100% at 20°C

One thing in common about these conditions is that not one includes a combined effect of high temperature (\geq 50°C) and maximized exposure to moisture (RH=100% or water immersion), unlike the other exposure conditions that wet-layup with putty specimens were exposed to. Therefore, data was divided into two subsets: one containing all data that was exposed for periods equal to or longer than 60 days, except for the aforementioned conditions (Data subset 1); and the other subset including the remainder of data (Data subset 2).

Figure 81 presents histogram and probability density function for Data subset 1. It is deemed that normal distribution is an appropriate representation of the population, which is supported by Q-Q plot in Figure 82.



Figure 81. Histogram and probability density estimate for Data subset 1



Figure 82. Q-Q plot for Data subset 1

Data subset 1 was subjected to Kolmogorov-Smirnov and Anderson-Darling statistical tests with a significance level α =0.05 to determine the suitability of theoretical normal distribution fit with mean μ =0.633 and standard deviation σ =0.127. Based on the test statistics it can be concluded that normal distribution is an appropriate fit for the data subset. Probability density function for normal statistical model fit for Data subset 1 is graphically represented in Figure 83.

	Normal		
	Kolmogorov-	Anderson-Darling	
	Smirnov		
Sample size	101	101	
Statistic	0.0783	0.5938	
Critical value (CV)			
for Significance	0.1511	2.5018	
level of 0.05			
P-value	0.539	N/A	
Rejection criterion (is Statistic>CV?)	No	No	

Table 38. Statistical tests results



Figure 83. Normal distribution fit for Data subset 1

Population distribution for Data subset 2 is graphically presented in Figure 84 and Figure 85. Again, it can be inferred from probability density function and Q-Q plot that data is distributed normally. The observed skew of data towards the higher bound shows that wet-layup with putty is resistant to exposures shorter than 60 days, or exposures that do not combine effects of high temperature and water immersion/100% relative humidity. A relatively low standard deviation of σ =0.086 further backs up this assumption.



Figure 84. Histogram and probability density estimate for Data subset 2



Figure 85. Q-Q plot for Data subset 2

Theoretical normal distribution with parameters μ =0.966 and σ =0.086 was tested against the empirical probability distribution function for the population to determine the goodness of statistical fit. Once again, Kolmogorov-Smirnov and Anderson Darling statistical tests with significance level of α =0.05 were utilized. Test results confirming that normal distribution is a satisfactory fit for data is shown in Table 39. Adopted statistical model is graphically presented in Figure 86.

	Normal		
	Kolmogorov- Smirnov	Anderson-Darling	
Sample size	99	99	
Statistic	0.0798	0.6679	
Critical value (CV) for Significance level of 0.05	0.1347	2.502	
P-value	0.528	N/A	
Rejection criterion (is Statistic>CV?)	No	No	

Table 39. Statistical tests results



Figure 86. Normal distribution fit for Data subset 2

To determine the difference between two subsets, statistical tests were performed. For the sake of comparison, normal distribution fits for data subsets are plotted together in Figure 87.

Levene's test and F-test yielded P-values lower than 0.05; therefore, it was concluded that variances for the two subsets are not equal. Due to this fact, ANOVA could not be utilized to compare the two populations. Welch's t-test, which allows for populations with different variances, had to be utilized.

Welch's t-test is an alternative to Student's t-test when variances are not equal. Welch's t-test determines whether the means of two groups are statistically different. This is determined by comparing difference in group means to variability of groups. However, since the variances of two groups are not equal, a non-pooled variance estimate is used (variance is calculated for each group separately). Commonly acceptable practice is to conclude that the groups are statistically different if obtained P-value is lower than 0.05.

The test returned a p-value of 0.000 for Data subset 1 and Data subset 2; the null hypothesis that means are equal between the two subsets was rejected. Therefore, two data subsets were looked at separately in further analyses.



Figure 87. Comparison of normal distribution models for two data subsets (wet-layup with putty)

5.3.5 CFRP Laminates

From the histogram and probability density function in Figure 88, it may be inferred that CFRP laminate data is distributed trimodally.



Figure 88. Histogram and probability density function for CFRP laminates

The reason for such distribution of data lays in fact that unexpected failure mode occurred in all CFPR laminate specimens. Namely, as early as 28 days of exposure in 60°C water and between 2 and 6 months in 30°C water, CFRP laminate decohesion or its debonding from epoxy occurred. It should be noted that data grouped around the highest peak in probability

density function corresponds to specimens exposed for short amounts of time (less than 60 days) or conditions with lower temperatures (30°C). The peak corresponding to specimens with the lowest bond strength indices relates to CFRP failure or adhesive failure between the laminate and epoxy.

Therefore, most data points in the plot above do not pertain to FRP-concrete bond properties, but they rather relate to CFRP material properties and/or its adhesion properties to epoxy. Therefore, further analysis of the data will not be conducted in this study as the gathered data points do not reflect the long-term behavior of the FRP-concrete bond.

5.3.6 Influence of Failure Mode on Bond Strength Index

For FDOT data, after each test, failure mode was recorded as a percent of surface that failed adhesively. Percentages were expressed in increments of 5% based on visual observation. Then, average for each exposure time was calculated. Final results for each composite system are presented in Figure 89. It should be noted that 0% adhesive failure would correspond to a completely cohesive failure and 100% would correspond to a fully adhesive failure (Figure 90, Figure 91 and Figure 92).

Adhesive failure characteristics were expected to increase as the intensity and duration of exposure increased. Such was the case in most adhesive systems except for Composite D04. Concrete used with this system had a compressive strength of approximately 4000 psi. The reason for such behavior may be that high porosity of 4,000 psi concrete allowed for deeper penetration of liquid epoxy, which was not the case in 10,000 psi concrete. Deeper penetration of epoxy minimized influence of reduced epoxy stiffness on stress transfer mechanism, which resulted in achievement of highly cohesive failure modes.

Epoxy transfers shear stresses from FRP to concrete. Generally, as the contact area increases, higher forces can be distributed into the concrete. Contact area is artificially increased by surface treatment techniques such as sandblasting, shotblasting, water-jetting, etc. All of these techniques damage concrete surface to create irregularities, and consequently, increase contact area. However, due to the heterogeneous nature of concrete (the presence of different sizes of aggregate particles, air voids, etc.) there is an intrinsic roughness associated with damaged concrete surface. As the treatment is applied, voids and crevices near the surface open up and become available for epoxy penetration. Generally, as concrete strength increases, porosity



Figure 89. Failure mode of concrete specimens



Figure 89-continued. Failure mode of concrete specimens



Figure 90. Cohesive failure mode (0% adhesive)



Figure 91. Adhesive failure mode (100% adhesive)



Figure 92. Partially adhesive failure mode (70% adhesive)

of concrete decays exponentially (Lian et al., 2011). Thus after the surface preparation, lower strength concrete will provide more area available for bonding (and frictional forces distribution) than high strength concrete. This, in turn, may influence the failure mode.

Based on the evidence from performed tests, failure mode appeared to be governed by surface preparation (which is a function of application technique and concrete porosity) rather than the concrete strength. In Group 3, all composite systems that were adhered to concrete beams cast from 10,000 psi concrete achieved predominantly (greater than 50%) adhesive failure mode, even in control samples. In addition to smaller amounts of epoxy used in specimen preparation, this may explain low bond strength index values from Group 1 NCHRP data where, due to conditioning, failure mode shifted from cohesive (0% adhesive) to completely adhesive after exposure. This suggests that the load required to produce adhesive failure; and therefore a more conservative bond strength index was produced. To support the hypothesis that change in failure mode corresponds to change in specimen capacity, failure modes and corresponding loads were compared in control samples from different groups for Composite B (Table 40). A shift in specimen ultimate capacity due to change in failure mode is apparent. Figure 93 explains low bond strength indices for Group 1 exposure to immersion at 30°C through 60°C by presenting load capacities of control and exposed specimens.

The purpose of three-point bend testing is to determine loss in adhesion properties of epoxy due to accelerated conditioning. This is accomplished best if predominantly adhesive failure mode is forced in both control and exposed sample so that loss in bonding properties is directly assessed. Therefore, for this study desirable failure mode in three-point bending is adhesive. Cohesive failure in control samples produces a more conservative bond strength index.

Test group	f'c (psi)	Average failure load	Adhesive failure (%)
Group 1	≈10,000	4476	0
Group 2	≈10,000	3469	90
Group 3	≈10,000	3349	77.6

Table 40. Comparison of failure loads and failure modes for control specimens



Figure 93. Comparison of control to conditioned (60 days immersion in water at 60°C) specimen load capacity for Composite B

5.3.7 Environmental Reduction Factor and Bond Durability Factor

Current ACI design guidelines for externally bonded FRP are based on limit-states design principles. Procedures for both serviceability limit states (such as deflections and cracking), and ultimate limit states (such as failure, fatigue, stress rupture) are defined. The FRP reinforcing system shall be designed to conform with ACI 318 strength and serviceability provisions, as per ACI 440.2R-08. However, additional reduction factors, defined in ACI 440.2R-08 design guidelines, must be applied to account for uncertainties relevant to FRP systems.

Environmental reduction factors (C_E) are recommended by ACI 440.2R-08 to account for influence of various exposure conditions on FRP systems (Table 41). The factor is less than one and is applied to the ultimate design tensile strength of FRP material to reduce the effective tensile strength used in design. Modulus of elasticity, however, is not reduced.

The source of these environmental reduction factors, however, is not clear. Based on anecdotal evidence, they were selected by Committee 440 based on the results from available durability studies on FRP materials and did not consider the Mode II adhesive bond to concrete. Ultimate useable tensile strain in bonded FRP reinforcement is limited to control debonding

Exposure conditions	Fiber Type	Environmental	
Exposure conditions	Fiber Type	reduction factor CE	
	Carbon	0.95	
Interior exposure	Glass	0.75	
	Aramid	0.85	
	Carbon	0.85	
Exterior exposure	Glass	0.65	
	Aramid	0.75	
A garagaina anvironment (abamical	Carbon	0.85	
Aggressive environment (chemical	Glass	0.50	
plants and wastewater treatment plants)	Aramid	0.70	

Table 41. Environmental reduction factors as per ACI 440.2R-08

when designing FRP reinforcement for flexure. C_E further limits this ultimate tensile strain to account for loss in strength due to weathering. Ultimately, this factor should have some rational basis either in a durability model or experimental evidence, or both.

As an intermediate step, the data from the present research was used to develop the bond durability factor (BDF). This factor provides experimental characterization of the durability of bonded FRP composite reinforcement based on the accelerated conditioning used in the small beam tests. One of the goals of bond durability factor (BDF) is to characterize degradation in bond properties due to exposure to different aggressive environments, and based on that provide an estimate of nominal bond capacity. Eventually, the intent is that this factor be used to provide rationale for the environmental reduction factor (CE) in design.

To determine an appropriate bond durability factor based on the available database, a method was developed that accounts for different exposure conditions, varying FRP systems, and laboratory variables. To form a systematic approach that accounts for each exposure condition, an analogy to adhesive anchors was established. Namely, adhesive anchors experience the same variability in possible failure modes as FRP reinforced systems. Cheok and Phan (1998) in the NISTIR report 6096 identified the following failure modes:

- Steel failure
- Concrete cone failure
- Bursting failure
- Splitting failure
- Pull-out failure
- Bond failure between anchor and bonding agent

ACI 318-11 approach to adhesive anchor design requires that a series of tests be conducted using the particular adhesive and anchor system. Nominal anchor strength is then based on the 5 percent fractile, which is the average test value reduced by a factor to account for the number of tests conducted and the variability of the data. This value is also defined as the characteristic strength (ACI 355.4-11). This approach results in an actual strength that is statistically likely to exceed the design strength (90 percent confidence that there is 95 percent probability of the actual strength exceeding the nominal strength). Since the statistical probability of failure is acceptable in the life-safety context of ACI 318-11, it is reasonable to adapt this approach for use in developing the characteristic bond durability factor (BDF). Furthermore, the similarity in application, materials, and failure modes between adhesive anchors and bonded FRP composites makes this approach uniquely suitable.

As such the approach given in ACI 355.4-11 for determining characteristic anchor strength based on testing has been adapted for determining the characteristic BDF as follows:

$$BDF_k = \overline{BSI}_{test,x} \cdot (1 - K \cdot v_{test,x})$$
 Equation 27

where:

K – tolerance factor corresponding to a 5% probability of non-exceedance with a confidence of 90%, derived from a noncentral t-distribution for which the population standard deviation is unknown. Values for specific samples sizes are provided in Appendix F, and are graphically represented in Figure 94, as per Hahn and Meeker (1991).

BDF_k - characteristic BDF (5% fractile), lb/lb

BSItest,x - mean bond strength index for test series x, lb/lb

 $v_{test,x}$ - coefficient of variation of the population sample corresponding to test series x, % This approach does not dictate a minimum number of replicate test specimens, but rather uses a factor that accounts for the increasing uncertainty with decreasing numbers of specimens.

All data for each exposure condition for exposure times of 60 days or more were combined for this analysis. This approach is based on the general trends observed in NCHRP data (Figure 95). Furthermore, all FDOT data (7, 14, and 60 days) were combined for wet-layup without putty. These observations were confirmed by performing ANOVA analysis with



Figure 94. Tolerance factor, K, vs. number of tests, n

significance level of α =0.05 (Table 42). For each exposure condition, bond strength indices were grouped in respect to time to test the hypothesis that loss in properties for NCHRP data stabilized in 60 days, and after 7 days in FDOT data. Null-hypothesis that means between different groups of data are equal can be rejected if obtained P-value is less than 0.05. Exception was made in wet-layup with putty that was based on observations made on FDOT data.



Figure 95. Illustration of bond strength index degradation with respect to time from NCHRP study (Deng, 2008)



Figure 96. Illustration of bond strength index degradation with respect to time from FDOT study

Characteristic BDF is associated with a specific accelerated conditioning protocol. BDF, on the other hand, is a property that relates to a range of different exposure conditions, and characterizes an overall performance of FRP-concrete bond.

To establish a bond durability factor for wet-layup without putty, analysis of data was performed based on the characteristic values for each exposure condition. As explained previously, data for each conditioning protocol was grouped according to assumption that loss in bond properties plateaued at 60 days for NCHRP data and at 7 days for FDOT data. All qualifying bond strength indices for a specific exposure condition were first incorporated into one characteristic conservative BDF_k (which included all qualifying data). In addition, a so-called overly conservative characteristic BDF_k was calculated. Overly conservative characteristic BDF_k was obtained from the longest exposure samples only. For example, if samples were subjected to a specific conditioning protocol for 7, 14, 60, and 120 days, only the bond strength indices obtained for 120 days of exposure were included in the calculation. The approached is termed overly conservative because the K value rapidly increases as the number of samples decreases. Terms "conservative" and "overly conservative" strictly and only relate to corresponding values of K: expected lower K-values are termed "conservative"; expected higher K values are termed "overly conservative". All data for wet-layup without putty,

Exposure condition	P-value	Reject null-hypothesis?
Group 1 Water 20C A	0.064	No
Group 1 75% RH 20C A	0.0001	Yes
Group 1 100% RH 20C A	0.0005	Yes
Group 1 100% RH Fog Room	N/A	N/A
20C A		
Group 1 Water Fog Room	0.629	No
20C A		
Group 1 Wet Dry 40C A	0.478	No
Group 1 Wet Dry 60C A	0.901	No
Group 1 Real Time Roof A	0.019 (12 mo + = 0.397)	No
Group 1 Water 60C D	N/A	N/A
Group 2 Water 30C A	N/A	N/A
Group 2 Water 40C A	N/A	N/A
Group 2 Water 50C A	N/A	N/A
Group 2 Water 60C A	N/A	N/A
Group 2 UV 50C A	N/A	N/A
Group 2 Alkaline 50C A	N/A	N/A
Group 2 Chloride 50C A	N/A	N/A
Group 2 Real Time Bridge A	0.564	No
Group 2 Water 30C D	0.345	No
Group 2 Water 40C D	0.484	No
Group 2 Water 50C D	0.187	No
Group 2 Water 60C D	0.394	No
Group 2 Water 30C E	0.556	No
Group 2 Water 40C E	0.063	No
Group 2 Water 50C E	0.966	No
Group 2 Water 60C E	0.085	No
Group 3 Water 30C A	0.973	No
Group 3 Water 60C A	0.844	No
Group 3 Water 30C D04	0.781	No
Group 3 Water 60C D04	0.854	No
Group 3 Water 30C F	0.461	No
Group 3 Water 60C F	0.582	No
Group 3 Water 30C D10	0.195	No
Group 3 Water 60C D10	0.965	No
Group 3 100% RH 60C A	0.520	No
Group 3 100% RH 60C D04	0.457	No
Group 3 100% RH 60C F	0.422	No
Group 3 100% RH 60C D10	0.0035	Yes

Table 42. Results of ANOVA analysis



Figure 97. Characteristic values for wet-layup without putty excluding Group 1 exposure to water immersion to 30°C through 60°C

1. Moisture conditioning at 20°C
Group 1 water immersion for Composite B
Group 1 RH=75% for Composite B
Group 1 RH=100% for Composite B
Group 1 Fog room RH=100% for Composite B
Group 1 Fog room water immersion
2. Moisture conditioning at 30°C
Group 2 water Immersion for Composite B
Group 2 water immersion for Composite D
Group 2 water immersion for Composite D-bad
Group 3 water immersion for Composite A
Group 3 water immersion for Composite B
Group 3 water immersion for Composite D
Group 3 water immersion for Composite D
3. Moisture conditioning at 40°C
Group 1 wet-dry cycling for Composite B
Group 2 water immersion for Composite B
Group 2 water immersion for Composite D
Group 2 water immersion for Composite D-bad
4. Moisture conditioning at 50°C
Group 2 water immersion for Composite B
Group 2 water immersion for Composite D
Group 2 water immersion for Composite D-bad
5. Moisture conditioning at 60°C
Group 1 wet-dry cycling for Composite B
Group 2 water immersion for Composite B
Group 2 water immersion for Composite D
Group 2 water immersion for Composite D-bad
Group 3 water immersion for Composite A
Group 3 water immersion for Composite B
Group 3 water immersion for Composite D
Group 3 RH=100% for Composite A
Group 3 RH=100% for Composite B
Group 3 RH=100% for Composite D
Group 3 RH=100% for Composite D
6. Chemical attack and UV at 50°C
Group 2 UV-water immersion cycling for Composite B
Group 2 alkaline water immersion for Composite B
Group 2 chloride water immersion for Composite B
7. Real-time exposure
Wyoming roof
Florida bridge

Table 43. Conditioning protocol subgroups for wet-layup without putty

excluding Group 1 exposure to water immersion to 30°C through 60°C, was included in the analysis. Group 1 exposure to water immersion to 30°C through 60°C (Data subset 2) was excluded from the analysis due to the previously described anomaly that caused low capacities in the test specimens. The results of the analysis are presented in a form of bar chart in Figure 97. Conditioning protocols were then separated into subgroups as per Table 43.

Data for each group is presented in whisker plots in Figure 99 and Figure 100. Meanings of whisker plot components are graphically explained in Figure 98.



Figure 99. Whisker plots for each subgroup for conservative characteristic values



Figure 100. Whisker plots for each subgroup for overly conservative characteristic values

Plots show that the spread of data is quite large, which was expected based on the method that was used. However, in Table 44 conservative case, mean values for all groups are relatively close, if not considering moisture conditioning at 20°C and real-time exposure. For moisture conditioning at 20°C, relatively higher values of bond strength index were expected, due to lower conditioning temperature. On the other hand, in moisture conditioning at 50°C subgroup, a low mean for characteristic BDF is probably due to the characteristic BDF for exposure of Composite B to water immersion which had a quite significant coefficient of variation (0.130) which, when coupled by a K factor of 5.311 (for 3 samples in the group), resulted in a very low characteristic value of 0.26. If this characteristic value were to be excluded from the analysis mean of conservative values for moisture conditioning at 50°C, the characteristic BDF would be 0.64 which is on par with the other 5 exposure conditions.

There is no significant difference in average characteristic values between moisture conditioning for different temperatures. This signifies that wet-layup without putty was primarily sensitive to moisture. If it is assumed that moisture equilibrium is reached after 60 days of constant exposure, and therefore, any additional loss in bond properties after that threshold may be accredited to increasing temperatures. This trend, however, is not inherent to wet-layup without putty.

Subgroup	Mean for conservative characteristic BDF _k	Standard deviation for conservative characteristic BDF _k	Mean for overly conservative characteristic BDF _k	Standard deviation for overly conservative characteristic BDF _k
Moisture conditioning at 50°C	0.72	0.06	0.64	0.20
Moisture conditioning at 30°C	0.67	0.22	0.56	0.32
Moisture conditioning at 40°C	0.68	0.09	0.58	0.25
Moisture conditioning at 50°C	0.52	0.22	0.35	0.28
Moisture conditioning at 60°C	0.66	0.15	0.49	0.20
Chemical attack and UV at 50°C	0.68	0.14	0.68	0.14
Real-time exposure	0.57	0.18	0.51	0.20

Table 44. Normal distribution parameters for conservative and overly conservative characteristic BDF_k

Real-time exposure characteristic values are on a conservative side. However, it should be noted that the harsh conditions that were picked for these experiments would not be experienced by FRP-concrete bond in most applications.

Means for overly conservative characteristic values show similar trends. Two conditions have the highest characteristic values: moisture conditioning at 50°C; chemical attack and UV at 50° C. In other moisture conditioning subgroups characteristic values decrease as the temperature increases. Real-time exposure characteristic value is again relatively low, but it is comparable to characteristic values for other subgroups.

To determine a bond durability factor for wet-layup without putty, the mean for all conservative, and overly conservative characteristic values including the real time exposure conditions is calculated. It was determined that mean for the conservative case is 0.66, and for overly conservative it takes the value of 0.54. If mean of conservative characteristic values is

regarded an upper bound for bond durability index, and mean of overly conservative characteristic values its lower bound, it is deemed appropriate to pick the value of 0.60 (average of the two) as a representative bond durability index.

To justify the choice of bond durability factor, a cumulative distribution function for normal distribution model for wet-layup without putty excluding Group 1 exposure to water immersion to 30°C through 60°C is plotted in Figure 101. From the model, it can be determined that the probability that the random bond strength index will be lower than the bond durability factor of 0.60 is 0.53%. More research is required to determine loss in bond capacity in structural scale members, and relate it to bond durability index. The recommended probabilities of not exceeding for bond durability factor of 0.60 are deemed appropriate. If bond durability factor were to be used in design, the choice of an appropriate probability of not exceeding it is up to the designer.



Figure 101. Fitted cumulative distribution function for wet-layup without putty excluding Group 1 exposure to water immersion to 30°C through 60°C

Characteristic value analysis was performed on wet-layup with putty test population to determine an appropriate bond durability factor. Only Data subset 1 was subjected to the analysis. Therefore, conditioning protocols identified as being non-detrimental to the FRP-concrete bond were not taken into account. Conservative and overly conservative characteristic values are presented in Figure 102.



Figure 102. Characteristic values for wet-layup with putty

To determine effects of different exposure conditions, critical values, for the purpose of further analysis, were separated into 6 subgroups. Again, a wide spread of characteristic values was obtained in most subgroups as presented in Whisker plots (Figure 103 and Figure 104). It should be noted that characteristic values for Group 2 water immersion for Composite C were excluded from the analysis because the samples for the condition yielded a negative conservative and overly conservative characteristic value of -0.44, due to a large coefficient of variation (0.36) of the population.

1.	Moisture conditioning at 30°C				
•	Group 1 water Immersion for Composite C				
•	Group 2 water immersion for Composite C				
•	Group 3 water immersion for Composite C				
2.	Moisture conditioning at 40°C				
•	Group 1 water immersion for Composite C				
•	Group 2 water immersion for Composite C				
3.	Moisture conditioning at 50°C				
•	Group 1 water immersion for Composite C				
•	Group 2 water immersion for Composite C				
4.	Moisture conditioning at 60°C				
•	Group 1 water immersion for Composite C				
•	Group 2 water immersion for Composite C				
•	Group 3 water immersion for Composite C				
•	Group 3 RH=100% for Composite C				
5.	Chemical attack and UV at 50°C				
•	Group 2 UV-water immersion cycling for Composite C				
•	Group 2 alkaline water immersion for Composite C				
•	Group 2 chloride water immersion for Composite C				
6.	Real-time exposure				
•	Wyoming roof				
•	Florida bridge				

Table 45. Conditioning protocol subgroups for wet-layup with putty

Both Whisker plots and means of characteristic values for subgroups (Table 46) show that wet-layup systems are sensitive to increasing exposure temperatures. Interesting fact is that moisture conditioning at 30°C (temperature likely to be experienced in the field applications), and real-time exposure conditions mean characteristic values are on par.

Bond durability factor is calculated based on the average of conservative and overly conservative characteristic values across all exposure conditions. Average for conservative case is 0.43, and for overly conservative case it is 0.42. Therefore, average of two is 0.425. However, the bond durability index was rounded to 0.40.



Figure 103. Whisker plots for each subgroup for conservative characteristic values





Bond durability index for wet-layup with putty is compared against normal cumulative distribution function fit for Data subset 1 of wet-layup with putty in Figure 105. It was found that probability of not exceeding the bond durability factor is 3.32%.

Subgroup	Mean for conservative characteristic BDF _k	Standard deviation for conservative characteristic BDF _k	Mean for overly conservative characteristic BDF _k	Standard deviation for overly conservative characteristic BDF _k
Moisture conditioning at 30°C	00.58	0.02	0.53	0.10
Moisture conditioning at 40°C	0.42	N/A	0.48	N/A
Moisture conditioning at 50°C	0.36	0.24	0.33	0.21
Moisture conditioning at 60°C	0.35	0.09	0.35	0.09
Chemical attack and UV at 50°C	0.38	0.18	0.38	0.18
Real-time exposure	0.54	0.025	0.51	0.025

Table 46. Normal distribution parameters for conservative and overly conservative characteristic values



Figure 105. Fitted cumulative distribution function for Data subset 1 for wet-layup with putty
5.4 Summary and Conclusions

Small beam specimens were used to study FRP-concrete bond performance when subjected to accelerated conditioning environments (immersion in water and exposure to high humidity at elevated temperatures). Bonded CFRP reinforcement was applied to small concrete beams, which were then conditioned and tested to failure under three-point bending. The bond strength index was determined by dividing the average conditioned strength by the average control strength. The characteristics of the bond failure were also noted, including the relative amount of adhesive or cohesive failure surfaces that were present.

Small beam specimens were exposed to the following accelerated conditioning environments, for 1, 2, and 8 weeks:

- Immersion to water at 30°C
- Immersion to water at 60°C
- Exposure to RH=100% at 60°C

Analysis of load-displacement data revealed difference in behavior between control and exposed samples. Furthermore, analysis of bond degradation over time showed that composite systems A, B, and D exhibited similar behaviors, while Composite C and Composite E had unique behavior, each.

The acquired data was grouped with data from the previous study by Dolan et al. (2008) that utilized the same FRP reinforced concrete test specimen. This formed a population of over 900 test results. Data were subjected to a rigorous statistical analysis to determine the distribution of data with respect to multiple variables.

The method used to experimentally determine a characteristic design value for adhesive anchors (ACI 355.4-11) was adapted to quantify the loss in bond capacity following accelerated conditioning. Bond durability factors of 0.4 and 0.6 were established for wet-layup with and without putty, respectively. The intent of presented work was to quantify the loss in bond properties over time. However, for the durability factor to be incorporated into design standards, the findings from this study need to be confirmed on large scale specimens and full-scale structural elements.

Finally, based on the presented work the following conclusions may be drawn:

- Statistical analysis showed that test data for different composite systems was normally distributed. Relatively low coefficients of variation (ranging from around 9-21%) were obtained in all subsets of data.
- FRP-concrete bond is vulnerable to combined effects of high temperature and humidity/water. Furthermore, it was determined that the amount of applied epoxy may have an effect on the bond durability in wet-layup without putty.
- 3. Loss in bond capacity for wet-layup FRP without putty plateaus after about 14 through 60 days of constant exposure to accelerated conditioning. FDOT data showed stabilization of bond degradation as early as of 7 days of exposure. Bond durability factor for these systems, based on the available database, was 0.6.
- 4. Data for wet-layup FRP with putty shows a possible change in failure mechanism between 2 and 8 weeks of exposure. Furthermore, sensitivity to increasing exposure temperature is noted in case of maximized moisture exposure (constant water immersion or constant RH=100%).Based on the gathered data, these systems are not recommended for application in infrastructure that is expected to be exposed to aggressive environments; the bond durability factor was found to be 0.40. However, only one commercially available composite system was included in the study. Testing on different composite systems is required.
- 5. All specimens reinforced with CFRP laminate showed a shift in failure mode from cohesive/adhesive in control samples, to material decohesion or adhesive failure between CFRP and epoxy in exposed samples. Bond durability factor analysis was not conducted for CFRP laminate as there was not enough long term exposure evidence of FRP-concrete bond performance. The one system that was included in the study is not recommended for use where exposure to aggressive environments is present.
- 6. Based on observed behavior of test specimens, 60 days of exposure to accelerated conditioning is deemed sufficient to estimate FRP-concrete bond degradation.
- 7. Overly conservative characteristic bond durability factor was based on 3-5 tests per exposure condition. To lower the level of uncertainty, and consequently the K factor that accounts for uncertainty in characteristic bond durability factor, it is

suggested to increase the number of specimens to a minimum of 6 to achieve a K value of 3.096 in future work.

8. Analysis of failure modes in wet-layup specimens confirmed the hypothesis that the ultimate load capacity of three-point bending specimen relates to the failure mode. Namely, cohesive failure mode corresponds to higher, while adhesive bond failure corresponds to lower, control specimen capacity. Adhesive failure mode is deemed desirable in both control and exposed specimens to provide a direct comparison of change in ultimate capacity within the same failure mode from control to exposed specimen.

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Temp	Exposure Time	Peak Stress		Modulus			
(°C)	(weeks)	(MPa)	Stdev	(GPa)	Stdev	Strain (%)	Stdev
Control	0	64.12	12.41	2.34	0.26	3.48	1.10
	2	71.71	8.96	2.47	0.23	3.38	0.30
	4	66.18	8.27	2.45	0.08	3.43	1.00
	6	68.26	9.65	2.48	0.20	2.95	0.60
	8	74.46	4.83	2.45	0.08	3.50	0.40
30	2	67.57	10.34	2.24	0.30	3.90	0.36
	4	66.88	4.14	2.19	0.10	3.75	0.40
	6	66.19	4.14	2.10	0.16	4.40	0.60
	8	64.12	2.07	2.13	0.16	4.56	0.76
40	2	64.81	6.21	2.12	0.26	4.47	0.80
	4	63.43	4.14	2.02	0.19	4.03	0.40
	6	64.81	2.07	2.04	0.12	4.20	0.40
	8	65.50	4.83	1.94	0.07	4.70	0.70
50	2	65.50	4.83	2.07	0.10	4.80	0.40
	4	67.57	4.83	2.17	0.17	4.50	0.40
	6	59.29	8.96	1.97	0.13	3.97	0.90
	8	67.57	6.21	1.91	0.15	5.10	0.90
60	2	57.23	5.52	2.01	0.08	6.05	3.80
	4	54.47	5.52	1.81	0.20	5.23	1.80
	6	55.16	0.69	1.81	0.19	4.49	0.45
	8	56.54	6.21	1.78	0.14	4.73	0.37
70	2	59.98	4.83	1.94	0.21	4.95	0.90
	4	54.47	4.83	1.92	0.20	4.70	1.30
	6	49.64	3.45	1.80	0.09	3.95	0.34
	8	48.95	3.45	1.65	0.07	4.52	0.73
80	2	47.57	2.76	1.77	0.15	4.30	0.70
	4	48.26	5.52	1.70	0.14	4.10	0.25
	6	51.02	4.83	1.74	0.14	4.20	0.32
	8	48.95	3.45	1.67	0.19	4.30	0.20
90	2	53.78	0.69	1.95	0.15	3.90	0.30
	4	46.19	2.76	1.72	0.15	3.70	0.50
	6	46.19	6.21	1.82	0.17	3.40	0.80
	8	46.19	4.14	1.62	0.17	4.20	0.50

7 Appendix A: Mechanical Properties of Model Epoxy After Exposure



8 Appendix B: Typical Load-Displacement Curves for Exposed Model Epoxy Samples

Figure 106. Typical load-displacement curve for unexposed epoxy samples after 8 weeks



Figure 107. Typical load-displacement curve for hygrothermally exposed epoxy samples after 8 weeks - immersion in water at 30°C



Figure 108. Typical load-displacement curve for hygrothermally exposed epoxy samples after 8 weeks - immersion in water at 40°C



Figure 109. Typical load-displacement curve for hygrothermally exposed epoxy samples after 8 weeks - immersion in water at 50°C



Figure 110. Typical load-displacement curve for hygrothermally exposed epoxy samples after 8 weeks - immersion in water at 60°C



Figure 111. Typical load-displacement curve for hygrothermally exposed epoxy samples after 8 weeks - immersion in water at 70°C



Figure 112. Typical load-displacement curve for hygrothermally exposed epoxy samples after 8 weeks - immersion in water at 80°C



Figure 113. Typical load-displacement curve for hygrothermally exposed epoxy samples after 8 weeks - immersion in water at 90°C

	Exposure Time	Peak Stress		Modulus			
Exposure	(weeks)	(MPa)	Stdev	(GPa)	Stdev	Strain (%)	Stdev
UV	1	73.77	0.69	2.22	0.09	5.22	0.53
	2	75.15	3.45	2.28	0.18	4.96	0.45
	4	65.50	13.10	1.97	0.11	4.61	1.47
	6	59.29	17.24	1.93	0.19	4.10	1.64
	8	42.75	11.72	2.27	0.21	2.02	0.49
UV +							
Water	1	66.19	4.14	2.20	0.09	4.77	0.30
	2	64.12	1.38	2.07	0.11	4.26	0.08
	4	61.36	6.21	2.04	0.28	4.29	1.09
	6	68.26	3.45	2.01	0.18	4.77	0.20
	8	50.33	9.65	2.03	0.04	2.82	0.93

9 Appendix C: Mechanical Properties of Model Epoxy After UV Exposure

Temperature (°C)	Exposure Time (weeks)	Peak stress (MPa)	Stdev	Modulus (GPa)	Stdev	Strain	Stdev
control	0	62.05	6.21	2.09	0.16	3.663	0.50
	2	63.43	11.03	2.12	0.18	4.106	0.41
	4	68.26	2.07	2.35	0.13	4.629	1.34
	6	65.50	4.14	2.29	0.20	3.611	0.17
	8	68.26	3.45	2.29	0.08	4.267	0.81
30	2	62.05	3.45	1.97	0.18	4.187	0.26
	4	56.54	4.14	2.02	0.07	5.616	0.38
	6	51.71	2.07	2.04	0.14	3.297	0.36
	8	56.54	2.76	2.00	0.22	4.153	0.82
40	2	56.54	6.89	1.90	0.13	4.240	0.48
	4	50.33	6.21	1.82	0.17	4.429	0.79
	6	48.26	4.83	1.80	0.22	3.688	0.62
	8	50.33	3.45	1.79	0.08	3.785	0.21
50	2	51.02	7.58	1.76	0.18	3.893	0.20
	4	44.13	3.45	1.63	0.16	3.885	0.49
	6	44.82	4.83	1.81	0.12	3.717	0.61
	8	46.88	2.76	1.74	0.11	3.874	0.24
60	2	46.19	4.14	1.71	0.08	3.923	0.38
	4	44.13	3.45	1.53	0.15	4.294	0.72
	6	42.75	4.14	1.70	0.13	6.924	4.41
	8	45.51	2.07	1.67	0.17	3.995	0.67
70	2	48.95	4.14	1.78	0.11	4.415	1.00
	4	44.13	2.07	1.61	0.08	4.128	0.31
	6	39.30	2.07	1.68	0.04	9.836	11.72
	8	42.06	2.76	1.61	0.11	3.642	0.27
80	2	44.82	2.76	1.61	0.15	3.785	0.25
	4	41.37	2.76	1.54	0.08	4.246	0.98
	6	39.99	3.45	1.68	0.09	5.212	3.85
	8	44.82	3.45	1.58	0.24	3.955	0.49

10 Appendix D: Mechanical Properties of Sikadur 300 After Exposure

11 Appendix E: ANOVA Results for Modulus of Model Epoxy After Exposure

Multivariate Tests ^c						
Effect		Value	F	Hypothesis df	Error df	Sig.
temperature	Pillai's Trace	.653	4.084 ^a	6.000	13.000	.016
	Wilks' Lambda	.347	4.084 ^a	6.000	13.000	.016
	Hotelling's Trace	1.885	4.084 ^a	6.000	13.000	.016
	Roy's Largest Root	1.885	4.084 ^a	6.000	13.000	.016
temperature * Control	Pillai's Trace	.613	3.434 ^a	6.000	13.000	.030
	Wilks' Lambda	.387	3.434 ^a	6.000	13.000	.030
	Hotelling's Trace	1.585	3.434 ^a	6.000	13.000	.030
	Roy's Largest Root	1.585	3.434 ^a	6.000	13.000	.030
temperature * Week	Pillai's Trace	.834	.962	18.000	45.000	.516
	Wilks' Lambda	.367	.879	18.000	37.255	.604
	Hotelling's Trace	1.224	.793	18.000	35.000	.694
	Roy's Largest Root	.665	1.662 ^b	6.000	15.000	.198

a. Exact statistic

b. The statistic is an upper bound on F that yields a lower bound on the significance level.

c. Design: Intercept + Control + Week

Within Subjects Design: temperature

Number of tests	К	Number of tests	К
n		n	
3	5.311	21	2.190
4	3.957	22	2.174
5	3.400	23	2.159
6	3.092	24	2.145
7	2.894	25	2.132
8	2.754	26	2.120
9	2.650	27	2.109
10	2.568	28	2.099
11	2.503	29	2.089
12	2.448	30	2.080
13	2.402	35	2.041
14	2.363	40	2.010
15	2.329	45	1.986
16	2.299	50	1.965
17	2.272	60	1.933
18	2.249	120	1.841
19	2.227	240	1.780
20	2.208	00	1.645

12 Appendix F: Tolerance Factors for Characteristic BDF

(Hahn and Meeker 1991)