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Alkaline durability tests for E-glass/vinyl ester-reinforced polymer with nanoclay

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ALKALINE DURABILITY TESTS FOR E-GLASS / VINYL ESTER
REINFORCED POLYMER WITH NANOCCLAY

by

Shu-Kai Yeh

Thesis submitted to the College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of

Masters of Science
in
Chemical Engineering

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2003

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simulated concrete solution, sustained load

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Abstract

Alkaline Durability Tests for E-Glass / Vinyl Ester Reinforced Polymer with Nanoclay

Shu-Kai Yeh

Two kinds of GFRP (glass fiber reinforced plastics) composite materials were prepared and used in this study. One was E-glass / vinyl ester glass fiber reinforced polymer (plain GFRP) and the other was nano-GFRP prepared with the addition of 1wt.% of Cloisite[®] 10A nanoclay. These samples were aged in an alkaline solution (pH 13.2) with 3560N (800-lbs), 2225N (500-lbs) and 885N (200-lbs) of sustained load, which were 50%, 31% and 12.5% of the tensile strength, respectively. Time to failure or tensile strength reduction was measured and used to determine durability of the samples in terms of Aging Index, which was proposed as the tensile strength reduction per day. The failed cross sectional areas of samples were examined by taking pictures with optical microscopes.

The nano-GFRP samples showed slightly higher durability than the plain GFRP samples under 2225N (500-lbs) sustained load. However, durabilities of the two kinds of samples were nearly the same under the 3560N (800-lbs) and 885N (200-lbs) sustained loads. It has been found that the Aging Index proposed in this study varies as function of the square of applied stress.

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Chapter I

Introduction

Glass fiber reinforced polymer (GFRP) composite is widely used as structural material in aerospace, automotive, marine, and electronic industries. Compared to traditional structural materials such as steel and metal alloys, GFRP composite has advantages such as ease of fabrication, high strength to weight ratio, low cost to weight ratio, corrosion resistance, and magnetic transparency.⁽¹⁾

Fiber reinforced polymer composite usually consists of two parts which are high strength fiber, and polymer binder. High strength fiber is bonded with polymer matrix. When sustained stress is applied to the composite, this stress is resisted by fibers through the polymer binder.

There are many kinds of polymers which have been used for polymer matrix in GFRP composite. Some polymers which are used commonly are listed in Table 1. There are two broad categories of polymer: one is thermoset polymer and the other is thermoplastic polymer. The difference in properties of these two polymers is due to their property of softening upon heating. The latter softens upon heating while the former does not because it is in a liquid form before cure and doesn't melt after heating due to high density of cross linkage. Typical thermoset resins include vinyl ester, epoxies, and phenolics and are widely used in GFRP processing because of their ease of processing, thermal stability, better creep resistance, and chemical resistance. On the other hand, thermoplastic polymers include nylons, polycarbonate and polyesters and are used less in GFRP processing because they have high viscosity in liquid and they are difficult to process. The void content of GFRP manufactured with thermoplastic polymer is higher than that with thermoset polymer. The fiber volume

content of GFRP with thermoplastic polymer, however, is usually lower than that with thermoset polymer. Therefore, most of the GFRP materials are manufactured with thermoset polymer.

Although GFRP composite materials have many advantages, they degrade when used particularly in concrete beams, bridge decks and road pavement. There are chemical aging and physical aging. Chemical aging includes dissolution of matrix, swelling of matrix and fiber-matrix debonding. All aging related changes can take place by some organic solvents. Also, high pH aqueous solution attacks glass fibers, which causes fiber-matrix debonding and thus reduces tensile strength of composite.⁽²⁾

Physical aging of GFRP is defined as the polymer and glass gradually approach their equilibrium state for their volume, enthalpy and entropy while the existing polymer and glass have higher values of their properties than those at equilibrium.⁽⁴⁾

The chemical aging mechanisms are specifically caused by moisture absorption and alkaline attack. Moisture is absorbed into GFRP from their environments. This absorption causes polymer to soften and amorphous leading to fiber-matrix delamination and fiber weakening.⁽⁵⁾

When GFRP composites are used as reinforcement in concrete, they are attacked by alkali solutions produced by dissolution of concrete in absorbed moisture. The average pH value of concrete pore solution is 13.4.⁽⁶⁾ High pH concrete pore solution diffuses thorough polymer matrix and dissolves glass fiber in GFRP material. The chemical reaction can be written as:⁽⁷⁾

Alkaline attack causes serious degradation problems of GFRP composites. Because of this degradation in the presence of high pH (>11) in concrete, the average life of non-modified E-glass / vinyl ester GFRP rebar is only between 0.5 to 1.7 years for the specimens under 10% of sustained tensile strength.⁽⁸⁾ However, the life span

would be much more extended if the resin is properly modified with urethane. This will be delineated later in this section.

Table 1. Polymeric Matrix Materials (Mallick, 1993)⁽³⁾

Thermoset Polymers (resins):

Epoxyes: principally used in aerospace and aircraft applications.

Polyester and Vinyl Esters: commonly used in automotive, marine, chemical and electrical applications.

Phenolics: used in bulk molding compounds.

Polyimides, polybenzimidazoles (PBI), polyphenylquinoxaline (PPQ): for high temperature aerospace applications (temperature range of 250 °C – 400 °C).

Thermoplastic Polymers:

Nylons (such as nylon 6, nylon 6,6), thermoplastic polyesters (such as PET, PBT), polycarbonate (PC), polyacetals: used in injection molded articles.

Polyamide-imide (PAI), polyether-ether ketone (PEEK), polysulfone (PSUL), poly-phenylene sulfide (PPS), polyether imide (PEI): suitable for moderately high temperature applications.

The chemical aging can be prevented by three methods: The first method is by adopting alkali resistant glass fibers. Owens Corning Inc. developed a glass fiber under a trade name of Adventex[®] which is resistant to alkali solution. It has been shown that GFRP manufactured with this alkali-resistant GFRP is much more durable than that manufactured with traditional E-glass fiber. ⁽⁹⁾

The second method is to modify polymer matrix with organic polymers and inorganic fillers. It has been proved that modifying vinyl ester polymer matrix with urethane would improve durability of non-modified E-glass / vinyl ester GFRP rebar in alkaline solution. Urethane-modified vinyl ester GFRP rebars showed almost

negligible tensile strength loss (0.8%) after 102 days of alkaline exposure with 25~33% tensile strength sustained loading,⁽¹⁰⁾ while vinyl ester GFRP rebars manufactured without urethane modification failed within one month with only 25% tensile strength sustained loading in alkaline solution.⁽⁸⁾ Furthermore, Reichhold Chemicals Inc. have developed urethane-modified vinyl ester GFRP which would be resistant to alkali attack. A bridge constructed with urethane-modified vinyl ester GFRP has been in service since 1996 and recent field inspections revealed that the bridge is of a very good service condition.

The third method was suggested in which montmorillonite nanoclay powders are dispersed into the polymer matrix of GFRP during the manufacturing process. The result is that the polymer matrix provides tortuous diffusion pathways in its structure.⁽¹¹⁾ Thus, the diffusion coefficient of moisture through the matrix decreases. A previous study showed that when 1wt.% Cloisite[®] 10A nanoclay was dispersed to vinyl ester resin in forming nanocomposites, water diffusion coefficient decreased by 60%.⁽¹²⁾

The major objective of this study is to determine the degradation of regular GFRP and polymer nanocomposites under sustained load in an alkali solution in terms of failure time and tensile strength reduction. In this study, the composite is made with epoxy vinyl ester resin and E-glass fiber. In addition, the polymer nanocomposite is made by adding 1wt.% Cloisite[®] 10A nanoclay to the regular GFRP.

Chapter II

Literature Review

Concrete is made of Portland cement (limestone), sand, water and aggregates. Several methods were developed to measure the alkalinity of concrete pore solution. Barneyback et al.⁽¹⁵⁾ developed an expression for alkalinity measurement using a pore fluid method in early 1980s. This method applied a pressure of 550MPa on concrete blocks placed in a 2” diameter cell made of SAE 4340 alloy steel. The high pressure was applied in order to squeeze out a pore solution from the concrete.

In 1997, Sagues et al.⁽⁶⁾ used in-situ leaching method to evaluate the pH value in concrete pore. Three holes of 5mm in diameter and 30mm in depth were drilled in perpendicular to each freshly-made concrete cylinder surface. After carefully cleaning the holes, 0.4mL of distilled water was injected to each hole with a syringe. The distilled water was sealed in concrete cylinder with acrylic washer and rubber stopper. The prepared specimen is shown in Figure 1.

Figure 1. Prepared concrete specimen sample for in-situ leaching method.⁽⁶⁾

The pH value of the solution in the holes was measured by a micro-pH glass electrode with a silver reference electrode. The measured pH value of the solution is given in Figure 2. After 15 days exposure, the pH value of the solution becomes around 13.4. These pH values are slightly higher than that measured by Barneyback et al. ⁽¹⁵⁾

Figure 2. pH evolution of the solution inside three holes on the same concrete cylinder CCTR 1-2-3 showing similar behavior (calibrated to 21°C). ⁽⁶⁾

The disadvantage of these two methods is that it is not easy to obtain enough pore solution to be used for actual experiments. Therefore, many previous research projects used several liters of simulated concrete pore solution of the GFRP alkaline environment. The simulated concrete pore solution usually contains three different chemicals, which are calcium hydroxide, potassium hydroxide and sodium hydroxide. There are various formulas suggested by various authors as to the composition of the simulated concrete pore solution. Karbhari et al. ⁽¹⁶⁾ collected these formulas which can be seen in Table 2.

The successful utilization of GFRP as a concrete reinforcement depends on the GFRP durability in concrete pore solution. When concrete pore solution diffuses through the GFRP polymer matrix, it not only etches the glass fiber inside the polymer matrix but also causes fiber-matrix debonding (see Figure 3). Thus the GFRP is seriously degraded by concrete pore solution.

Table 2. Examples of Previously Used Simulated Concrete Solutions.⁽¹⁶⁾

Investigators	Details of Solution	Reference
Uomoto and Nishimura	NaOH solution at 1 mol/l at 40 °C	(17)
Rotasy	Saturated solution of $\text{Ca}(\text{OH})_2$ + 0.4N KOH for a pH 13 Level	(18)
Hawkins, Steckel, Baucer and Sultan	CaCO_3 solution at 23°C to get pH 9.5	(19)
Christensen, Mason, and Jennings	0.32 mol/L KOH, 0.17 mol/L NaOH and 0.07 mol/L of $\text{Ca}(\text{OH})_2$ in distilled water	(20)
Vijay. GangaRao	0.2% $\text{Ca}(\text{OH})_2$, 1% NaOH, 1.4% KOH by weight (pH 13)	(21)
Conrad, Bakis, Boothby and Nanni	Saturated Solution of $\text{Ca}(\text{OH})_2$	(22)
Ton-That, Benmokrane, Raham and Robert	118.5 g of $\text{Ca}(\text{OH})_2$, 0.9g NaOH and 4.2g of KOH in 1 liter of deionized water	(23)

Figure 3. Degradation of interface showing pitting of fiber and fiber-matrix debonding due to immersion in concrete pore solution.⁽¹⁶⁾

Research has been carried out in the past to investigate durability of GFRP in

simulated concrete pore solution. ^(1, 8, 9, 24, 25 and 26) Some of them used commercially available cylindrical GFRP rebars in their sustained stressed alkaline exposure tests ^(1, 7, 8), while others used rectangular coupons in their non-stressed alkaline exposure tests. In both studies, durability of the composite was determined by measuring time to failure or residual tensile strength. Particularly in the latter study, diffusion coefficient of simulated concrete pore solution through the composite matrix was determined ^(24, 25, and 26).

In the first study which used commercially available cylindrical GFRP rebars, samples were placed in a PVC pipe which contained a simulated concrete pore solution. The samples were sealed with O-rings and washers. The sustained loads were applied on the samples by springs, lever arms ⁽⁹⁾ and threaded bolts ^(1, 8). As mentioned previously durability of the cylindrical samples was determined by measuring time to rupture under sustained stress. In some cases, samples were taken off before failure and durability was determined by measuring residual tensile strength. Both cases took microscopic pictures and used them as an evidence of alkaline attack of GFRP samples (See Figure 4 and 5).

Figure 4. SEM pictures of untested GFRP specimens. ⁽⁸⁾

Figure 5. SEM pictures of GFRP specimens applied for 25% of tensile strength for 30 days. ⁽⁸⁾

Previous studies suggested that the properties of GFRP, particularly durability in alkaline solution be studied more extensively for better utilization in infrastructures such as bridge decks ^(1, 8, 9, 24 - 26). The test results with commercially available cylindrical GFRP rods suggest that the stress level of the GFRP rods be less than 25% of their guaranteed tensile strength which is defined as the ultimate tensile strength minus three times of the standard deviation. ⁽⁹⁾

In Reference (8) R. Sen et al. further used an equation developed by Katsuki ⁽²⁷⁾ et al. which is based on Fick's first law of diffusion to predict the residual life of GFRP rods. The prediction of remaining life for the test specimens is between 1.6 to 4.6 years (unstressed) and 0.5 to 1.8 years for the specimens stressed to 10% of their tensile strength. Vijay and GangaRao obtained similar results with non-urethane-modified vinyl ester / E-glass GFRP composites (P. V. Vijay and H. V. S. GangaRao, Construction Facilities Center West Virginia University, personal contact).

As previously mentioned, the diffusivity of concrete pore solution through polymer matrix is one of the factors, which affects durability of GFRP materials.

Therefore, if we can decrease the diffusion coefficient of concrete pore solution through polymer matrix, the degradation rate of GFRP may be reduced. One of the ways for reduction of GFRP degradation is to modify GFRP to nanocomposites by including micro-sized clay particles. It is known that the diffusion of pore solution through the nanocomposites matrix is much hampered and thus the degradation of the composite is much retarded.

Like all other composites, the term “nanocomposites” is defined as a two or more phase system where one phase is dispersed into other phases. Although polymer clay interaction has been studied during the sixties and the early seventies, the concept of polymer-clay nanocomposites has not been proposed until the early nineties.⁽²⁸⁾ The researchers from Toyota found that it is possible to build a nanostructure between nylon-6 polymer and organophilic clay hybrid in 1990.⁽²⁹⁾ As compared to nylon-6 polymer, their new hybrid materials showed enormous improvements in mechanical properties, barrier properties and thermal resistance with only 4 wt.% clay loading.

Among numerous clays tested, montmorillonite is the most effective nanofiller because it has flat plate-like structure, and high aspect ratio to give an enormous surface area. In addition, montmorillonite is abundant in nature. A montmorillonite platelet usually includes aluminum or magnesia atoms in the center of an octahedral sheet which is fused with two external silica tetrahedron layers. This sandwich structure layers is called a unit layer. An idealized structure of montmorillonite unit layer is given in Figure 6. The thickness of unit layer is around 1 nanometer and the lateral dimensions of the platelet ranges from several hundred nanometers to several thousands nanometers. Clays are composed of so many such layers stacked in parallel to one another and held by Van der Waals forces.

In many types of clay, the lateral Si^{4+} atoms as shown in Figure 6 are partly

replaced by trivalent atoms such as Al^{3+} and/or the central Al^{3+} atoms are also partly replaced by some divalent atoms such as Fe^{2+} and Mg^{2+} . Because of that, lack of positive charges on clay platelet surface is usually compensated by adsorbing Na^+ and Ca^{2+} ions present in water. These cations can be exchanged by other cations that are present in solution. This property of clay makes it possible to replace inorganic cations on the unit layer surface with organic cations by ion exchange mechanism, and thus makes the clay develop affinity with an organic phase such as polymer. Generally onium ion and amine salt are the two typical cations used in clay modification.

Figure 6. Idealized structure for montmorillonite. ⁽²⁸⁾

Clay filled polymers are classified as three types of composites based on their morphology, which are conventional composite, intercalated composite and exfoliated / delaminated composite. This classification is determined by the interaction of polymer and clay. When the polymer chains are not able to penetrate through the gaps between the unit clay platelets, the stacks of clay remain in the original aggregates, and it is known as conventional or macroscopic composite. In some other polymer-clay composites, polymer chains are intercalated into unit clay platelets gaps but the platelets are still not able to disperse in the polymers. This type of morphology

is called intercalated composite. When the clay platelets are randomly dispersed into polymers and the gaps between each platelet are expanded, this structure is called exfoliated or delaminated composite. A schematic diagram of these morphologies is shown in Figure 7. Among these three types of morphologies, exfoliated morphology gives the maximum benefits, because the montmorillonite clay has a high surface area (around $750 \text{ m}^2/\text{g}$).⁽³⁰⁾ Property enhancement is decided by the molecular level interactions between clay surface and polymer. Since montmorillonite clay platelets present the largest surface area in exfoliated morphology, the property enhancement of polymer nanocomposite is very significant even with very small clay loading.

Figure 7. Types of nanocomposites morphologies.⁽²⁸⁾

The high surface area of montmorillonite clay plays an important role in property enhancement of polymer nanocomposites. In both exfoliated and intercalated nanocomposites, dispersed nanoclay platelets create a tortuous structure inside the polymer matrix. The effective diffusion path for a diffusing molecular is longer. Therefore, polymer nanocomposites have very good diffusion barrier properties for liquid and gas (see Figure 8).⁽¹²⁾ The diffusion coefficient of water through vinyl ester-clay nanocomposite is reduced as the clay content is increased as can be seen in

Figure 9. ⁽¹²⁾ It is seen from the figure that the diffusivity is reduced by 85% with only 5 wt.% clay loading.

Figure 8. Different diffusion paths in polymer and polymer nanocomposites. ⁽¹²⁾

Figure 9. Measured values of moisture diffusivity through unsaturated vinyl ester resin. ⁽¹²⁾

Chapter III

Experimentation

3.1 Materials

Dow Chemical DERA-KANETM *Momentum* 411-350 epoxy vinyl ester resin was obtained from Eastech Chemical Company and used as the polymer matrix in this study. The resin contains 45% of styrene monomer. This resin was cured for polymerization at room temperature by adding 1 wt.% of methyl ethyl ketone peroxide (MEKP, initiator) and 0.03wt.% cobalt naphthenate (catalyst for polymerization). Both of these additives were obtained from Sigma-Aldrich Company. Typical properties of this resin before and after polymerization are provided in Tables 3 and 4, respectively.

The E-glass fiber mats used in this study are 0°/90° bi-directional woven mats, and the fabric weight is 814 g/m² (24 ounces per square yard). It is obtained from PPG Industries. Figure 10 shows a schematic representation of woven pattern of the glass fiber mats. Nanocomposites were made with Cloisite[®] 10A nanoclay, which was obtained from Southern Clay Company. Cloisite[®] 10A is a natural montmorillonite modified with quaternary ammonium salts. The chemical and physical properties of Cloisite[®] 10A nanoclay are listed in Appendix I.

**Table. 3. Typical Properties of DERA KANETM Momentum
411-350 Epoxy Vinyl Ester Resin, Before Polymerization.⁽³¹⁾**

Dynamic Viscosity @ 25°C (77°F), MPa.s ¹	370
Styrene Content, %	45
Special Gravity	1.046
Shelf Life ² , dark, @ 25°C (77°F), months	12

¹ Typical properties; not to be construed as specifications.

² No additives, promoters, accelerators, etc.

**Table. 4. Typical Room-Temperature Properties of DERA KANETM
Momentum 411-350 After Polymerization.⁽³¹⁾**

Tensile Strength, MPa (psi)	86 (12,000)
Tensile Modulus, GPa (10 ⁵ psi)	3.2 (4.6)
Tensile Elongation, %	5.0-6.0
Flexural Strength, MPa (psi)	150 (22,000)
Flexural Modulus, GPa (10 ⁵ psi)	3.4 (4.9)
Specific Gravity	1.14
Heat Distortion Temperature, °C (F°) at 1.82 MPa applied stress (at 264 psi applied stress)	105 (220)
Barcol Hardness	35

Figure 10. Schematic of woven pattern of the glass fabric.⁽²⁶⁾

3.2 Sample Preparation

In preparing a plain GFRP sample plate, 120 grams of DerakaneTM 411-350 *Momentum* epoxy vinyl ester resin was mixed with 1 wt.% of MEKP (initiator) and 0.03wt.% of cobalt naphthenate by a chop stick. Mixed resin was placed in a vacuum chamber and degassed in a vacuum for 10 minutes. In order to facilitate the release of the sample plate from the aluminum plates after it is solidified, one layer of Frekote[®] FMS sealer and Frekote[®] 700-NC release agent were applied on the aluminum plate before resin was poured on an aluminum plate. These chemicals were obtained from Loctite Company. After the sealer and the release agent were applied, resin was poured on an aluminum plate of 1'×2'×3/8". One layer of E-glass fabric of 12.5" long and 6.25" wide was placed on the poured resin and excess resin was rubbed out with a chop stick. Then the second layer of identical E-glass fabric was stacked on top of the first layer and more resin (approximately 60g) was poured on top of the second layer of fabric. Again, excess resin was rubbed out with a chop stick before another identical aluminum plate was placed on the top. This whole assembly was pressurized by placing two lead blocks, each with 10.2kg (22.5-lbs). The GFRP plate was cured at room temperature for 24 hours. Then, GFRP sample plate was released from the cage of the aluminum plates and post-cured at 100 °C for additional 3 hours. The thickness of the cured plate was around 0.052". This value was consistent from plate to plate.

Nannocomposite sample plates were prepared by adding 1 wt.% of Cloisite[®] 10A nanoclay into liquid resin and dispersing with an agitator for one hour. Heat was produced during agitation and in order to negate the effect, some ice cubes were placed around outside the resin cup. The agitated resin was degassed in a vacuum chamber for 30 minutes. Then, the same procedures as before were taken to prepare nano GFRP plates.

Both sample plates of GFRP and nano GFRP plates were cut into 1" x 11.5"

strips with a tile saw. Each sample weighed in the range of 15.6~16.4g. Five strips were produced from each GFRP sample plate.

3.3 Tension Tests

The prepared GFRP or nano GFRP specimens were physically strengthened to be suitable for tension tests (ASTM D3039⁽³²⁾). Each end of a GFRP specimen was reinforced with two 2" x 1" tapered tabs. Both ends of the specimen and four tabs (1" x 2" x 1/8") were sandpapered with a 150 grit sand paper. Then the surfaces were cleaned with acetone. An epoxy adhesive, Elementis 7895, was used to glue the tabs to both ends of specimen. The glue was cured for one day. The cross sectional area of the sample was measured at three different places, at the center and at the two positions of 1.75" away from the center. The values were averaged and used to determine the cross-sectional area. Applied stress on the sample was calculated by dividing the load by the average cross-sectional area.

Tension tests were conducted by an Instron 8500 tension test instrument and by placing an extensometer on the sample. The instrument assembly provided the load / strain information which were recorded simultaneously on a computer. The Young's modulus was calculated based on the stress-strain relationship. The picture of Instron 8500 is given in Figure 11. In the measurement, only 25% of tensile strength was applied. Also, measurement repeated more than once to assure that there was no slip between the sample and the grip. If there was, the Young's modulus would not be consistent from analysis to analysis. Both nano-GFRP samples and plain GFRP samples showed similar Young's modulus and tensile strength. Fifteen nano-GFRP samples and 17 plain GFRP samples were tested.

Figure 11. Instron 8500 tension test instrument.

3.4 Fiber Volume Fraction and Void Fraction of GFRP composites

Generally, the tensile strength and Young's modulus of composite materials are largely dependent on fiber volume fraction and void content in the composite materials. The fiber weight fraction of GFRP sample plate was determined by ignition loss methods (ASTM D2584⁽³²⁾). Also, the sample void content was calculated by measuring the density of GFRP sample and unreinforced resin (ASTM D2734⁽³⁴⁾). A 1" x 1" sample was cut from the corner of each GFRP sample plate. Every sample was put in a crucible and ignited in a muffle furnace at 575°C for 2-6 hours until the reinforced resin disappears. Before the sample was placed into muffle furnace, the volume and the weight of the sample were determined in order to determine the density of the sample. After 2 - 6 hours, the crucible was taken out and placed in a desiccator for 10 minutes. Then the unburned fiber was determined by weighing empty crucible and loaded crucibles with unburned E-glass fiber. Then the fiber and resin volume fractions were determined using the density of E-glass fiber of 2.54 to 2.59 g/cm³, which was obtained from ASTM D2734. The void content of GFRP sample plates was calculated by Equation (2).

$$V = 100 - M_d \left(\frac{r}{d_r} + \frac{g}{d_g} \right) \dots\dots\dots (2)$$

where:

V = void fraction, volume %,

M_d = measured density of composite sample, g/cm^3

r = weight % of resin in the composite

g = weight % of fiber in the composite

d_r = density of resin, g/cm^3

d_g = density of fiber, g/cm^3

The density of resin was determined by solidifying DerakaneTM *Momentum* 411-350 epoxy vinyl ester resin into a 3.2 mm I.D. and 30 mm high cylinder. The resin was also cured at room temperature for 24 hours and post-cured at 100°C for 3 hours. The rough surface of the post-cured resin was sandpapered by 400-grits until no significant voids on the surface was detected by naked eyes. The height and diameter of the sample were measured at various places in order to determine the average volume. Then the density of post-cured resin was determined by its weight and volume.

3.5 Sustained-Load Frame Design

A frame was designed to be used for conducting sustained-load tests. The frame consists of a flanged pipe (2" diameter x 18" high) and two circular flanges (6" diameter) with four 3/4" holes on each. Two sets of yoke end linkage were used to connect a specimen to the flange. Stress was applied from squeezing a die spring on the flange as shown in Figure 12. The loads applied were 3560N (800-lbs), 2225N (500-lbs) and, 885N (200-lbs) in experiment. These corresponded to 50, 31 and 12.5% of the tensile strength of specimen, respectively. Two kinds of springs which were suitable for each sustained load were used. The spring constants were measured by Instron 8500, which were 175kN/m (1000 lb/inch) and 385kN/m (2200 lb/inch).

Figure 12. Sustained-load frame.

3.6 Alkaline Sustained-Load Exposure Tests

The alkali solutions used in this study consisted of 0.32 mol/L KOH, 0.17 mol/L NaOH and 0.07 mol/L $\text{Ca}(\text{OH})_2$. This composition was according to Christensen et al.⁽¹⁸⁾ The pH was claimed to be 13.4 but the measured pH value was 13.2 in the study. In order to conduct alkaline exposure tests, FERNCO[®] 2" rubber QWIK caps were installed on samples with EPOWELD[®] epoxy adhesive. After caps were installed, 1" by 1.875" tabs were glued on both end of the sample (See Figure 13). A 2" PVC pipe of 7.5" in length was used as an alkali solution reservoir in sustained-load alkaline exposure tests. Samples were sustained at 3560N, 2225N and 885N (800, 500, and 200-lbs) load. After the load was applied, a 350 ml alkaline solution (pH 13.2) was poured in the PVC pipe. In order to prevent alkaline solution evaporation and carbon dioxide dissolution, the pipe was sealed by 3M Scotch[®] masking tape. The experiments which were conducted with 3560N (800-lbs) and 2225N (500-lbs) used 16 plain GFRP samples and 16 nano-GFRP samples. In the case of 885N (200-lbs) test, experiments used 12 plain samples and 12 nano-GFRP samples. The whole assembly of this pipe under the load is shown in Figure 14.

Figure 13. A prepared specimen for alkaline sustained-load exposure samples.

Figure 14. Alkaline sustained-load experiments.

3.7 Residual Tensile Strength Measurement

The life cycle of GFRP composites was determined by time to failure and/or residual tensile strength measurement. For 3560N (800-lbs) and 2225N (500-lbs) sustained-load exposure tests, time to failure was used to evaluate the aging. On the other hand, for the 885N (200-lbs) sustained-load tests, the residual tensile strength was measured after 3-month alkaline exposure. The aged samples were taken off from the sustained-load flanges. The rubber caps and PVC pipes were removed from each sample. The tapered red tabs on both ends of the sample were also cut by the tile saw. Then the same procedures mentioned in Chapter 3.3 were taken to modify the

specimen to be suitable to measure the residual tensile strength.

3.8 Optical Microscopic Pictures

The cross sectional areas of aged and non-aged GFRP samples were cut into 3/4" x 1" pieces and mounted on a mold of epoxy resin of 3.2 mm diameter. The samples were polished by Buehler Ltd. Automat[®] semi-automatic polisher (see Figure 15). Mounted samples were polished in sequence by 320, 400, and 600 grits sandpapers. Then samples were polished by 9 μm and 3 μm Buehler METADI[®] Supreme diamond suspension fluid.

Figure 15. Buehler Automat[®] 2 semi-auto polishing machine.

An optical microscope which was manufactured by Brodersen Instrument Inc. was used to observe the polished sample dyes (see Figure 16). Also, the optical microscope was connected to a CCD camera and thus the observed images were converted to digital signal which can be recorded on a computer. The magnification with the microscope ranged from 100 to 500. Microscopic pictures are shown in Chapter 4.

Figure 16. Brodersen Instrument optical microscope

Chapter IV

Results and Discussion

4.1 Tension Tests

Tables 5 and 6 present physical properties including Young's modulus and tensile strength of non-aged plain GFRP and nano-GFRP samples, respectively. Samples were named by batch such as 2A, 2B, 2D... for plain samples and 2CA, 2CB, 2CC for nano-GFRP samples. As can be seen from the tables, the average Young's modulus and tensile strength values between the two kinds of composite samples are almost the same.

The last columns of the tables also show the modes of failure by the place where the failure occurred. It can be seen that the number of samples broken in the middle is almost the same as the number of samples broken in the tab for plain GFRP samples; however, the number of samples broken in the middle is twice as many as the number of samples broken in the tab for nano-GFRP samples. The reason for this occurrence is not clear.

If we select those samples which were failed in the middle, the average tensile strengths are 219.1MPa (31.8ksi) and 210.1MPa (30.5ksi) for plain GFRP samples and nano-GFRP samples, respectively. These values are not significantly different from each other. Also, the standard deviation values on Young's modulus and tensile strength between the two kinds of composite samples are not significantly different.

4.2 Fiber Volume Fraction and Void Fraction of GFRP Samples

Void fraction and fiber volume fraction of the plain GFRP samples were determined using Equation (2). The results are given in Table 7. The standard deviation values of the fiber volume percent and void fraction among these samples

are also provided. The void fraction of GFRP samples shows a large variation from 4.9% to 7.74% with the standard deviation of 0.88%; however, the fiber volume fraction shows a much smaller variation from 27.52% to 32.84% with the standard deviation of 1.62%. The high magnitude of void fraction of GFRP samples (4.9% to 7.74%) and its large variation are considered to be due to the manual manufacturing method (hand-lay-up) of the specimens because rubbing the resin with chopsticks tends to produce more bubbles and can not be performed in a controlling fashion.

Table. 5. Young's Modulus and Tensile Strength of Plain GFRP Samples

Sample	Young's Modulus (GPa)	Failure Load (N)	Average Thickness (cm)	Average Width (cm)	Average Cross-sectional Area (cm ²)	Tensile Strength (MPa)	Failure Mode
2A-1	15.17	6843	0.132	2.497	0.3298	207.45	Tab
2A-3	14.55	7239	0.132	2.631	0.3475	208.17	Middle
2A-4	13.51	6767	0.132	2.637	0.3483	194.35	Middle
2B-1	15.31	7087	0.124	2.639	0.3285	217.22	Tab
2B-2	14.34	7114	0.132	2.626	0.3469	204.98	Middle
2B-3	14.27	6581	0.135	2.639	0.3553	185.24	Middle
2B-4	13.93	7434	0.135	2.644	0.3559	208.75	Tab
2B-5	15.31	7301	0.127	2.619	0.3323	218.10	Tab
2D-1	13.58	6630	0.135	2.598	0.3498	189.48	Tab
2D-2	13.72	6998	0.135	2.614	0.3519	200.19	Tab
2D-3	14.62	6959	0.130	2.596	0.3363	208.25	Middle
2D-4	14.27	6896	0.127	2.593	0.3294	207.95	Middle
2E-1	14.82	7234	0.130	2.565	0.3323	217.65	Middle
2F-1	13.10	7408	0.145	2.555	0.3699	201.37	Tab
2K-1	13.58	7376	0.130	2.576	0.3336	219.69	Middle
2M-1	15.10	7243	0.130	2.598	0.3366	216.62	Tab
2N-1	14.82	6358	0.127	2.591	0.329	191.84	Tab
Average	14.34	7028	0.132	2.601	0.342	205.73	
STD	0.669					10.36	

Table. 6. Young's Modulus and Tensile Strength of Nano-GFRP Samples

Sample	Young's Modulus (GPa)	Failure Load (N)	Average Thickness (cm)	Average Width (cm)	Average Cross-sectional Area (cm ²)	Tensile Strength (MPa)	Failure Mode
2CA-1	14.89	7537	0.130	2.619	0.339	217.79	Middle
2CA-2	14.48	7301	0.135	2.614	0.352	207.40	Middle
2CA-3	14.27	7911	0.135	2.601	0.350	224.45	Middle
2CA-4	14.20	7026	0.135	2.609	0.351	200.00	Middle
2CA-5	15.17	7572	0.137	2.629	0.361	211.62	Tab
2CB-1	15.31	6630	0.130	2.598	0.337	198.29	Tab
2CB-2	14.48	7217	0.135	2.598	0.350	207.62	Middle
2CB-3	12.48	7373	0.132	2.601	0.344	215.86	Middle
2CB-4	13.79	7297	0.137	2.583	0.354	206.36	Tab
2CB-5	14.55	7239	0.132	2.588	0.342	199.49	Tab
2CC-1	13.72	7443	0.137	2.596	0.356	208.94	Middle
2CC-2	13.65	7203	0.135	2.560	0.345	207.64	Middle
2CC-3	15.38	6630	0.132	2.548	0.336	196.90	Middle
2CC-4	14.69	7368	0.130	2.588	0.335	218.28	Middle
2CC-5	15.58	6015	0.124	2.588	0.322	185.44	Tab
Average	14.41	7184	0.132	2.596	0.345	207.07	
STD	0.758					9.67	

Equation (2) was not suitable to determine the void fraction of nano-GFRP samples. The reason was that weight of clay and thus the weight of fiber could not be determined by igniting the specimen at 575°C. This was because clay particles included in the sample contained surfactant up to 39% of its weight and during ignition the surfactant might be lost by vaporization; thus the weight of surfactant-modified clay particles could not be determined.

The density of post-cured resin was determined by determining its weight and volume. Three different post-cured resin cylinders were made and used to determine their average density. The results are given in Table 8. The density of three different

samples showed a consistent results from sample to sample. The average density value over those of the three samples was substituted for d_f in Equation (2) to calculate the void fraction.

Table. 7. Fiber Volume Fraction and Sample

Void Content of Plain GFRP Samples

Sample	Sample Weight(g)	Sample Volume(cm ³)	Fiber Weight(g)	Fiber wt. %	Fiber Volume (%)	Void Content (%)
2Q-1	1.3683	0.9107	0.6953	50.81	29.76	4.9
2R-1	1.3404	0.8836	0.7002	52.24	30.89	5.02
2S-1	1.3635	0.91	0.7014	51.44	30.05	5.6
2T-1	1.3297	0.8881	0.6843	51.46	30.04	5.69
2U-1	1.4049	0.9633	0.6816	48.52	27.58	6
2V-1	1.3367	0.9079	0.645	48.25	27.7	4.91
2W-1	1.4534	0.9893	0.6983	48.05	27.52	4.99
2X-1	1.3943	0.9522	0.6991	50.14	28.62	6.8
2Z-1	1.3343	0.8833	0.7291	54.64	32.18	7.21
2AA-1	1.3943	0.9476	0.7258	52.05	29.86	7.74
2AB-1	1.2953	0.8401	0.7076	54.63	32.84	5.29
2AC-1	1.3621	0.91	0.6904	50.69	29.58	5.14
2AD-1	1.3784	0.9126	0.7387	53.59	31.56	6.44
2AE-1	1.3483	0.8913	0.7113	52.76	31.11	5.68
Average	1.3813	0.9283	0.7007	50.85	29.56	5.74
STD				2.08	1.62	0.88

Table. 8. Density of Post-Cured Resin Cylinders

Sample Cylinder	(1)	(2)	(3)
Weight	14.254	14.1402	14.5391
Height 1 (cm)	1.654	1.65	1.708
Height 2 (cm)	1.687	1.66	1.72
Height 3 (cm)	1.669	1.664	1.716
Height 4 (cm)	1.669	1.64	1.716
Average Height	1.67	1.654	1.715
Diameter (cm)	3.101	3.127	3.121
Density g/cm ³	1.1306	1.113	1.108

4.3 Optical Microscopic Pictures for Non-aged Samples

Non-aged samples with and without nanoclay were used as non-aged reference samples. The pictures which were taken with 100x and 300x magnifications were shown in Figures 17 and 18, respectively.

In Figure 17, the white cylinders inside the polymer matrix were vertical glass fiber strands and the white strips are horizontal fiber strands. Polymer matrix as shown in Figure 18 has many irregularly shaped clay particles which are well dispersed inside the polymer matrix.

Figure 17. Non-aged plain GFRP sample with 100x magnification.

Figure 18. Non-aged nano-GFRP sample with 300x magnification.

Figures 19 and 20 show vertical fiber strands with a larger magnification of 500 of non-aged plain GFRP and nano-GFRP samples respectively. The fiber strands of the two pictures look almost the same.

Figure 19. Non-aged plain GFRP sample with 500x magnifications

Figure 20. Non-aged nano-GFRP sample with 500x magnifications

4.4 Sustained-Load Tests with 3560N (800-lbs)

Thirty two samples were used to conduct 3560N (800-lbs) sustained-load tests. This load corresponded to 50% of the tensile strength. Sixteen plain GFRP samples and 16 nano-GFRP samples were used to conduct the tests. The time to failure for plain GFRP samples and nano-GFRP samples were given in Tables 9 and 10, respectively. It can be seen from the tables that the time to failure are varied in a wide

range for both kinds of composite samples. This phenomenon has been reported in literature.⁽⁷⁾ From Table 9, the average day to failure for all the samples is 12.5 days. If we only count the six samples which were failed in the middle, the average days to failure is 15.83 days. Also, from Table 10, the average days to failure for all the samples are 12 days. If we only count the seven samples which were failed in the middle, the average days to failure is 15.75 days. Those two sets of data are virtually identical, and thus it is concluded that nanoclay does not contribute against the aging process when 50% of tensile strength is applied.

Table. 9. Time to Failure with 3560N (800-lbs)

Sustained Load for Plain GFRP Samples

Sample	Sample Weight(g)	Failure Days	Failure Mode
2K-2	15.7	24	Middle
2K-3	15.8		Sample leak
2K-4	15.7	7	Middle
2K-5	15.7	24	Middle
2M-2	15.8	14	Tab hole
2M-3	16.1		Sample leak
2M-4	16.1	10	Tab & leak
2M-5	16.2	18	Middle
2N-2	15.8	13	Middle
2N-3	16		Sample leak
2N-4	16.1		Fail in the beginning
2N-5	16.3	6	Tab
2O-2	16.3	10	Tab
2O-3	16.4	7	Tab
2O-4	15.5	9	Tab (leak once)
2O-5	15.8	9	Middle

Table. 10. Test Results for 3560N (800-lbs) Alkaline Sustained-load Tests

Sample	Sample Weight(g)	Failure Days	Failure Mode
2CD-2	15.6	9	Tab
2CD-3	15	6	Tab
2CD-4	14.7	9	Tab
2CD-5	15.7	16	Middle(slow leak)
2CE-2	16.5	6	Tab
2CE-3	16.5	14	Middle
2CE-4	16.4		Leak
2CE-5	15.8	12	Middle
2CG-2	16.4	10	Middle
2CG-3	16.6	13	Tab
2CG-4	16.4	14	Middle
2CG-5	16.4	17	Middle
2CH-2	16	30	Middle
2CH-3	16.2	11	Tab
2CH-4	16.1		Leak
2CH-5	16.2	13	Middle

It was observed that the alkali solution leaked from the solution reservoir on both kinds of the composite samples. This may be because the glass fiber strands are debonded from the polymer matrix under this high load and micro-channels are developed through which alkali solution migrates, attacks the fiber strands and causes aging. The development of such channels under 3560N (800-lbs) load for composite is seen in Figure 21.

Cracks are developed very extensively on the plain and nano GFRP samples under 3560N (800-lbs) load as can be seen from Figures 21 and 22, respectively. The crack development looks almost the same for plain and nano-GFRP specimens. One can see from these pictures that micro-cracks are connected to form long channels. These channels may serve as a path for alkaline solution to reach fiber surface easily,

which may lead to extensive aging of the composite materials.

Figure 21. Crack development on a nano-GFRP specimen
under 3560N (800-lbs) load (100x).

Figure 22. Cracks development on a plain GFRP specimen
under 3560N (800-lbs) load (100x).

Figure 23 shows a sever case of channeling or a rupture on a plain GFRP samples under 3560N (800-lbs) load. The expanded picture of alkaline attack on a

nano-GFRP sample under 3560N (800-lbs) load with 500x magnifications is seen in Figure 24. The picture shows thick dark lines around the glass fiber strands. These lines may be due to alkaline attacks. This attack may contribute to debonding of the fiber glass from the matrix, and thus cause the aging.

Figure 23. Polymer matrix rupture on a plain GFRP sample surface (100x).

Figure 24. Alkaline attack on a glass fiber inside a nano-GFRP sample sustained with 3560N (800-lbs) load (500x).

4.5 Sustained-Load Tests with 2225N (500-lbs)

Thirty two samples were used to conduct 2225N (500-lbs) alkaline sustained-load tests. Sixteen plain GFRP samples and 16 nano-GFRP samples were used to conduct the tests. The results are shown on Tables 11 and 12 for GFRP and nano-GFRP samples, respectively.

The average time to failure for plain GFRP samples is 73.1 days that is calculated by the data in Table 11. As can be seen from Table 12, the time to failure for nano-GFRP samples give different values with respect to different batches. For example, sample sets of 2CK and 2CL yielded the average time to failure as 119 days while sample sets 2CI and 2CJ yielded the time to failure as 54.5 days. This huge difference may be related to the dispersion of clay particles in the polymer matrix during the preparation step. It is considered that the sample sets yielding longer time to failure had better dispersed and exfoliated clay platelets through out the polymer matrix than the sample sets yielding shorter time to failure. The average time to failure for all sets of nano-GFRP samples is 83 days which is slightly longer than that of plain GFRP samples (73.1 days). It is interesting to note that nano-GFRP samples (2CK-3) has not been broken for 180 days and is still going on as of November 11, 2003.

. The optical microscopic pictures of an aged plain composite sample sustained with 2225N (500-lbs) load is shown in Figure 25. This picture shows much less cracks than those of Figure 22 which is a counter part for 2225N (800-lbs) sustained load. Also, Figure 26 shows much less cracks on a nano-GFRP specimen developed under 2225N (500-lbs) load than those of Figure 24 which is a counterpart for 3560N (800-lbs) sustained-load.

Table. 11. Time to Failure with 2225N (500-lbs)

Sustained Load for Plain GFRP Samples

Sample	Sample Weight(g)	Failure Days	Failure Mode
2Q-2	15.7	65	Middle
2Q-3	15.7	49	Middle
2Q-4	15.6	56	Middle
2Q-5	15.7	60	Middle
2R-2	16	83	Middle
2R-3	16	73	Middle
2R-4	15.8	65	Middle
2R-5	15.8	83	Middle
2S-2	15.6		Leaking
2S-3	15.9	73	Middle
2S-4	15.5	92	Middle
2S-5	15.8	73	Middle
2T-2	15.8	74	Middle
2T-3	15.8	74	Middle
2T-4	15.6	103	Middle
2T-5	15.5	74	Middle

Figure 25. Micro cracks on a plain GFRP sample
sustained with 2225N (500-lbs) load (100x).

Figure 26. Alkaline attack on glass fiber inside a nano-GFRP sample sustained with 2225N (500-lbs) load(500x).

Table. 12. Time to Failure with 2225N (500-lbs)

Sustained Load for Nano-GFRP Samples

Sample	Sample Weight(g)	Failure days	Failure Mode
2CI-2	16	41	Middle
2CI-3	16.1	69	Middle
2CI-4	16.1	55	Tab
2CI-5	15.9	60	Middle
2CJ-2	15.6	45	Middle
2CJ-3	15.9	53	Middle
2CJ-4	16	57	Middle
2CJ-5	16.4	56	Middle
2CK-2	15.4	73	Middle
2CK-3	15.8	Running	
2CK-4	15.8	87	Middle
2CK-5	15.9	141	Middle
2CL-2	16	113	Middle
2CL-3	15.8	151	Middle
2CL-4	15.8	98	Middle

4.6 Sustained-Load Tests with 884N (200-lbs)

Twenty-four samples were used to conduct 885N (200-lbs) sustained-load tests. Twelve plain GFRP samples and 12 nano-GFRP samples were used to conduct the tests. These samples were aged for three months using the same procedures as before. Then these samples were tested for the ultimate tensile strength with Instron 8500. The results for plain GFRP and nano-GFRP samples were provided in Table 13 and 14, respectively. The average tensile strengths of aged plain GFRP and nano-GFRP samples under 885N (200-lbs) load for 3 months became 181.9Mpa (26.4ksi) and 174.1Mpa (25.3ksi), respectively.

4.7 Aging Index of Alkaline Sustained-Load Tests

In order to standardize the aging effect on both plain GFRP and nano-GFRP samples, Aging Index is proposed.

$$A.I. = \frac{\sigma_0 - \sigma_a}{d} \dots\dots\dots (3)$$

where:

A.I. = Aging Index, MPa /day

σ_0 = Tensile strength of non-aged sample, MPa

σ_a = Failure stress or residual tensile strength of aged sample, MPa

d = Failure days or exposure, days

In the case of 3560N (800-lbs) and 2225N (500-lbs) alkaline sustained load tests, σ_a is the applied stress as 3560N (800-lbs) and 2225N (500-lbs) divided by the average cross-sectional area of test specimens. On the other hand, σ_a is the residual tensile strength of the aged sample with 885N (200-lbs) sustained-load tests which was measured with Instron 8500 machine.

Table.13. Residual Tensile Strength with 885N (200-lbs)**Sustained-Load for Plain GFRP Samples**

Sample	Failure Load		Residual Tensile Strength		Failure Mode
	lb	N	ksi	MPa	
2AA-2	1344	5980	25.2	173.7	Tab
2AA-4	1622	7217	29.2	201.2	Middle
2Y-2	1434	6380	24.9	171.7	Middle
2Y-3	1524	6781	28.3	195.3	Tab
2Y-4	1462	6504	26.2	180.6	Middle
2Y-5	1574	7003	28.0	192.9	Tab
2Z-2	1413	6287	25.5	176.1	Middle
2Z-3	1541	6856	26.9	185.7	Middle
2Z-4	1354	6024	23.7	163.4	Tab
2Z-5	1528	6879	26.1	179.7	Middle
Average			26.4	181.9	
STD			1.7	11.74	

Table.14. Residual Tensile Strength with 885N (200-lbs)**Sustained-Load for Nano-GFRP Samples**

Sample	Failure Load		Residual Tensile Strength		Failure Mode
	lb	N	ksi	MPa	
2CS-2	1546	6879	26.7	183.9	Tab
2CS-3	1544	6870	28.1	193.8	Tab
2CS-4	1541	6856	26.7	184.1	Tab
2CP-2	1249	5557	23.1	159.4	Tab
2CP-3	1440	6407	25.7	176.9	Tab
2CP-4	1407	6260	24.4	168.5	Tab
2CP-5	1329	5913	23.8	164.4	Tab
2CQ-2	1370	6096	26.2	180.7	Middle
2CQ-3	1460	6495	26.5	182.5	Middle
2CQ-4	1255	5584	21.7	149.9	Middle
2CQ-5	1477	6572	24.9	171.4	Tab
Average			25.3	174.1	
STD			1.88	12.8	

An empirical equation has been established to relate the Aging Index to the applied stress as given:

$$A.I. = a\sigma^2 + b \dots\dots\dots(4)$$

where “a” and “b” are constants., and σ is the applied stress. Note that in the case of 3560N (800-lbs) and 2225N (500-lbs) sustained-load tests, σ_a and σ are the same.

Figure 27. Linear relationship between Aging Index and square of the applied stress for plain and nano GFRP materials.

The Aging Index values were plotted against σ^2 according to Equation (4) as can be seen from Figure 27. A good linear relationship is established with R^2 value of 0.9931 for plain GFRP samples. In this figure, there are three data points for 2225N (500-lbs) for nano-GFRP samples. The upper one is for less durable samples (sample sets 2CI and 2CJ), the bottom one is for more durable samples (sample sets 2CK and 2CL), and the middle one is the average between those two. The time to failure data

for these samples are given in Table 12.

For the plain GFRP samples, “a” equals to $6 \times 10^{-4} \text{ (MPa} \times \text{day)}^{-1}$ and “b” equals to -0.4316 MPa/day. The intercept value of “b” shows a negative value. This is apparently an error since A.I. can not be negative. The empirical equation shows that A.I. is a function of σ^2 . The second order with respect to σ may be due to the fact that the stress contributes to the aging in two fold. First, it may contribute directly to the aging and second, it may contribute to a phenomenon that can be developed indirectly such as increase of void fraction to result in aging. The increase of void fraction might contribute to the aging by accelerating the diffusion rate of the alkaline solution through the matrix.

Aging Index is not constant but decreases probably exponentially as the number of days increases. ^(8, 35) However, in the present study, the average failure time with 2225N (500-lbs) load is 73.1 days for plain GFRP samples and 84 days for nano-GFRP samples. These failure times are close to 90 days of exposure time for evaluation of tensile strength reduction with 885N (200-lbs) load. Thus the time constraints imposed for evaluating Aging Index for these two cases may be eliminated. However, the failure time with 3560N (800-lbs) load is 15.8 days for plain GFRP samples and nano-GFRP samples. This failure time is the longest and can not be extended to the time frame of 73 and 90 days. In this context, the Aging Index with 3560N (800-lbs) load should be compared with those of less loads evaluated with longer time frame.

Chapter V

Conclusion

1. At 3560N (800-lbs) sustained-load tests, the average days to failure for plain GFRP and nano-GFRP samples are 15.83 and 15.75 days, respectively. The results of these tests showed that durability of the two samples were almost the same under 3560N (800-lbs) sustained load. The microscopic pictures of aged plain GFRP and nano-GFRP samples showed many cracks in the polymer matrix. It seems that these cracks formed channels through which alkaline solution arrived at the surface of glass strands freely and attacked the strands. Thus, the addition of nanoclay into polymer matrix was not affected to retard the alkaline attack because the addition of nanoclay was designed to retard the diffusion of the alkaline solution through polymer matrix.
2. In the tests of 2225N (500-lbs) sustained-load tests, the nanocomposites samples are slightly more durable with 83 days of failure time than plain composite samples with 73 days of failure time. However, in the case of nano-GFRP samples, the average days to failure of some samples (7) is 119 days while that of other samples (8) is 54.3 days. It is considered that the more durable samples have clay platelets which are more exfoliated in the polymer matrix than those in the less durable samples.
3. In the tests of 885N (200-lbs) alkaline sustained-load tests, the residual strengths are 181.9Mpa (26.4ksi) and 173.6Mpa (25.2ksi) for the plain GFRP and nano-GFRP samples, respectively. Compared to the tensile strength of non-aged samples which is 208.7Mpa (30.3ksi). The effect of alkaline solution attack is significant. However, these residual strengths of plain GFRP samples and

nano-GFRP samples are almost the same.

4. An Aging Index was proposed as the tensile strength reduction per day. It is found that the Aging Index is a function of the square of the applied stress in an empirical equation. This second order with respect to applied stress relationship can be considered as a combination of direct effect and indirect effect such as increasing void fraction under applied stress.

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APPENDICES

APPENDIX I

Physical and Chemical Properties of Cloisite® 10A Nanoclay

Description:

Cloisite® 10A is a natural montmorillonite modified with a quaternary ammonium salt.

Table. 14. Typical Properties of Cloisite® 10A nanoclay

<u>Treatment/Properties:</u>	Organic Modifier (1)	Modifier Concentration	% Moisture	% Weight Loss on Ignition
Cloisite® 10A	2MBHT	125 meq/100g clay	< 2%	39%

Where HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14)

Anion: Chloride

(1) 2MBHT: dimethyl, benzyl, hydrogenatedtallow, quaternary ammonium

Table. 15. Typical Dry Particle Sizes of Cloisite® 10A

nanoclay (microns, by volume)

10% less than:	50% less than:	90% less than:
2μ	6μ	13μ

Color: Off White

Table. 16. Density of Cloisite[®] 10A nanoclay

Loose Bulk, lbs/ft ³	Packed Bulk, lbs/ft ³	Specific Gravity, g/cc
10.21	16.52	1.90

X Ray Results: $d_{001} = 19.2\text{\AA}$

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