SHORT TERM CHARACTERISTICS AND ENVIRONMENTAL AGING OF BIO-RESIN GFRP TESTED IN TENSION AND FOR CONFINEMENT OF CONCRETE CYLINDERS

by

Amanda Eldridge

A thesis submitted to the Department of Civil Engineering

In conformity with the requirements for

the degree of Masters of Applied Science

Queen's University

Kingston, Ontario, Canada

(August, 2013)

Abstract

Conventional fiber reinforced polymers (FRPs) require polymers such as epoxies that are not biodegradable, which have a significant impact on the environment. The first phase of the thesis aims at replacing conventional polymers with sustainable bio-polymers. The tensile mechanical properties of glass-FRP (GFRP) laminates using two types of organic furfuryl alcohol bio-resins extracted from renewable resources, such as corncobs, were investigated. Results are compared to control specimens fabricated using conventional epoxy resin. It was shown that by careful selection of viscosity of bio-resin, and type and dosage of catalyst, similar mechanical properties to epoxy-GFRP can be achieved.

The second and third phases consisted of durability testing of the bio-resin GFRP. A total of 160 tension coupons and 81 unconfined and confined concrete cylinders wrapped with bio-resin-GFRP were studied. Conditioning was achieved by immersion of the specimens in saline solutions with 3% salt concentration, at 23^o, 40^o and 55^oC, for up to 300 days. Specimens were compared to epoxy-GFRP specimens aged in the same environment. Deterioration was quantified by tensile testing of the coupons and compression testing of the cylinders at various stages of exposure. The bio-resin-GFRP showed 33% less tensile strength retention than the epoxy-GFRP. The epoxy-GFRP and bio-resin-GFRP wrapped cylinders had the same un-aged confined axial compressive strength ($f_{cc}^{'}$), essentially a strengthening ratio ($f_{cc}^{'}/f_{c}^{'}$) of 2.24. After 300 days, the ($f_{cc}^{'}/f_{c}^{'}$) ratio retentions for the bio-resin-GFRP was 73% at all temperatures. Using the Arrhenius model, it was predicted that 61% retention in tensile strength of the bio-resin-GFRP and 65% retention of the compressive strength of wrapped cylinders would occur after 100 years in an environment with a mean annual temperatures of 10^o.

Acknowledgements

I would like to thank Dr. Fam for all of his support, guidance and encouragement throughout my time doing my Masters research. Special thanks go to Dave Lynch and Neil Porter for their excellent technical knowledge and support over the past two years.

I would also like to thank Mark Nelson, Kenneth Mak and all the other graduate students in Ellis Hall for their advice and a helping hand and for all the memorable times we had in the last two years.

I also wish to acknowledge the financial support provided by Ontario Ministry of Agriculture, food, and Rural Affairs (OMAFRA).

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

1.1 GENERAL

Fibre reinforced polymers (FRPs) have been used in many applications over the years, from new construction to retrofitting. Their lightweight properties, corrosion resistance and high strength make them ideal for these applications. FRPs are comprised of two basic components: fibres and resin. The fibres provide the strength and stiffness of the composite while the resin acts as a matrix, allowing stress to be uniformly distributed among the fibres. Carbon, glass and aramid are among the most widely used fibres, and vinyl ester, polyester and epoxy are the most common resins used in practice for civil applications. Each combination of resin and fibres provides a different set of mechanical and environmental characteristics.

Unfortunately, conventional resins such as epoxies are unsustainable. In order to reduce the environmental impact, the epoxy can be replaced with a more "green" alternative. This is a step towards a more sustainable FRP. Many natural thermosetting polymers are based from corn, soybean and tung oil [Lu et al, 2005; Li et al, 2003; Casado et al, 2009]. Numerous studies have been done on natural resins in combination with natural fibres [Wollerdorfer and Bader, 1998; Wambua et al, 2003; O'Donnell et al, 2004]. However, most natural fibres do not have the mechanical properties to be used in structural applications.

FRPs can be used to retrofit concrete columns to increase their axial strength. This is accomplished by encasing or wrapping columns with FRP. The FRP wrap is oriented primarily in the hoop direction in order to restrain the dilation of the column at high

strains, thereby increasing the column's capacity. This type of retrofitting is a very economical option compared to concrete jacketing of the column.

Short- and long-term mechanical characteristics are needed to fully understand how a material behaves before it is applied in the field. Long-term tests evaluate the durability of a material by exposing it to different environments. Many research studies have been conducted on FRPs being exposed to freeze/thaw, wet/dry and alkaline environments [Al-Zahrani et al, 2002; Rivera et al, 2010; Robert et al, 2012; Chen et al, 2007; Cromwell et al, 2010]. In marine environments, FRPs would be exposed to saltwater at varying temperatures.

This research focuses on the short- and long-term mechanical properties of a bio-resin GFRP based from furfuryl alcohols. In the first phase of the project, many combinations of bio-resin and catalysts were investigated in order to determine the ideal mix proportions that produce the greatest strengths. Other parameters were investigated as well, including curing time, lap splice length and catalyst dosage. The next phase of this research consisted of long-term testing by exposing the bio-resin GFRP to three saltwater baths at three different temperatures. Epoxy GFRP was also aged in these baths as control specimens to compare the bio-resin GFRP results to. At 14, 29, 97, 182 and 300 days, five bio-resin- and five epoxy- GFRP coupons were removed from the tanks and tested in tension. The last phase of this research consisted of fabricating and aging 72 concrete cylinders. Some were retrofitted with bio-resin and epoxy-GFRP, while others were unconfined. After 29, 97, 182 and 300 days, cylinders were removed from the tanks and tested in axial compression. Results were compared to additional nine un-aged control specimens.

1.2 OBJECTIVES

The objectives of this research are as follows:

1. To determine the ideal mix proportion and curing time of the bio-resin and catalyst based on the mechanical properties.
2. To examine the effect of saltwater baths at different temperatures on bio-resin GFRP and bio-resin GFRP wrapped concrete cylinders over 300 days.
3. To compare the bio-resin GFRP results to conventional epoxy GFRP.
4. To predict the property retention of the bio-resin GFRP and bio-resin GFRP wrapped concrete cylinders over their service life.

1.3 SCOPE

The scope of this thesis consists of developing the short- and long-term characteristics of a bio-resin GFRP. The tensile properties of a bio-resin GFRP were determined and durability testing was conducted.

The experimental work was divided into three phases. Phase I of this research was designed to determine the ideal bio-resin, catalyst type, dosage and curing time of a "green" GFRP. A total of 87 coupons were fabricated examining these parameters. Tensile tests were conducted and results were compared to conventional epoxy GFRP.

Phase II addressed the long-term properties of the bio-resin GFRP coupons. Durability of this structural material was examined by exposing the bio-resin GFRP composites to a saline solution with 3% salt concentration, at 23^{o}, 40^{o} and 55^{o}C, for up to 300 days. A total of 150 bio-resin and epoxy GFRP coupons were fabricated and exposed to this environment. Deterioration of these composites was quantified by tensile testing at various stages of exposure and compared to conventional epoxy GFRP.

Phase III of this thesis research focused on the durability of bio-resin GFRP wrapped concrete cylinders. Conditioning was achieved by immersion of various groups of GFRP wrapped 153 x 305 mm cylinders in saline solutions with 3% salt concentration, at 23^{o}, 40^{o} and 55^{o}C, for up to 300 days. The groups included nine control specimens fabricated with conventional epoxy resin for comparison and plain concrete cylinders. A total of 72 confined and unconfined cylinders were conditioned. Specimens were then tested in axial compression periodically, at 29, 97, 182 and 300 days.

1.4 THESIS FORMAT

This thesis consists of 5 main chapters. Chapter 1 provides a brief description of the overall research, scope of the project and background information of GFRP composites, retrofitting applications and durability testing. Chapter 2 describes the first phase of this research, which consists of examining bio-resin GFRP coupons over different parameters. Chapter 3 provides the second phase of this research and describes the environmental testing of bio-resin and epoxy GFRP coupons in saltwater baths. Chapter 4 presents the last phase of the project, which consists of the environmental testing of bio-resin GFRP wrapped concrete cylinders. Lastly, Chapter 5 consists of the conclusions.

Chapter 2: Mechanical Characteristics of Glass Fibre Reinforced Polymer made of Furfuryl Alcohol Bio-resin[1]

2.1 INTRODUCTION

Fiber Reinforced Polymers (FRPs) are commonly used in structural retrofitting applications as well as in new construction. There are many benefits associated with using FRPs, such as its lightweight properties, ease of construction and corrosion resistant features [Karbhari, 2001]. However, polymeric resins used in FRPs, such as epoxies, are primarily composed of chemicals which are unsustainable. By replacing the matrix of the FRP with a bio-based resin, the environmental impact associated with producing FRPs will most likely be reduced. In order to continue having the superior structural characteristics conventional FRPs have, glass, carbon or aramid fibres still need to be incorporated into the FRP system. There have been many studies done on replacing synthetic fibres, like glass, with natural fibres [Wollerdorfer et al, 1998; Wambua et al, 2003; O'donnell et al, 2004; Adekunle et al, 2011; Williams et al, 2000]. These natural fibre composites have limited structural mechanical properties in terms of strength and stiffness, compared to FRPs with conventional fibers. However, it is possible to achieve comparable mechanical characteristics to conventional FRPs by using glass, carbon or aramid fibres with bio-resin matrices, which is the subject of the present study.

Within the last decade, research had been conducted on producing a bio-based resin made from natural oils [Khot et al, 2001; Miyagawa et al, 2005; Miyagawa et al,

[1] This chapters has been accepted for publication as the following journal paper:
Fam, A. and Eldridge, A. Misra, M. (2013) "Mechanical characteristics of glass fibre reinforced polymer made of furfuryl alcohol bio-resin." Journal of Materials and Structures, in press.

2006; Petrovic et al, 2005; Vroman et al, 2009; Li et al, 2002]. Corn, soybean, linseed and tung oils are some of the varieties of natural oils used to make thermosetting polymers [Lu et al, 2005; Li et al, 2003; Mosiewicki et al, 2005; Casado et al, 2009]. The bio-resins used in the present study are furfuryl alcohol based. Furfuryl alcohol resins are produced by condensing furfuryl alcohols in the presence of acid catalysts [JAFFE, 1962]. They are organic compounds derived from renewable resources such as, corn cobs and sugar canes [PennAKem]. For example, in Ontario there is a surplus of corn cob waste and therefore, could be used in this application.

The main objective of the present study is to establish the short-term mechanical properties of glass-FRP (GFRP) laminates produced using two different types of furfuryl alcohol bio-based resins at room temperature. Tensile tests have been conducted on these specimens to determine the ultimate strength and Young's modulus. Results have been compared to conventional GFRP composites, using epoxy resin, which represents the current state of practice. The study aims to establish the optimal curing time and optimal percentage of catalyst necessary for completing the curing process. The study also aims to establish the optimal length of over-lap splices of two laminates, which is required in certain structural applications such as wrapping concrete columns.

2.2 EXPERIMENTAL PROGRAM

2.2.1 Materials

One type of conventional continuous glass fiber fabric, three types of polymer resins including a conventional epoxy resin and two bio-resins, as well as two catalysts, were used in this study. The details of each type of material are provided next.

Glass Fibers: The continuous glass fibres used in this study are commercially available Tyfo® SEH-51A. This unidirectional 1.3 mm thick fabric comes in a 1.37 x 45.72 m roll. The reported tensile strength and modulus of the dry fibers by the manufacturer are 3240 MPa and 72.4 GPa, respectively.

Bio-Resins: Commercially available QuaCorr1001 and QuaCorr1300, referred to in this study as Q1, Q3, have been used. Both QuaCorr resins are furfuryl alcohol based, which is derived from renewable resources such as corn cobs. QuaCorr 1001 is a diluted version of QuaCorr 1300, which allows it to have a lower viscosity. Two different catalysts were used to cure the bioresins; p-Toluenesulfonic acid monohydrate 97.5%, and commercially available QuaCorr2001, which will be referred to as pTam and Q2001, respectively, in this study.

Epoxy-Resin: The epoxy resin used as a control in this study was Tyfo® S Epoxy resin, which is commercially produced to be used with the Tyfo® SEH-51A glass-fiber fabric. This two-part epoxy resin is mixed with a ratio of 100 parts of component A to 34.5 parts of component B by weight. The manufacturer reports a tensile strength and elastic modulus of the epoxy-resin as 72.4 MPa and 3.18 GPa, respectively.

2.2.2 Test Specimens and Parameters

A total of 87 coupon specimens were fabricated and tested in this study. Table 2-1 presents the test matrix. The parameters studied are: 1) type of bio-resin, 2) type of catalyst, 3) dosage of catalyst, 4) curing time, 5) number of glass fiber layers, and 6) length of lap-splice. Parameters 1 to 5 were studied using tension coupons and compared with control epoxy-based coupons in terms of the tensile strength and modulus. Parameter 6 was studied for tension coupons with different overlap lengths between two

layers to establish the optimal overlap. This arrangement represents certain structural applications where the GFRP laminates is used to wrap columns and an overlap region occurs.

Epoxy-GFRP coupons used as control specimens consisted of single layer fibres as well as double layer fibers in order to establish if a difference in the number of layers affected the strength of the coupon. A sample of these coupons is shown in Figure 2-1.

All bio-resin coupons were fabricated using a single layer of glass fiber fabric. The effect of catalyst type and dosage was investigated to determine its impact on strength and stiffness. QuaCorr1300 resin was combined with 1%, 3% and 6% pTam catalyst by weight, referred to in Table 2-1 as 1-pTam-Q3, 3-pTam-Q3, and 6-pTam-Q3 specimens, where the number in front of the abbreviations represents the percentage of catalyst used. QuaCorr1001 resin was combined with 3% pTam catalyst and 3% and 6% Q2001 catalyst, referred to in Table 2-1 as 3-pTam-Q1, 3-Q2001-Q1, and 6-Q2001-Q1. Figure 2-2 shows a typical bio-resin GFRP coupon.

Young's modulus and strength development over time is an important property of the bio-resin GFRP. Ten 3-Q2001-Q1 coupons were fabricated, and tested in three groups at three time intervals representing two days, four days and thirteen days curing time. These test results were compared to the strength and Young's modulus of similar 3-Q2001-Q1 coupons tested at 23 days.

Lap splice lengths were investigated to determine the optimal overlap length. Twenty five 3-Q2001-Q1 coupons were tested with 25 mm, 50 mm, 100 mm, 200 mm and 300 mm overlap lengths. The series aims to determine the minimum overlap length required in wrapping and strengthening applications.

2.2.3 Fabrication of Test Specimens

The fabrication of all coupons followed ASTM D3039 (2007). The lap splice coupons followed ASTM D7616 (2011). The bio-resin was prepared and mixed with a certain percentage of catalyst. It was then poured on to the glass fibre sheet and spread throughout. The glass fibre sheet was then flipped over and more resin was poured on to the surface. Once it was certain that the resin had fully saturated the glass fibres it was placed in between two HDPE smooth boards. Weights were then put on top of the boards. After seven days, the bio-GFRP composite was removed. The lap splice coupons were fabricated in a similar way. Two glass fibre sheets were saturated with resin, and then overlapped each other with the respective overlap length and cured. All coupons were cut parallel to the fibres using a diamond blade saw, to a width of 25±1.5 mm.

In order to facilitate gripping of the coupons at both ends during tension tests, each coupon had a set of tabs bonded to the ends of the coupon to eliminate the possibility of failure in the grips. Tabs were made of epoxy-GFRP plates adhered to the coupons with the fibres perpendicular to the fibres in the coupon. Sikadur 30 viscous epoxy was used to adhere the tabs to the coupons. Measurements of the width and thickness of each coupon were taken at both ends and the middle, in order to get an average. The measured width along with the manufacture's nominal thickness was used to calculate the cross sectional area and stresses. The length of the coupons between tabs was 130 mm, and the length of each tab was 56 mm. The thickness of the cured epoxy-GFRP single- and double-layer coupons was 1.32±0.07 mm and 2.33±0.13 mm, respectively. The thickness of the cured single-layer Q1001 bio-resin GFRP coupons was 1.20±0.19 mm.

2.2.4 Test Setup and Instrumentation

All coupons were tested in an Instron universal testing machine (model 8808), which had a maximum capacity of 250 kN. The hydraulic grips on the Instron were set to a grip pressure of 600 psi. Coupons were loaded in uniaxial tension. Each coupon was tested at a rate of 2 mm/min in accordance with ASTM D3039 (2007). The test setups for epoxy-coupons and 3-Q2001-Q1 bio-resin coupons are shown in Figure 2-3(a) and (b). Electric resistance strain gauges were applied to some of the initial sets of coupons, along with an extensometer. Once it was determined that the strain gauges and the extensometer produced similar results, only the extensometer was used on subsequent coupon tests. The stress strain plot of the strain gauge and extensometer results are shown in Figure 2-4. The extensometer used was removed from the coupons at specified loads prior to failure. This was to ensure that no damage was done to the extensometer during tests.

2.3 EXPERIMENTAL RESULTS AND DISCUSSION

A summary of test results of all tension and lap-splice coupon tests, in terms of the ultimate strength and modulus, including the average and standard deviation values is provided in Table 2-1. The following sections provide details of test results and the impact of various parameters on the mechanical properties.

2.3.1 Results of Control Specimens

Initial tensile tests on epoxy-GFRP coupons were completed to establish the reference mechanical properties of the current conventional system and also to determine if a difference in number of layers affected strength and elastic modulus properties. Figure 2-5 shows the stress-strain curves of the single layer and the double layer epoxy-GFRP coupons. The difference in ultimate strength is within 4%, therefore, all subsequent

testing using bio-resin GFRP coupons was carried out on single layers and compared to the single layer epoxy-GFRP. The ultimate strength of the epoxy-GFRP single layer coupons are also presented in Figure 2-6 and Table 2-1, along with the variation in results. The error bars shown in Figure 2-6 represent the maximum and minimum strengths for each type of coupons. A constant thickness of 1.3 mm was used to calculate the stress for all coupons in this study. This thickness represents the manufacturer specifications. The ultimate strength of the epoxy-GFRP was 525 MPa. Figure 2-7 (a) shows a picture of the failed epoxy-GFRP typical coupon. Fibres alone would not be able to produce these strengths without the matrix. This is because the matrix in the FRP distributes the force throughout the fibres, otherwise the fibres would fail one by one instead of load sharing.

2.3.2 Results of Bio-Resin GFRP Tension Coupons

In this investigation two different types of bio-resin and catalyst were examined. In order to determine the most suitable resin type and catalyst proportion, a variety of combinations were tested. A comparison between the different types of coupons and their corresponding ultimate strengths is displayed in Figure 2-6, along with the maximum and minimum test results. All coupon tests were tested 23 days after fabrication.

Effect of Catalyst Dosage on Strength: The catalyst dosage is an important factor that greatly affects the tensile strength of the resulting FRP. QuaCorr1300 was mixed with 1%, 3% and 6% pTam catalyst and used to produce bio-GFRP coupons (specimens 1-pTam-Q3, 3-pTam-Q3 and 6-pTam-Q3 in Table 2-1). Figure 2-8 shows the variation of ultimate tensile strength of bio-resin GFRP coupons and the dosage of pTam catalyst in

terms of its percentage by weight of the QuaCorr1300 bio-resin. The figure shows that the 3% catalyst produced the highest tensile strength. Additional catalyst resulted in the resin being over-catalyzed and hence a negative effect. This was the case when 6% catalyst was added, resulting in the bio-GFRP composite having low tensile strengths and high variance. In this case, the polymer began to crosslink before it had time to saturate the glass fibres. The 1% catalyst also produced poor results. This amount is simply too low to complete the curing of all the QuaCorr1300 resin. When all data was analysed, a trendline could be applied. This third degree polynomial trendline produced a peak at 2.5%, suggesting that this was the optimal dosage of catalyst, where a maximum tensile strength of 435 MPa was obtained. It should be noted that this was still 17% lower than the epoxy-GFRP tensile strength of 525 MPa. Based on this information it was determined that the QuaCorr1300 resin has its limitation in matching the tensile strength produced by epoxy resin. This was in fact due to the glass fibres not being fully saturated by the resin because of the resin's high viscosity. Upon careful visual inspection of the coupons after failure, it was revealed that fibres were dry at the core of the coupon as shown in Figure 2-7 (b). In this case, the glass fiber fabric was sandwiched between two layers of the bio-resin, but was not fully penetrated by the resin.

Effect of Bio-Resin and Catalyst Type on Strength: QuaCorr1001 resin was also tested because it had a more comparable viscosity to epoxy, allowing it to better saturate the glass fibres. The resin was mixed with a 3% pTam catalyst (specimens 3-pTam-Q1 in Table 2-1), which produced a higher GFRP coupon tensile strength (438 MPa) than the 3-pTam-Q3 GFRP coupons (417 MPa). QuaCorr1001 resin was also mixed with 3% and 6% Q2001 catalyst (specimens 3-Q2001-Q1 and 6-Q2001-Q1 in Table 2-1) and produced

tensile strengths of 520 and 508 MPa, respectively. This resin/catalyst mixture (i.e. specimens 3-Q2001-Q1) produced very comparable strength (520 MPa) to the epoxy-GFRP coupons (525 MPa). As such, the 3-Q2001-Q1 was considered the best combination because of its high strength and low variance. It was used throughout all subsequent tests. The GFRP coupons with QuaCorr1001 bio-resin also experienced an explosive failure but in contrary to the QuaCorr1300 coupons, all fibres were saturated, as shown in Figure 2-7 (c).

Effect of Bio-Resin and Catalyst Type and Dosage on Modulus: Figure 2-9 shows the stress-strain curves of the epoxy-GFRP and the 3-Q2001-Q1 bio-GFRP coupons. The data presented illustrates the similarity in Young's modulus and peak strength. The strain measured from the extensometer was used in determining the Young's modulus of all coupons. The extensometer was removed at the same load for each set of coupons. The strain range used to calculate the Young`s modulus for all coupons was from 0% to 0.5% (4 coupons from the series 6-pTam-Q3 and 1 coupon from the series 3-Q2001-Q1 50mm used a strain range of 0%-0.4% due to the extensometer being removed prematurely). The elastic modulus remained relatively constant throughout each set of tests completed. Figure 2-10 displays the effect of different resin/catalyst combinations on the elastic modulus. The average elastic modulus is shown with error bars representing the maximum and minimum modulus values for each set of coupons. The 1-pTAM-Q3 and 3-pTam-Q1 GFRP coupons showed the lowest modulus and the largest variability.

Effect of Curing Time on Strength and Modulus: An investigation of the time it took for the 3-Q2001-Q1 bio-GFRP composite to reach ultimate strength was completed. After 2, 4 and 13 days a set of three coupons were tested (specimens 3-Q2001-Q1 2days, 3-Q2001-Q1 4days, and 3-Q2001-Q1 13days in Table 2-1). By the second day the 3-Q2001-Q1 bio-GFRP coupons reached 84% of the full ultimate tensile strength as shown in Figure 2-11. After four days, 93% of the strength was reached, suggesting that most of the curing occurs within the first 4 days following fabrication. The full strength is achieved at about 12-14 days. Young's modulus was also monitored over time as shown in Figure 2-12. On the fourth day during one of the tests, the extensometer was not clamped to the coupon properly, which produced inaccurate strain results. This was considered an outlier in the data set. It can be concluded that there is a much lower variation of tensile modulus compared to strength during the time the 3-Q2001-Q1 coupons were cured.

2.3.3 Results of Bio-Resin GFRP Lap-Splice Coupons

In practice, GFRP sheets could be used to rehabilitate columns through wrapping. If this is the case, the overlap length needs to be determined, in order to provide a sufficient anchorage. Initially, lap splice lengths of 25 mm, 50 mm, and 100 mm (specimens 3-Q2001-Q1 25mm, 3-Q2001-Q1 50mm, and 3-Q2001-Q1 100mm in Table 2-1) were tested and the failure strength did not reach the ultimate tensile strength of the 3-Q2001-Q1 bio-GFRP tension coupons, as shown in Figure 2-13 (i.e. bond failure occurred at the overlap as shown in Figure 2-14 before tensile failure occurs outside the overlap region). There was a clean separation of the two GFRP sheets. Subsequently, the lap splice was increased to 200 mm and 300 mm (specimens 3-Q2001-Q1 200mm and 3-Q2001-Q1

300mm in Table 2-1). These lengths produced higher values of tensile strength, as shown in Figure 2-13, but still did not reach the ultimate tensile strength of the 3-Q2001-Q1 coupons. Once the lap splice reached around 200 mm, the strength started to plateau at a strength of about 68% of the potential full tensile strength. The failures of the 200 and 300 mm lap slice coupons remained the same as the previous failures shown in Figure 2-14.

2.4 SUMMARY

Conventional fiber reinforced polymers (FRPs) require polymers such as epoxies that are not biodegradable, which have a significant impact on the environment. This study aims at replacing conventional polymers with bio-polymers which are more sustainable. The study investigates the tensile mechanical properties of glass-FRP (GFRP) laminates fabricated by wet layup using two types of organic furfuryl alcohol bio-resins extracted renewable resources, such as corncobs. Results are compared to control specimens fabricated using conventional epoxy resin. The study investigates the effects of catalyst type and dosage as well as the curing time on the tensile strength and modulus of the GFRP. The study also investigates the optimal overlap splice of the laminates. It was shown that by careful selection of viscosity of bio-resin, and type and dosage of catalyst similar mechanical properties to epoxy-GFRP can be achieved. The optimal catalyst proportion was 3% by weight. Full strength occurred after 13 days curing but 84% occurred in two days. The optimal lap splice length was 200 mm, however, the maximum strength was only 68% of the full ultimate tensile strength as bond failure always governs at the splice.

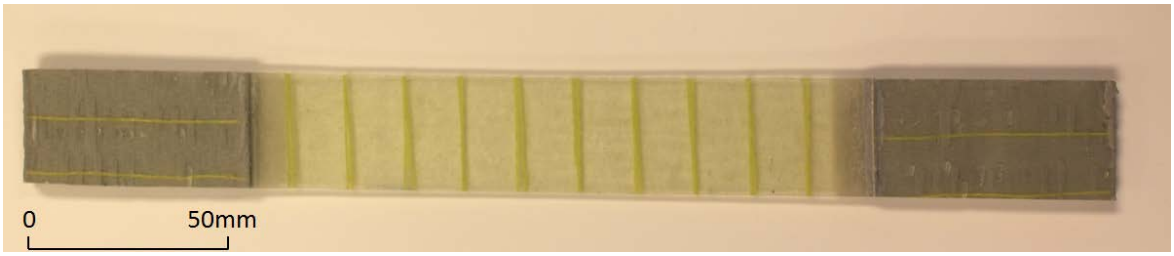


Figure 2-1: Epoxy-GFRP control coupon

Figure 2-2: Sample bio-resin GFRP coupon

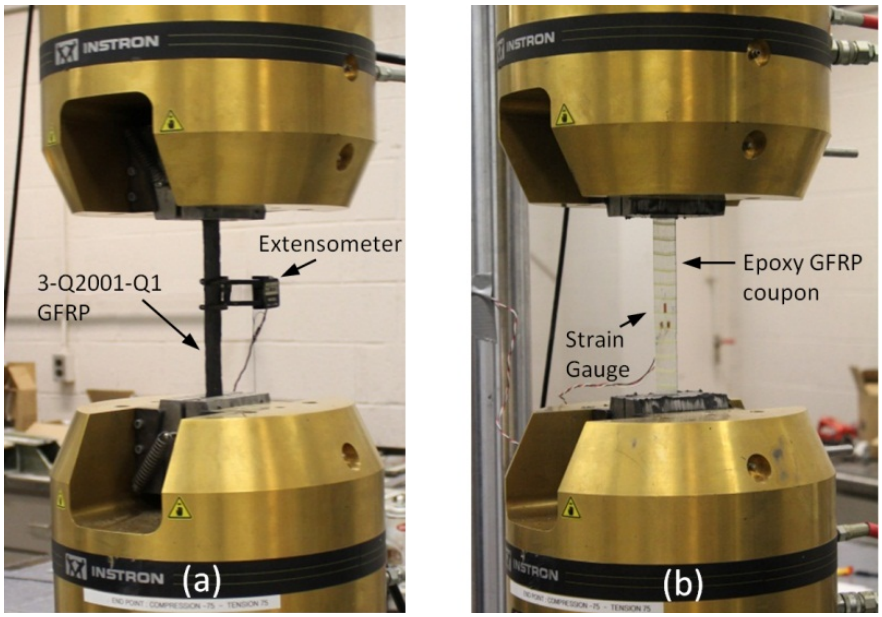


Figure 2-3: Test setup and instrumentation of (a) bio-resin GFRP coupons; and (b) Epoxy-GFRP coupons

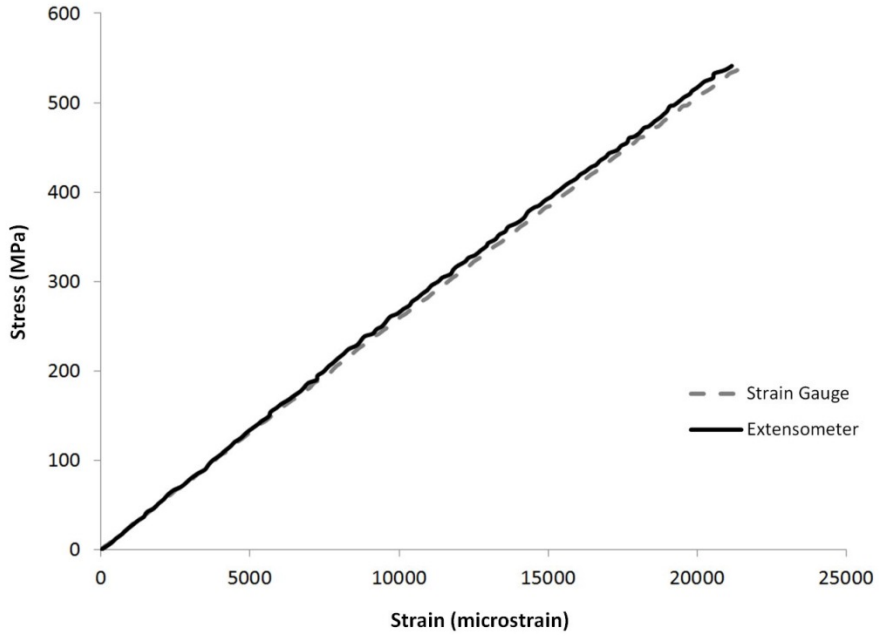


Figure 2-4: Stress strain plot of strain gauge and extensometer

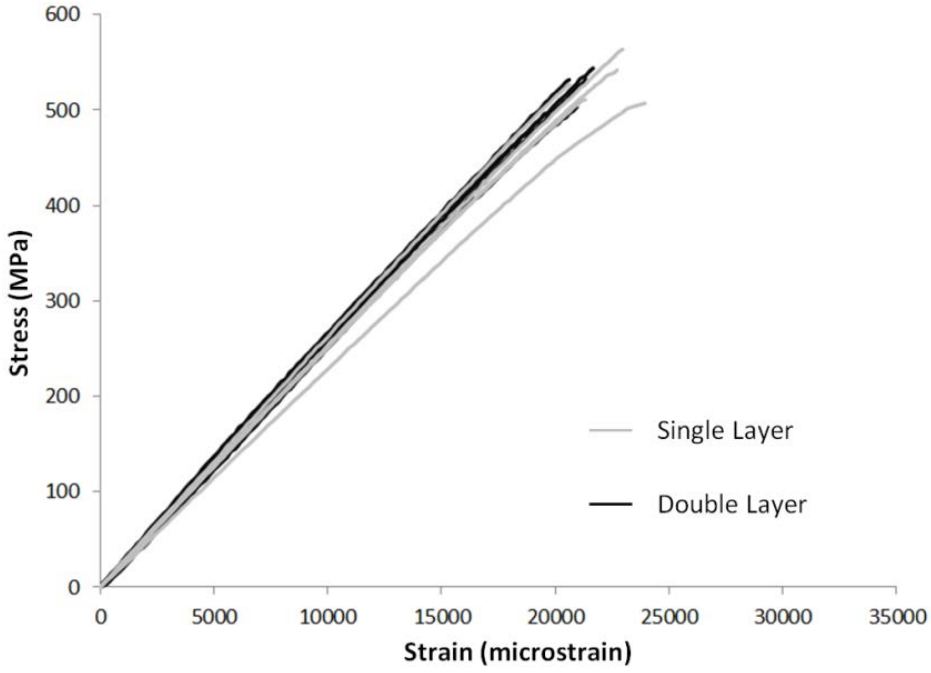


Figure 2-5: Stress-strain curve for epoxy-GFRP single and double layer coupons

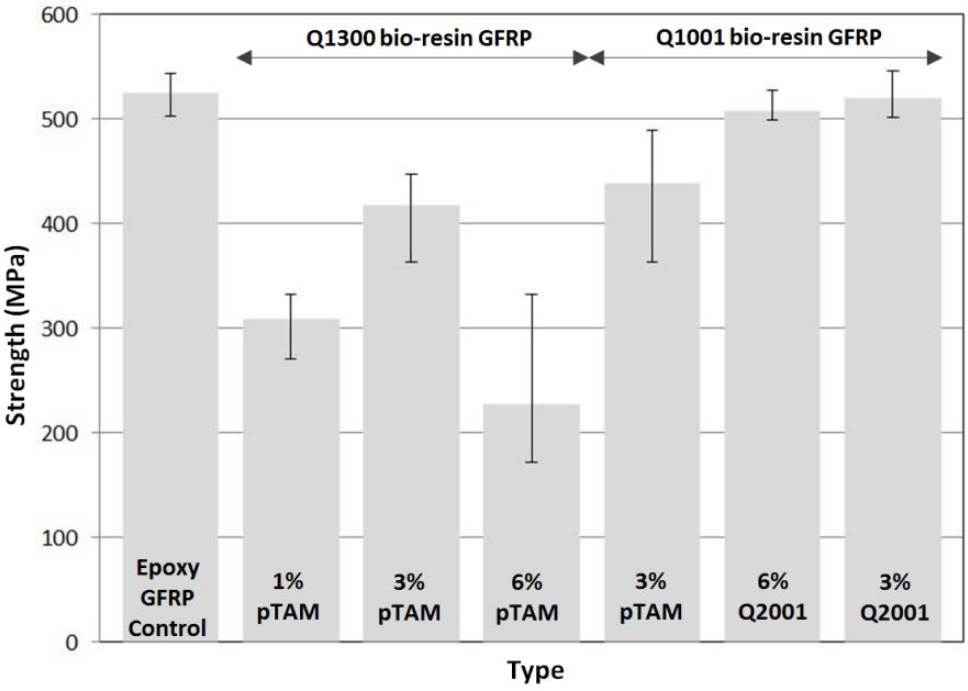


Figure 2-6: Ultimate strength of all types of GFRP coupons studied in this paper

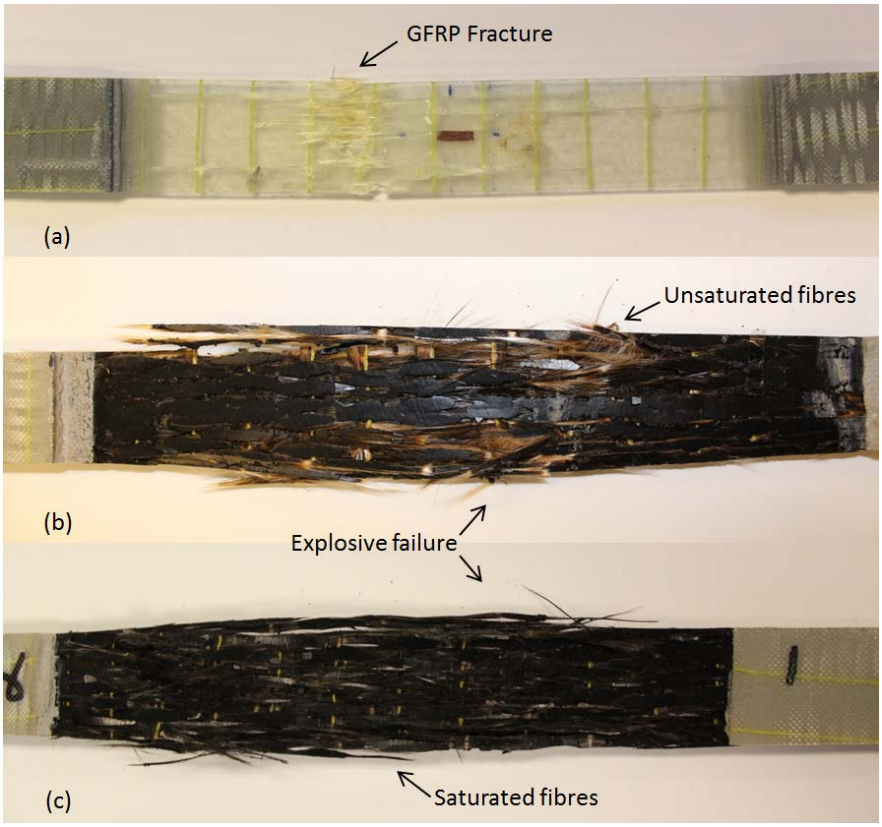


Figure 2-7: Failure modes of GFRP tension coupons: (a) epoxy-GFRP coupons, (b) QuaCorr1300 bio-resin GFRP coupons, and (c) QuaCorr1001 bio-resin GFRP coupons

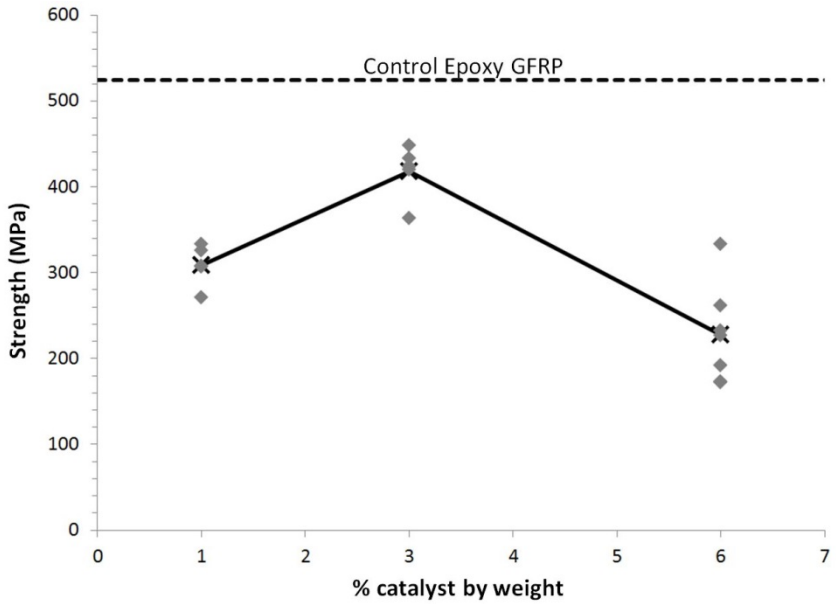


Figure 2-8: Variation of ultimate tensile strength of GFRP coupons with dosage of catalyst for QuaCorr1300 bio-resin

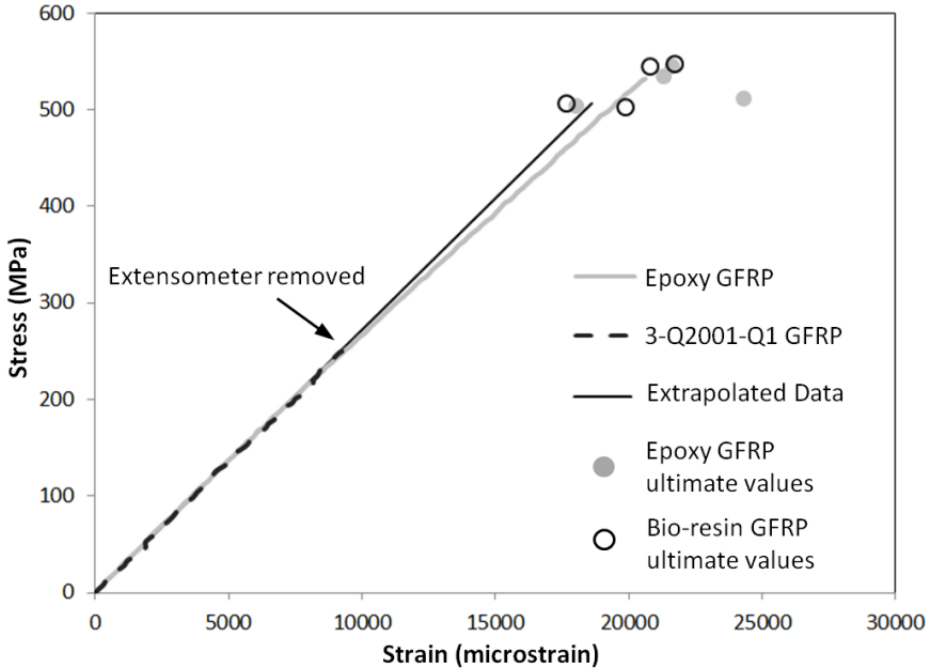


Figure 2-9: Stress-strain curve of epoxy-GFRP and 3-Q2001-Q1 bio-resin GFRP coupons

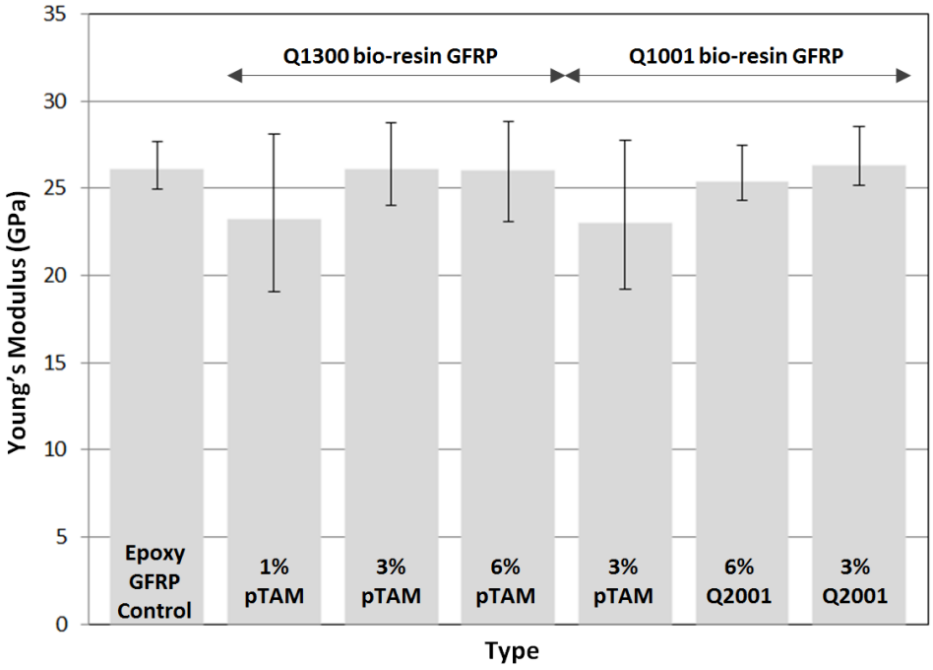


Figure 2-10: Effect of resin and catalyst types and dosage on elastic modulus of GFRP coupons

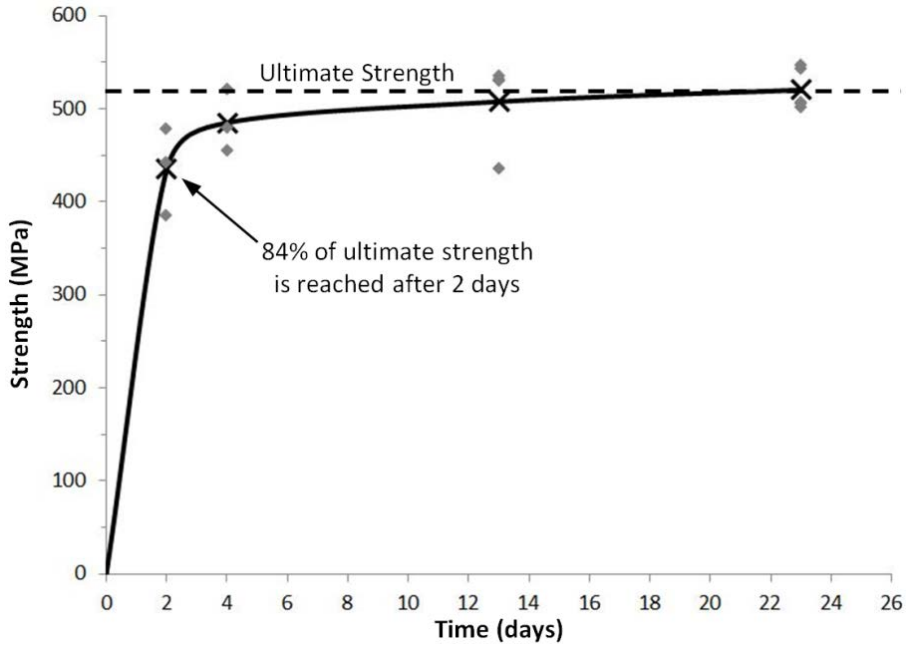


Figure 2-11: Variation of ultimate tensile strength of 3-Q2001-Q1 GFRP coupons with curing time

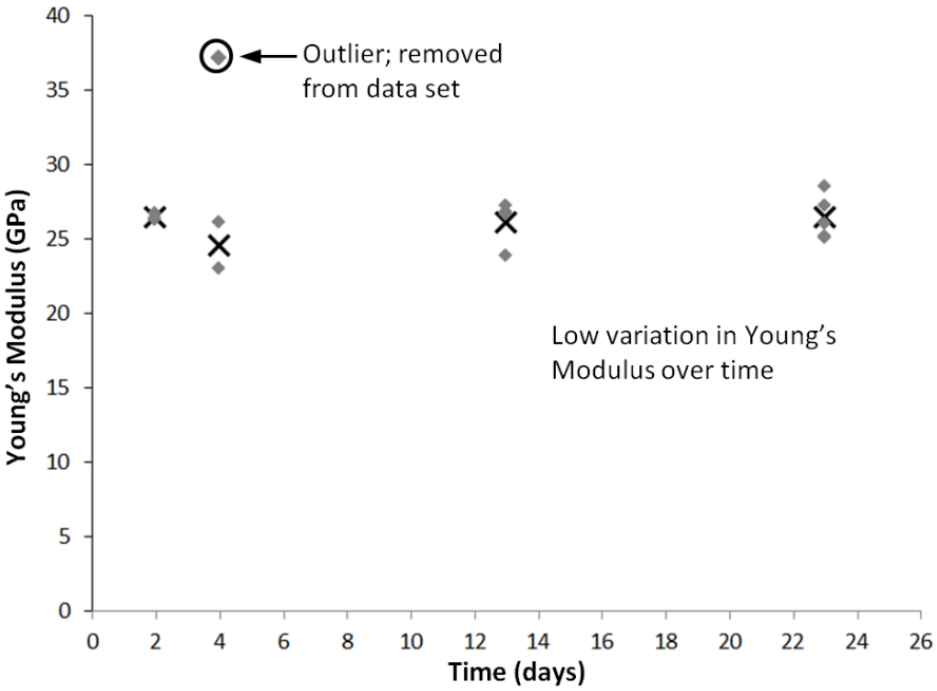


Figure 2-12: Variation of elastic modulus of 3-Q2001-Q1 GFRP coupons with curing time

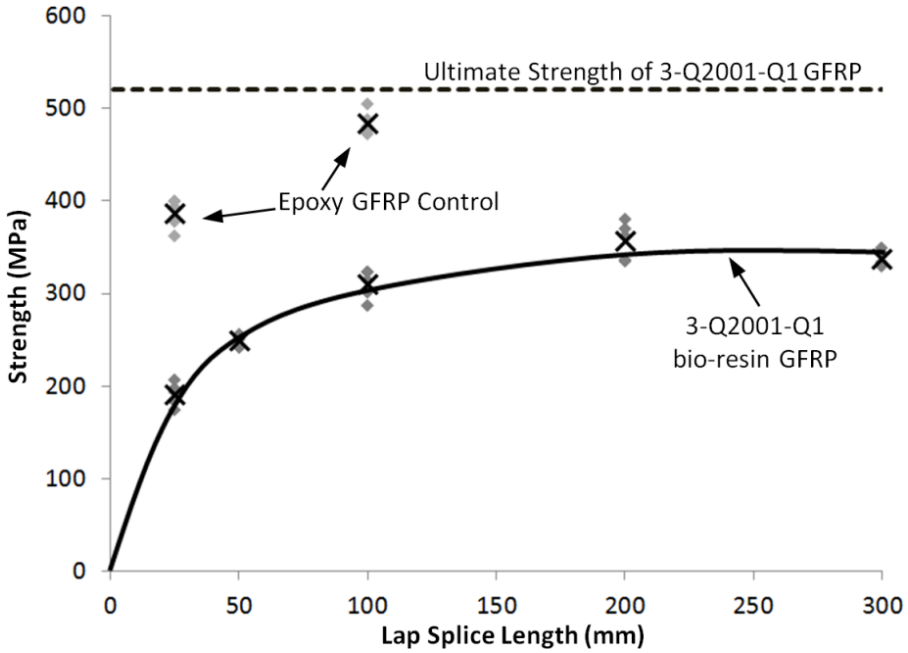


Figure 2-13: Variation of ultimate tensile strength with lap splice length for bio-resin- and epoxy- GFRP coupons

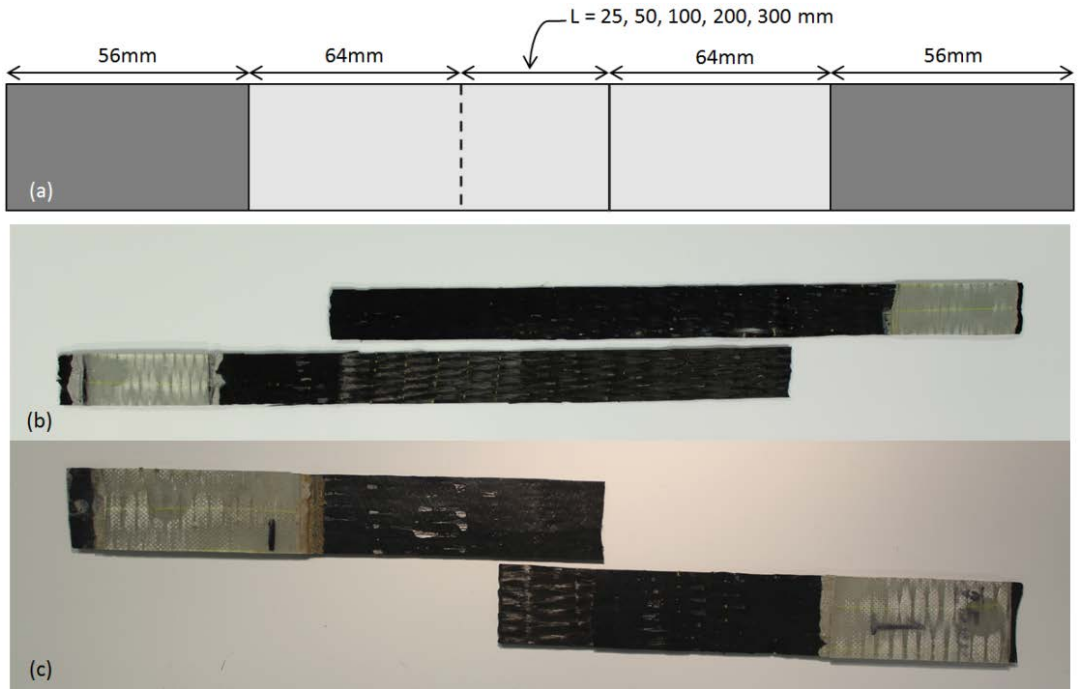


Figure 2-14: Lap Splice Coupons (a) schematic of lap splice coupons (b) 200 mm lap splice failure; (c) 25 mm lap splice failure

Table 2-1: Overview of test matrix and summary of test results

Coupon Type	No. of coupons used in calculation of mean	Mean maximum strengths (MPa)	Standard deviation (MPa)	Mean Young's Modulus (GPa)	Standard deviation (GPa)
Control Tension					
Epoxy Single Layer	5	525	17	26.78	1.5
Epoxy Double Layer	5	545	26	25.63	0.61
Control Lap Splice					
Epoxy 25 mm	5	386	16	25.89	0.82
Epoxy 100 mm	5	484	13	26.36	1.81
Bio-Resin Type & Catalyst Dosage					
1-pTam-Q3	5	309	24	22.70	4.01
3-pTam-Q3	5	417	32	25.86	1.57
6-pTam-Q3	7	227	57	26.04	2.11
3-pTam-Q1	5	438	48	22.99	3.24
3-Q2001-Q1	5	520	22	26.58	0.97
6-Q2001-Q1	5	508	11	25.32	1.46
Time Variant					
3-Q2001-Q1 2days	3	435	47	26.45	0.21
3-Q2001-Q1 4days	3	485	33	24.52	2.18
3-Q2001-Q1 13days	4	508	48	26.12	1.53
Lap Splices					
3-Q2001-Q1 25 mm	5	191	13	25.33	1.74
3-Q2001-Q1 50 mm	5	249	6	27.18	1.69
3-Q2001-Q1 100 mm	5	310	16	24.98	1.91
3-Q2001-Q1 200 mm	5	356	21	27.09	2.97
3-Q2001-Q1 300 mm	5	337	9	24.98	1.10

Chapter 3: Environmental Aging Effect on Tensile Properties of GFRP made of Furfuryl Alcohol Bio-Resin Compared to Epoxy[2]

3.1 INTRODUCTION

Fibre reinforced polymers (FRPs) have been used in numerous structural retrofit applications in recent years. Concrete beams and columns are commonly rehabilitated with adhesively bonded carbon- or glass-fibre reinforced polymers (GFRPs). Their advantageous properties, such as the ease of handling and corrosion resistance, make them ideal for these types of applications. Short- and long- term mechanical characteristics are needed to fully understand the performance of these materials and enable design over their full service life. Externally bonded FRPs will naturally be exposed to a variety of harsh environmental conditions such as freeze-thaw, salt water exposure, alkaline solutions and temperature. Research and testing has been conducted to simulate these conditions [Al-Zahrani et al, 2002; Rivera et al, 2010; Robert et al, 2012; Chen et al, 2007; Cromwell et al, 2010]. It was concluded that the most effective way to accelerate the aging process was to increase the temperature [Al-Zahrani et al, 2002].

Recently, Robert et al. (2010) conducted a durability study on glass fiber reinforced polypropylene thermoplastic composite laminates. The composite was exposed to saltwater, with a concentration of 3% NaCl by weight, to simulate the presence of de-icing salt. This was compared to immersion in tap water. It was determined that immersion in the salt water had a greater impact on the flexural

[2] This chapter has been submitted for publication as the following journal paper:
Eldridge, A. and Fam, A. (2013) "Environmental Aging Effect on Tensile Properties of GFRP made of Furfuryl Alcohol Bio-Resin Compared to Epoxy", *ASCE Journal of Composites for Construction*, Under review.

characteristics, compared to the tap water over 168 days. Another study was conducted on the durability of GFRP bars for concrete structures by Chen et al. (2007). These bars were immersed in five different solutions; water, three types of alkaline solutions and a saline solution. Elevated temperatures were used to accelerate the aging process. Some of the specimens in these solutions went through wetting/drying and freeze/thaw cycles. It was concluded that the GFRP bars experienced a significant strength loss when exposed to the simulated environments at 60^{o}C. As well, wetting/drying and freeze/thaw cycles had negligible impact on the GFRP bars.

Cromwell et al. (2010) tested several FRP systems, including CFRP and GFRP composites. A variety of environmental conditions were considered; immersion in water, salt water, alkaline and diesel as well as dry heat and freeze/thaw conditions. Tension tests along with other testing methods were conducted to assess the effects of these environmental conditions. Immersion in salt water and immersion in an alkaline solution were found to be the most suitable methods for evaluating the effects of environmental conditioning on FRP material. Kajorncheappunngam et al. (2002) conducted several long-term tests on GFRP composites. Tensile tests were conducted throughout the aging process to assess the deterioration of the composite. Distilled water, 30% salt water, acid and base solutions were used to age the specimens at temperatures of 23 and 60^{o}C. There was greater damage to the GFRP composites exposed to the solutions at 60^{o}C. The results verified that the durability of GFRPs was dependant on the chemical resistance of the glass fibres and integrity of the interface.

Extensive work has been done to develop procedures and models to predict the long term strength of FRP composites [Dejke, 2001; Chen et al, 2006; Porter et al, 1997].

When aging a specimen in an aqueous environment, the Arrhenius model can be used to predict its service life at a given average temperature [Bank et al, 2003]. This model can be used to predict degradation, only when the material is exposed to at least three temperatures, followed by measuring the property retention over time [Bank et al, 2003; Gerritse, 1998]. Robert and Fam (2012) applied this technique to concrete filled GFRP tubes aged in saltwater at temperatures of 23, 40 and 50^{o}C. Based on the results, the Arrhenius model was used to predict the GFRP property retention over service life. In all studies stated thus far, the FRPs examined are comprised of traditional fibres and resins. Carbon, glass and aramid fibres are conventionally used in combination with epoxy or vinlyester resin to form the composite. As such, there is a substantial body of knowledge surrounding the durability of conventional FRP composites.

3.1.1 Background of Bio-Resins

Conventional resins such as epoxies are unsustainable. By replacing the epoxy with a "green" natural alternative, the environmental impact of the expanding use of FRPs could be decreased. Many natural thermosetting polymers are based from corn, soybean and tung oil [Lu et al, 2005; Li et al, 2003; Casado et al, 2009]. Numerous studies have been done on natural resins in combination with natural fibres [Wollerdorfer and Bader, 1998; Wambua et al, 2003; O'donnell et al, 2004]. Most natural fibres used, however, do not have the necessary structural properties (i.e. strength and stiffness) for rehabilitation applications. Therefore, it is the authors' opinion that if the industry was to move towards 'green' composites in heavy structural applications, the focus should be on replacing the matrix and not the fibers. By combining bio-resins and conventional fibers, a compromise can be struck between environmental sustainability and adequate structural

performance. Ironically, it is also the matrix that is most susceptible to environmental exposures and degradation concerns. As such, durability studies are crucial in this case.

Furfuryl Alcohol Based Bio-Resin: Fam et al (2013) conducted a comprehensive study on the short-term mechanical characteristics of two types of furfuryl alcohol based bio-resin of two different viscosities. The resins were derived from renewable resources such as sugar cane and corn cobs. The study assessed GFRP laminates made from these bio-resins in terms of tensile strength and Young's modulus. The study examined different catalysts along with the effects of the dosage of the catalyst and the curing time on mechanical properties. The study also established the length of the overlap splice necessary to achieve the optimal strength of the composite. The study concluded that the low-viscosity type bio-resin, which has 1.22 specific gravity and 300-600 cps viscosity, was the most successful in that it resulted in a similar tensile strength to epoxy-GFRP coupons, when a 3% by weight catalyst was used. It was also proven to be the most suitable for the hand layup fabrication technique, unlike the viscous resin of 1.29 specific gravity and 12000-16000 cps viscosity. The latter did not properly saturate the glass fibres, and as a result, it produced tensile strength 19% lower than the epoxy-GFRP composite, when the optimal catalyst dosage was used. Two days after fabrication, the low-viscosity bio-resin GFRP reached 84% of its maximum tensile strength, and the full strength was reached at about 13 days. The various parameters studied were shown to have little effect on Young's modulus but significant effect on tensile strength. It was concluded from this initial investigation that the low-viscosity bio-resin has a great potential and promise in structural engineering applications, and hence it was decided to

launch a long-term durability study on this type of bio-resin GFRP, which is the subject of this paper.

3.2 EXPERIMENTAL PROGRAM

The experimental program in this study consisted of the fabrication, aging and testing of 160 GFRP standard coupons, 80 of which were fabricated using the bio-resin polymer, while the remaining used conventional epoxy resin. All coupons contained a comparable volume of glass fibers; given a hand lay-up process was used. Coupons were tested at various time intervals after aging and compared to control unconditioned coupons. The following is a detailed description of the experimental program.

3.2.1 Materials

Glass Fibres: Unidirectional E-glass fibre fabric was used as the reinforcement in the GFRP composites. This fibre is commercially available Tyfo® SEH-51A and comes in a 1.37x45.72 m roll. The manufacture reports a tensile strength and elastic modulus of 3240 MPa and 72.4 GPa, respectively.

Bio-Resin and Bio-Catalyst: The low-viscosity bio-resin used in this investigation is an organic compound, commercially available as QuaCorr1001 [PennAKem, 2010]. It is furfuryl alcohol based, derived from renewable resources such as sugar cane and corn cobs. It has a dark-reddish to brown color. It also has the following physical characteristics: a specific gravity of 1.22, a viscosity of 300-600 cps and a gel time of 18-24 minutes at 25^{o}C, and a flash point of 75.6^{o}C. The bio-catalyst used is also commercially available as QuaCorr 2001, which is a $C_8H_4O_4Cl_2$ phthaloyl chloride and $C_{10}H_{10}O_4$ dimethyl phthalate of a light yellow color. A 3% by weight catalyst was used to cure the resin.

Epoxy-Resin: Tyfo® S Epoxy-resin was used as a control in this study. This particular resin is commercially produced to be used with Tyfo® SEH-51A glass-fiber fabric. The epoxy-resin consists of two-parts with a ratio of 100 parts of component A to 34.5 parts of component B by weight. The tensile strength and elastic modulus of this resin based on manufacturer specifications are 72.4 MPa and 3.18 GPa, respectively.

3.2.2 Test Specimens and Parameters

A summary of the test matrix is given in Table 3-1. The objective of this study was to determine the durability of bio-resin GFRP composites and compare it to epoxy-GFRP by exposing them to saltwater baths with varying temperatures. This was accomplished by fabricating and testing standard 250x25 mm uniaxial coupons in tension, following ASTM D3039 (2007). Ten of the 160 coupons were tested with no environmental aging to act as reference control specimens. Three environmental tanks at different temperatures were used to age all other specimens. Each tank contained 3% salt solution and was set to a temperature of 23^{o}, 40^{o} and 55^{o}C, respectively. Twenty five bio-resin- and 25 epoxy-GFRP coupons were placed into each tank. Five bio-resin- and five epoxy-GFRP coupons were taken out of the tank to be tested at various time intervals, namely, at 14, 29, 97, 182 and 300 days.

3.2.3 Fabrication of Test Specimens

The bio-resin- and epoxy-GFRP coupons were fabricated in similar fashions. This process followed guidelines from ASTM D3039 (2007). The QuaCorr1001 bio-resin was mixed with 3% catalyst, as established by Fam et al (2013). The glass fibre sheets were laid out on plastic sheets. The resin was then poured onto the fabric and spread throughout the fibres as shown in Figure 3-1(a and b). The sheet was then flipped over

and more resin was added (Figure 3-1(c and d)). Once it was ensured that the resin had saturated the fibres, the sheets were placed between two smooth and heavy HDPE boards and left to cure. After one week, the GFRP sheets were removed and cut using a diamond blade saw into 25 mm by 250 mm coupons, with the fibres parallel to the blade. Individual coupons were then stored at room temperature in dry air for 14 weeks until they were placed into the conditioning tanks.

At each time interval, coupons were removed from the tank and dried for one day. GFRP tabs of a length of 56 mm and 25 mm width were then attached to both sides, at both ends of the coupons in order to prevent grip failures when tested [ASTM D3039, 2007]. The tabs were made of epoxy-GFRP and adhered to the coupons with Sikadur30 viscous epoxy. A schematic of the coupons is displayed in Figure 3-2(a). Samples of the epoxy- and bio-resin-GFRP coupons are also shown in Figure 3-2(b and c). Detailed measurements of every coupon, namely the width and thickness, were taken at various locations to calculate the cross sectional area and stresses.

3.2.4 Test Setup and Instrumentation

The long-term testing procedures followed the specifications from Bank et al. (2003). A total of three tanks were set-up for environmental aging. Two of the tanks were heated by a screw-plug heater on the side of the tank and controlled by an electronic temperature controller, which can be seen in Figure 3-3(a). These two tanks were also insulated around the sides and the top cover to reduce the amount of heat and moisture that would escape. As well, each tank was lifted off the ground by placing them on wood pallets to keep the heat from escaping. The two heated tanks had circulation pumps to circulate the hot water. The third tank contained water at room temperature and was sealed with a

plastic sheet on top. This tank was placed in a room with a constant 23^{o}C air temperature, therefore no insulation was required.

At each time interval, 10 coupons, 5 bio-resin GFRP and 5 epoxy GFRP, were removed and tested to determine their tensile strength and modulus. An Instron universal testing machine (model 8808) was used to complete the uniaxial tension tests. Each coupon was tested at a rate of 2 mm/min as per the ASTM D3039 standard (2007). The test set-up is shown in Figure 3-3(b). An extensometer with a 25 mm grip gauge length was calibrated and used to measure the strain in the GFRP coupons. It was removed from the specimen at a specified load prior to failure. This was to ensure that the extensometer was not damaged.

3.3 EXPERIMENTAL RESULTS AND DISCUSSION

A summary of results of all tension coupon tests, in terms of the ultimate strength and modulus, including the average, standard deviation and percent reduction values is provided in Table 3-2. The following sections provide details of test results and the impact of environmental aging on the mechanical properties of the bio-resin- and epoxy-GFRPs.

3.3.1 Results of Control Specimens

In this investigation control specimens were tested to establish the baseline properties to compare with subsequent aged test results. Five epoxy-GFRP coupons were tested and average tensile strength and modulus of 525 MPa and 26.6 GPa, respectively, were determined. Also, five bio-resin-GFRP coupons were tested and resulted in very similar properties to the epoxy-GFRP, namely, tensile strength and modulus of 520 MPa and 26.3 GPa, respectively. Figure 3-4(a) shows the control un-aged stress-strain curve of the

bio-resin-GFRP, in comparison to the epoxy-GFRP. All subsequent aged coupons were compared to the control ones and results were expressed in terms of percent retention of mechanical properties.

3.3.2 Results of Environmentally Aged Specimens

The tensile strength of both the bio-resin- and epoxy-GFRP coupons reduced as time progressed. Table 3-2 reports the average tensile strength and Young's modulus results of all coupons tested in this study. As well, it reports the percent reduction in strength, and standard deviations. The abbreviations used in this table denote each set of tests that were completed and describes the type of GFRP, the water temperature it was exposed to and the length of time it was in that environment. For example, B-40-97; 'B' represents the bio-resin GFRP coupon, '40' represents the 40^{o}C tank and '97' represents the number of days the coupon was exposed to that environment. Figure 3-5(a and b) displays the tensile strengths of the bio-resin (B)-GFRP and epoxy (E)-GFRP coupons, at various temperatures over 300 days. Also shown are the maximum and minimum values to reflect the range of variation (standard deviations are reported in Table 3-2). Sample stress-strain curves of the B-GFRP and E-GFRP at 97 and 300 days, at the highest temperature of 55^{o}C, are shown in Figure 3-4(b and c).

Behavior in 23^{o}C Tank: The 23^{o}C saltwater did not affect the strength of the E-GFRP immediately. The reduction went from 2% to 4% to 2%, over 14, 29 and 97 days in the tank, respectively. The B-GFRP coupons experienced similar effect for the 23^{o}C saltwater environment. The change in strength went from an increase of 2% to a decrease of 8% to 4%, over 14, 29 and 97 days, respectively. These are relatively small fluctuations, therefore, it can be concluded that over 97 days minimal degradation was

present. Strength reduction of the E-GFRP and B-GFRP coupons was first seen beyond 97 days in the 23^{o}C saltwater environment.

Behavior in 40^{o}C Tank: The 40^{o}C saltwater environment decreased the strength of the E-GFRPs after 14 days by 3%. From 29-182 days the strength decreased steadily at a rate of about 1% every 10 days. A different behaviour was observed for the B-GFRPs. After 14 days, there was no decrease in strength. The majority of the reduction took place between 14 and 97 days, where a 44% loss in strength occurred. Over the last 203 days the B-GFRP and E-GFRP followed a similar reduction trend.

Behavior in 55^{o}C Tank: The 55^{o}C saltwater environment had a greater impact on the E-GFRPs than the B-GFRPs over the first 29 days, with reductions in strength of 24% and 11%, respectively. From 29 to 97 days a significant decrease in strength in the B-GFRP coupons was experienced, with a 53% reduction. The E-GFRPs at this time interval only had a 36% decrease in strength. Over the next 203 days both B-GFRPs and E-GFRPs strength plateaued, reducing by only 8% and 3%, respectively.

Tensile Strength Retention: Figure 3-6 summarizes the test results in terms of standard strength retention-versus-time curves, at the three different temperatures. Overall, when comparing the B-GFRP to the E-GFRP, it can be seen that E-GFRP coupons performed better than the B-GFRP coupons after 300 days of exposure. The strength retention values of B-GFRP at 23, 40 and 55^{o}C were 80, 44 and 39%, respectively, while for the E-GFRP were 86, 72 and 61%, respectively.

Failure Modes: The failure modes of the E-GFRP coupons, in terms of the nature and pattern of fiber rupture remained the same throughout all tests at various ages and temperatures, as shown in Figure 3-7(a). However, the B-GFRP failure modes changed

slightly from an explosive and spread failure at early stages, as shown in Figure 3-7(b), to a localized non-explosive failure as aging and temperature increased, as shown in Figure 3-7(c).

Elastic Modulus: The strains measured from the extensometer were used to calculate Young's modulus. The strain range used was 0-0.5%. Figure 3-4(b and c) show sample stress-strain curves at various stages of aging at the highest temperature. Also, Figure 3-8(a and b) displays the values of Young's modulus at various temperatures over time, for the E-GFRP and the B-GFRP coupons, along with the maximum and minimum test results. It is clear that Young's modulus of both the B-GFRP and E-GFRP coupons remained fairly constant throughout the entire durability investigation. Since the elastic modulus did not change over time, it can be concluded that the ultimate rupture strain reduced proportionally to the peak tensile strength of each test.

3.3.3 Prediction of Long-Term Behaviour using Arrhenius Relationship

The strength retention of the composite can be predicted over its service life for a certain site temperature by using the Arrhenius model. The linearized form of Arrhenius equation is written as follows [Meyer et al, 1994]:

$$\ln\left(\frac{1}{k}\right) = \frac{E_a}{R}\frac{1}{T} - \ln(A) \quad (1)$$

where k=degradation rate (1/time); A=constant relative to the material and degradation process; E_a=activation energy; R=universal gas constant; T=Temperature (Kelvin). It can be observed that ln(A) is the intercept of the y-axis with the regression line and (E_a/R) is the slope in Arrhenius plot. Therefore, E_a and A can be determined once Arrhenius model is plotted. A number of assumptions are made in this mode: only one chemical degradation mode can dominate over the aging process and this mode cannot change with

time or temperature, and the FRP must be aged in an aqueous solution, not a dry environment [Bank et al, 2003]. At least three elevated temperatures are necessary to get accurate results from the Arrhenius model [Gerritse, 1998]. In this current study, the reduction in strength of the bio-resin GFRPs is predicted over its service life at three mean annual temperatures of 3^{o}, 10^{o} and 20^{o}C, representing Central Canada, southern parts of Canada and southern parts of the United States, respectively.

The procedure used to determine the long-term strength retention of the B-GFRPs and E-GFRPs was outlined by Bank et al [Bank et al, 2003]. The first step is to produce a graph that illustrates the relationship between property retention, expressed in percentage of the original strength, and the natural logarithm of time for given exposure temperatures. This is shown in Figure 3-9(a) for the B-GFRPs and Figure 3-10(a) for the E-GFRPs. Each data set is fit to a trend line and equations are produced as also shown in the figures. It can be seen that the trend lines at 23^{o}C in particular had R^2 values of 0.75 and 0.53 for the B-GFRP and E-GFRP, respectively. These values are lower than the minimum of 0.8 recommended by Bank et al (2003). By careful examination of the five data points in Figure 3-9(a) and Figure 3-10(a), it can be seen that the 97 days data points appear to be outliers, since they show unexpectedly higher strengths than the interval immediately before (at 29 days). As such, it was decided to neglect the data points at 97 days and use the remaining four points to establish the trend lines at 23^{o}C, which still satisfies the minimum number of four data points recommended by Bank et al (2003). The resulting trend lines showed R^2 values of 0.96 and 0.75 for the B-GFRPs and E-GFRPs, respectively, which can be considered acceptable to proceed with the analysis.

The equations of the regression lines are then used to produce the Arrhenius plots, seen in Figure 3-9(b) and Figure 3-10(b), which describes the relationship of the natural logarithm of time over the inverse of temperature, expressed in 1000/K for given property retentions. This graph is then used to predict the property retention over its service life at selected temperatures lower than those used in the experiments. Predictions of tensile strength retentions of B-GFRP composites immersed in saltwater at site temperatures of 3^o, 10^o, 20^oC are shown in Figure 3-11. The following Equations represent the strength retention over service life:

$$\left(\frac{f_u(t)}{f_u(t=0)}\right) x100 = -4.36\ \ln(t) + 85.16 \qquad \text{(B-GFRP at T = } 3^o\text{C)} \qquad (2)$$

$$\left(\frac{f_u(t)}{f_u(t=0)}\right) x100 = -4.92\ \ln(t) + 83.33 \qquad \text{(B-GFRP at T = } 10^o\text{C)} \qquad (3)$$

$$\left(\frac{f_u(t)}{f_u(t=0)}\right) x100 = -6.30\ \ln(t) + 78.57 \qquad \text{(B-GFRP at T = } 20^o\text{C)} \qquad (4)$$

where $f_u(t)$ is the tensile strength at a given time t, where t is in years and $f_u(t=0)$ is the short term tensile strength. After 100 years in service, immersed in saltwater at 3^o, 10^o and 20^oC, the tensile strength retentions are estimated to be 65, 61 and 50%, respectively. Results also clearly show that the majority of the reduction occurs early in service life, regardless of site temperature. For example, in the 10^oC environment, after 5 and 50 years, the bio-resin GFRP will retain 75 and 64% of its strength. The E-GFRP composite tensile property retention was also predicted at the 10^oC, as shown in Figure 3-12 in comparison with the B-GFRP, and given by equation (5):

$$\left(\frac{f_u(t)}{f_u(t=0)}\right) x100 = -2.59\ \ln(t) + 92.88 \qquad \text{(E-GFRP at T = } 10^o\text{C)} \qquad (5)$$

After 100 years, the E-GFRP shows 81% tensile strength retention, which is a 33% higher retention than the B-GFRP composites exposed to the same environmental condition.

3.4 SUMMARY

Bio-composites are emerging as a sustainable alternative in structural applications, and as a result, a major focus should be on their durability. This study focuses on the environmental aging of bio-resin glass fibre reinforced polymer (GFRP) through immersion in saltwater at elevated temperatures. The resin is furfuryl alcohol based, derived from renewable resources, such as corncobs and sugarcanes. Deterioration was quantified by tensile testing of unidirectional bio-resin-GFRP coupons at various stages of exposure, and compared to conventional epoxy-GFRP coupons under the same conditions. A total of 150 specimens were exposed to three different environments, namely 23^{o}, 40^{o} and 55^{o}C water with 3% salt concentration, for up to 300 days. It was found that the bio-resin GFRP retained 80, 44 and 39% of its original strength at the three temperatures, respectively. On the other hand, the epoxy-GFRP exhibited 86, 72 and 61% strength retentions, respectively. No reductions occurred to the Young's moduli. The Arrhenius model was applied, assuming environments with mean annual temperatures of 3^{o}, 10^{o} and 20^{o}C, representing different regions in North America. It was estimated that bio-resin GFRP strength retentions after 100 years, at the three mean temperatures, are 65, 61, and 50%, respectively. In comparison, the 100 years estimated strength retention of epoxy-GFRP at the 10^{o}C is 81%.

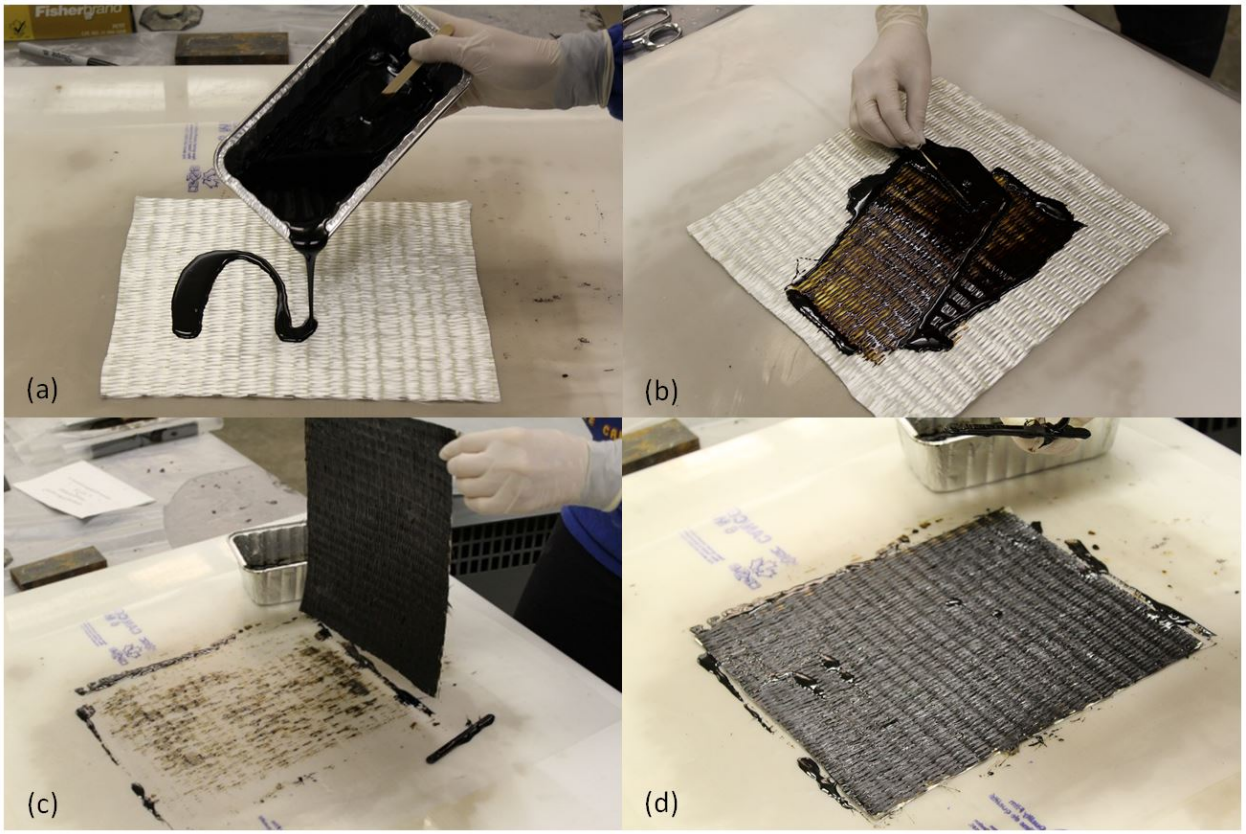


Figure 3-1: Fabrication of bio-resin GFRP laminates

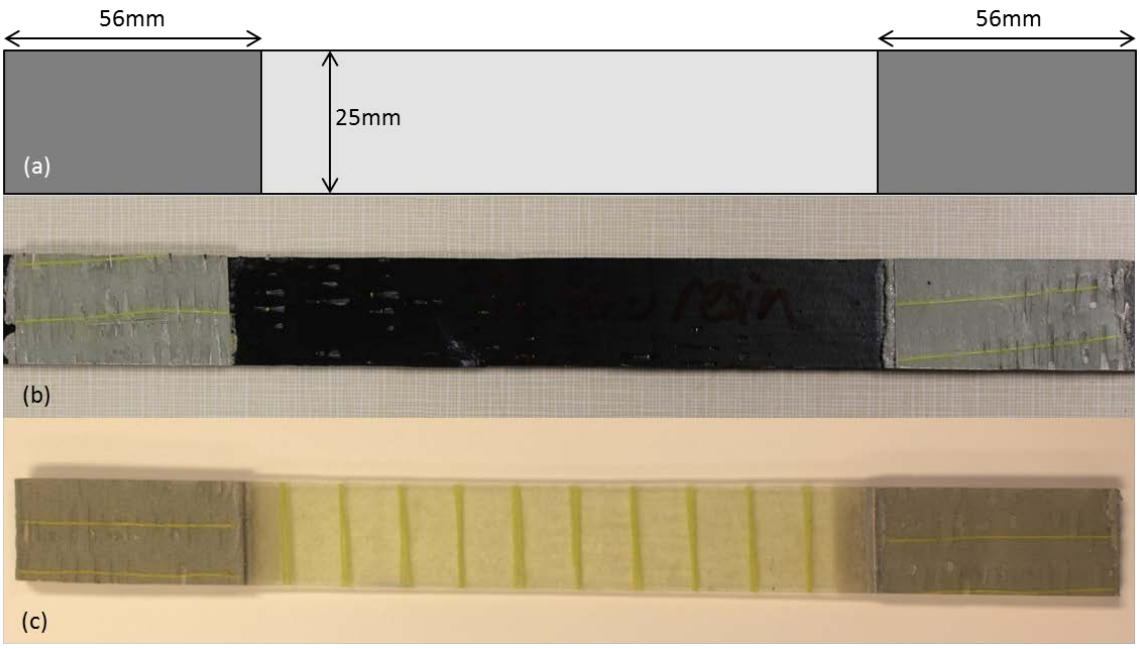


Figure 3-2: (a) Schematic of GFRP coupon; (b) Sample bio-resin (B)-GFRP coupon; (c) Sample epoxy (E)-GFRP coupon

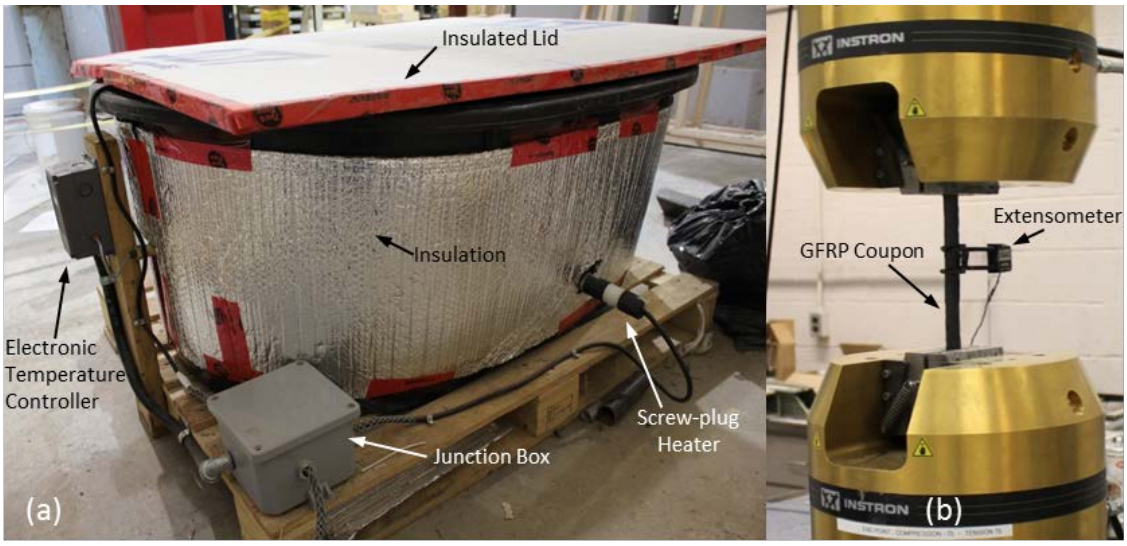


Figure 3-3: (a) Environmental chamber set-up; (b) Test-set-up and instrumentation of the coupons

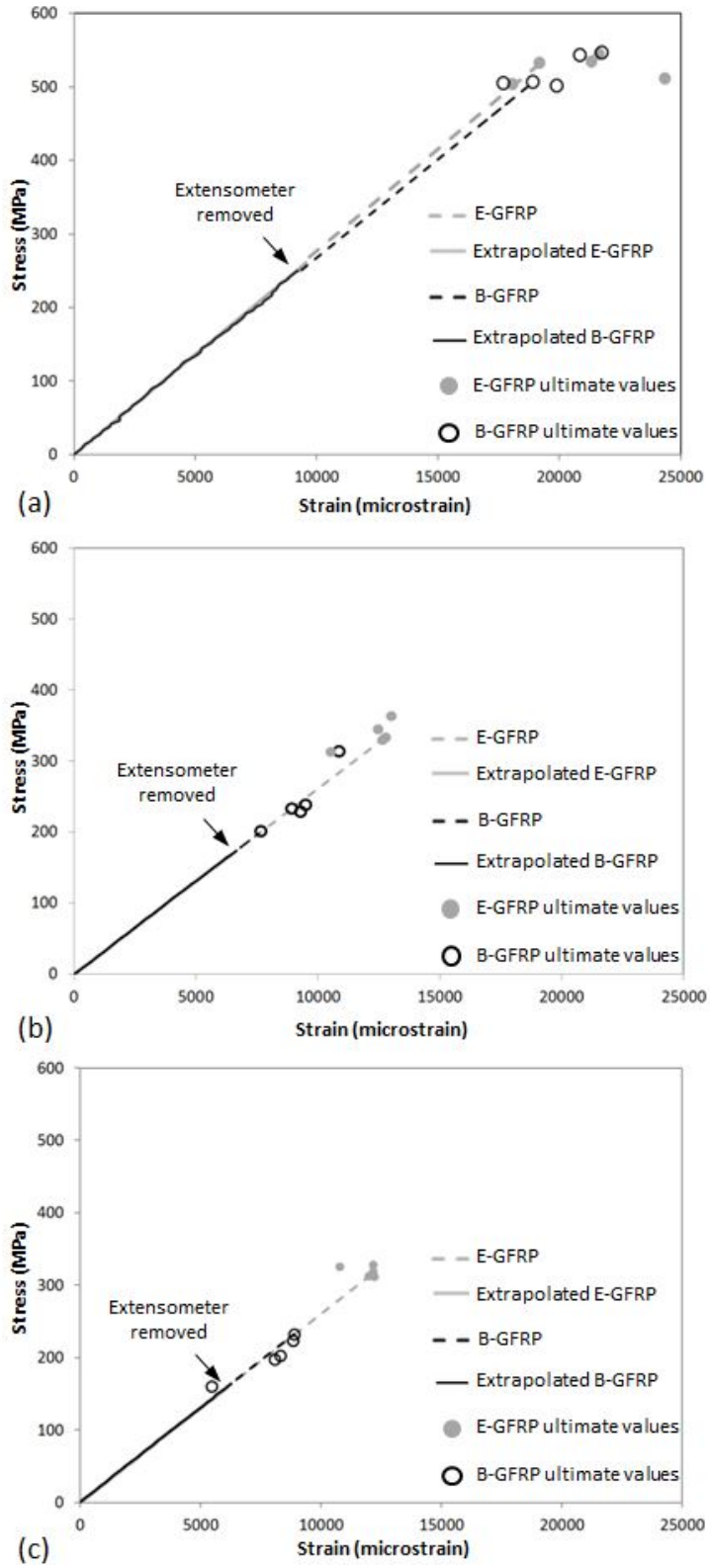
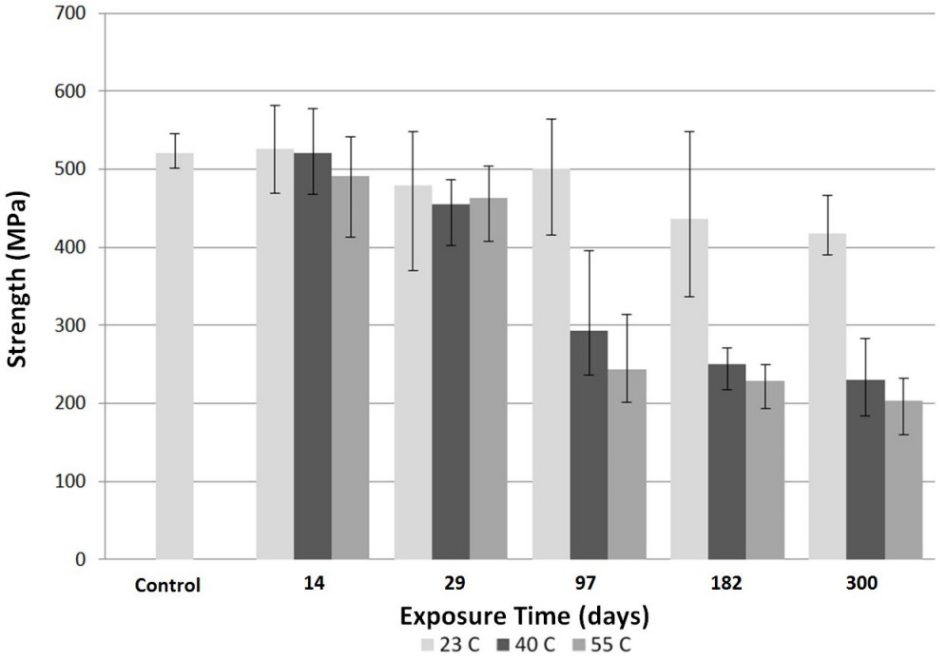
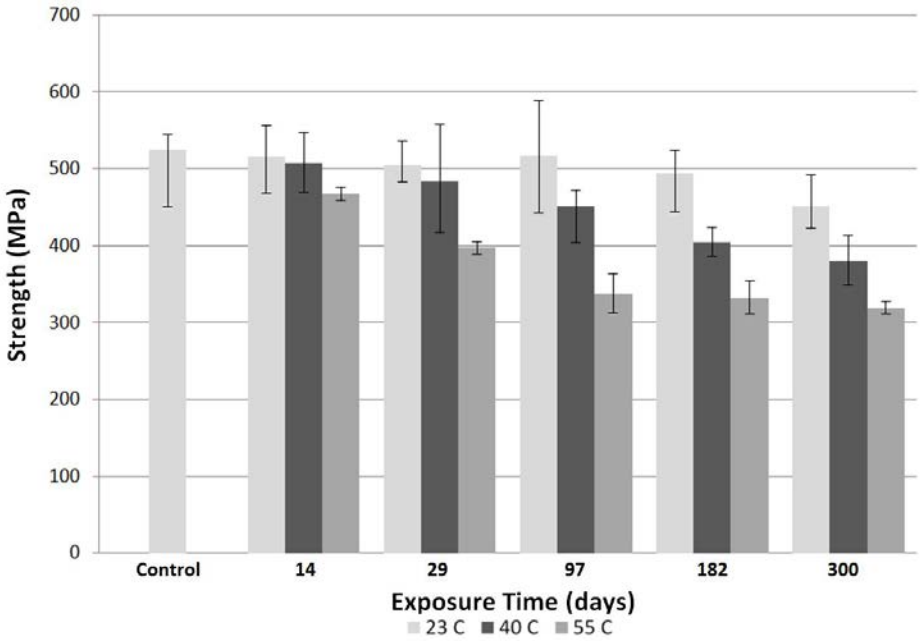


Figure 3-4: Sample stress-strain curves of epoxy (E)- and bio-resin (B)-GFRP coupons: (a) control un-aged, (b) after 97 days at 55°C, and (c) after 300 days at 55°C



(a) Bio-resin (B)-GFRP Composites



(b) Epoxy (E)-GFRP Composites

Figure 3-5: Tensile Strengths of B-GFRP and E-GFRP coupons aged in salt solution at 23, 40 and 55°C

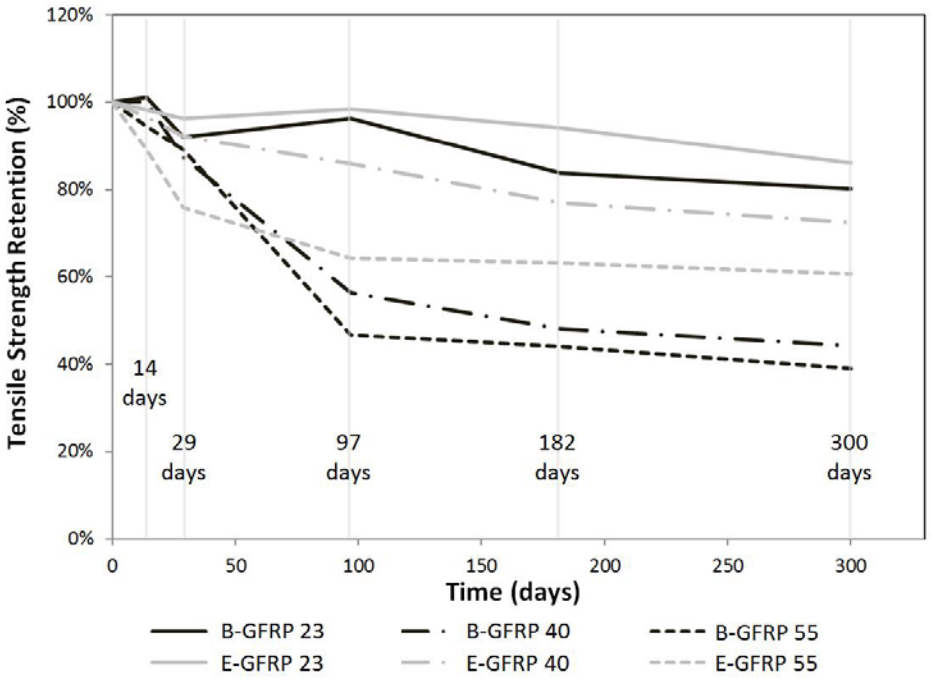


Figure 3-6: Tensile strength retention for epoxy- and bio-resin-GFRP coupons over 300 days

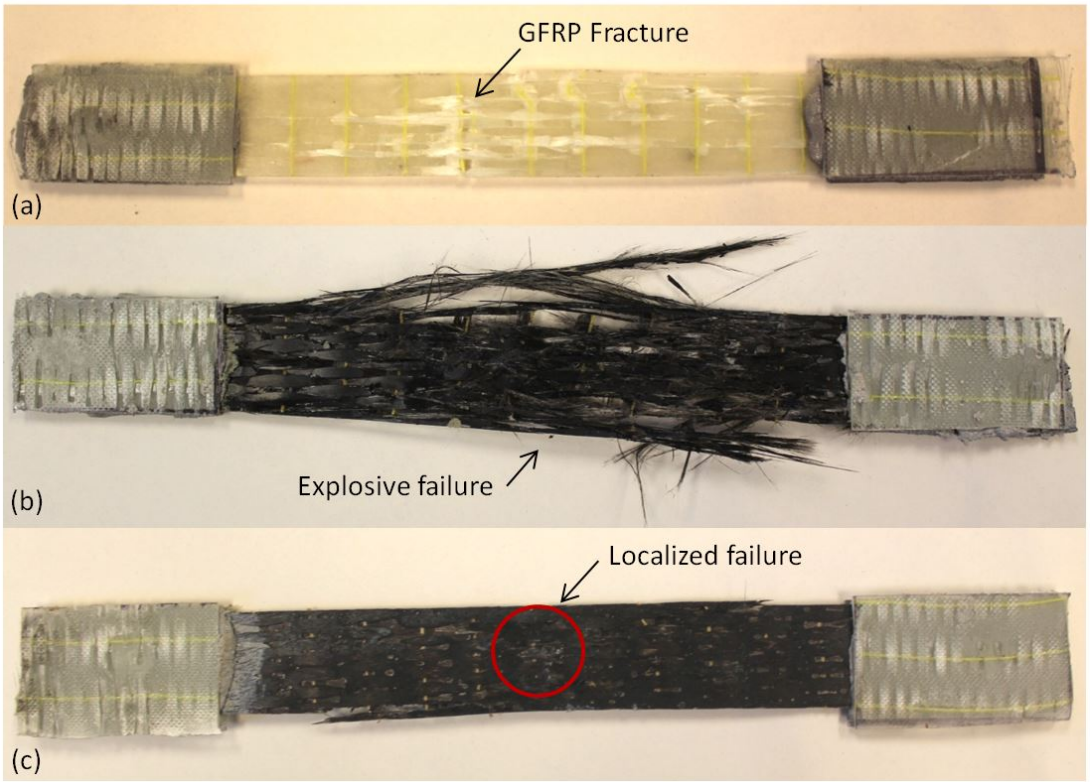
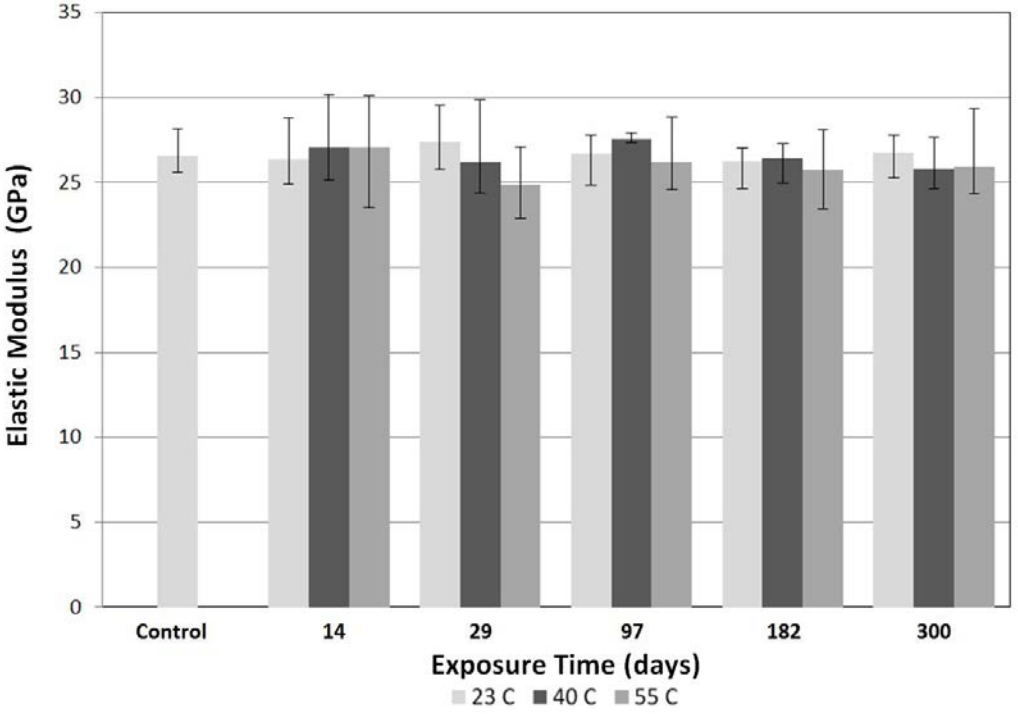
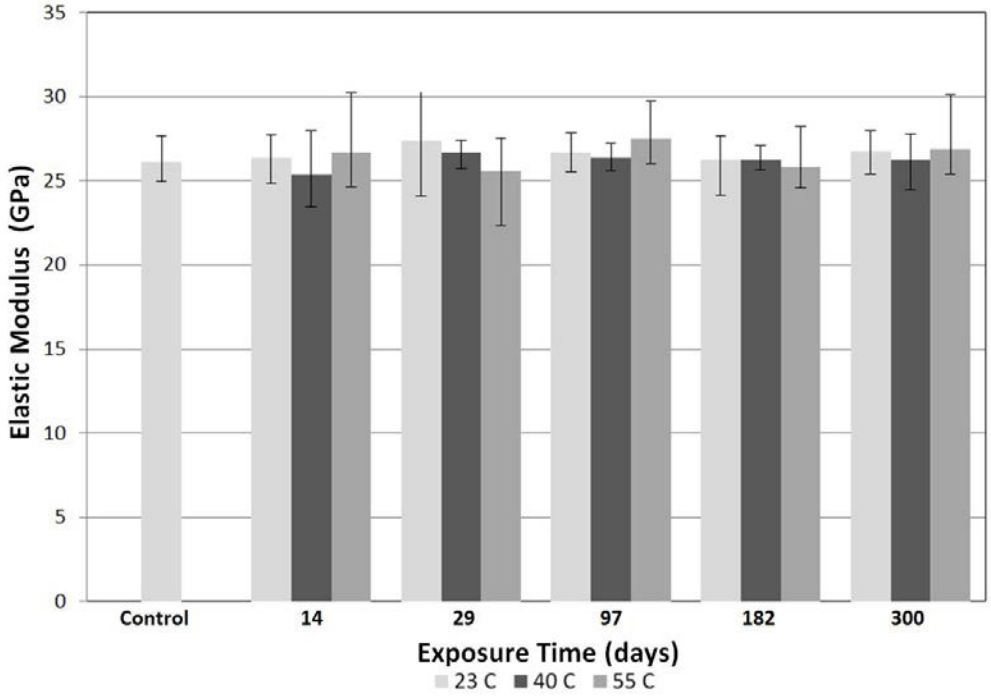


Figure 3-7: Failure modes: (a) E-GFRP coupons, (b) B-GFRP coupons in the beginning of aging, and (c) B-GFRP coupons towards the end of aging

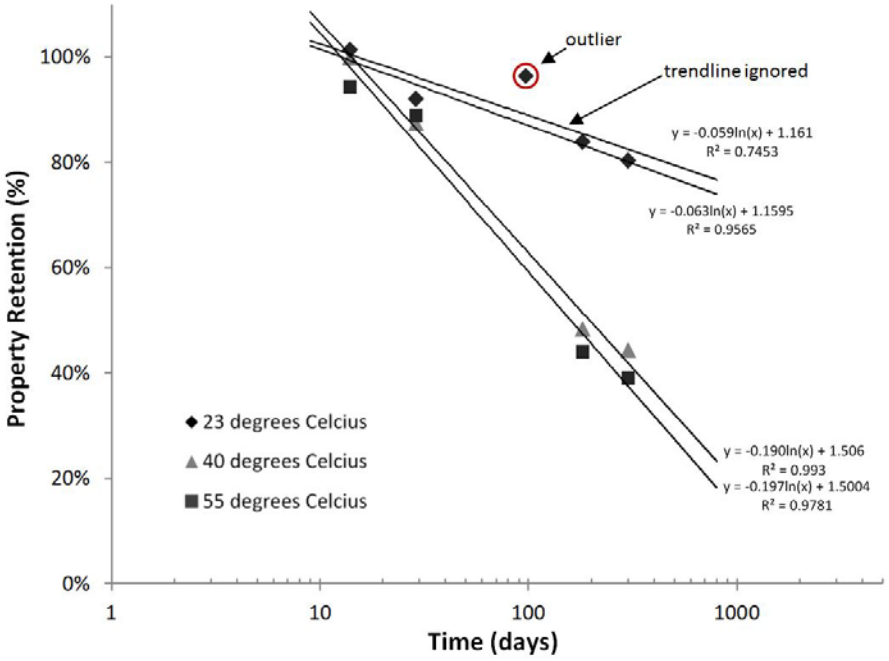


(a) B-GFRP Composites

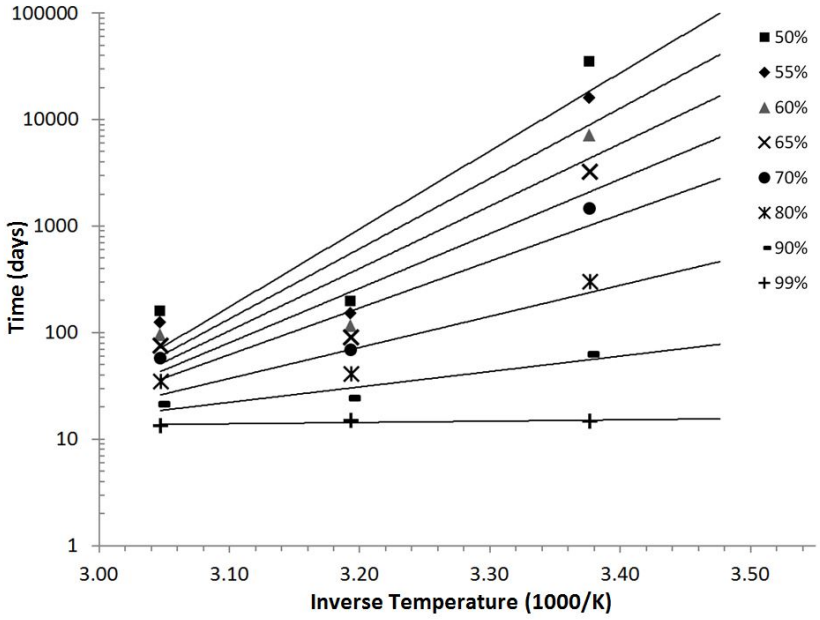


(a) E-GFRP Composites

Figure 3-8: Elastic Modulus of B-GFRP and E-GFRP coupons aged in salt solution at 23, 40 and 55°C

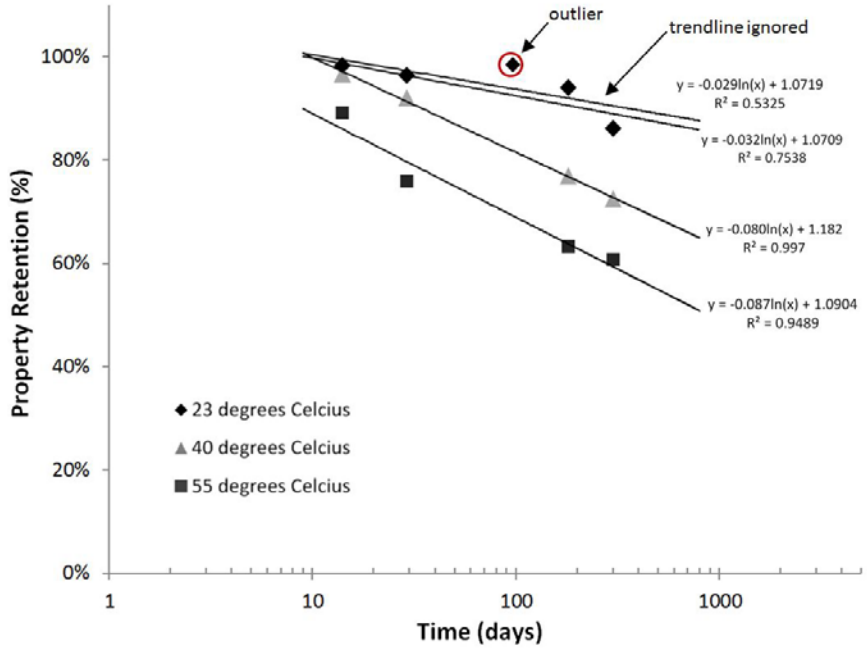


(a) Variation of property retention with logarithm of time

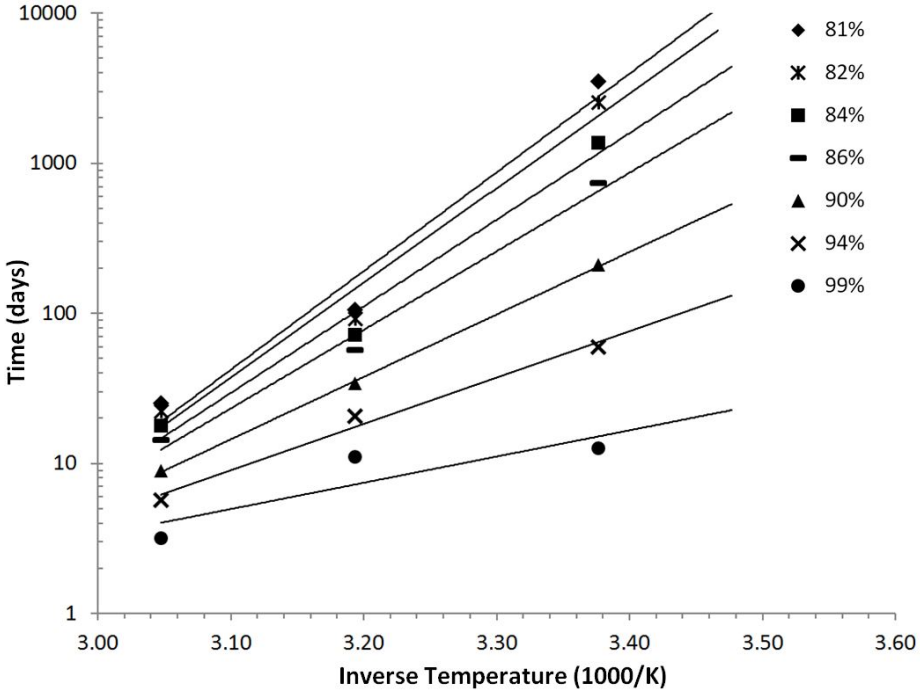


(b) Arrhenius plot

Figure 3-9: Process for generating a generalized form of tensile strength retention with time for B-GFRP composites



(a) Variation of property retention with logarithm of time



(b) Arrhenius plot

Figure 3-10: Process for generating a generalized form of tensile strength retention with time for E-GFRP composites

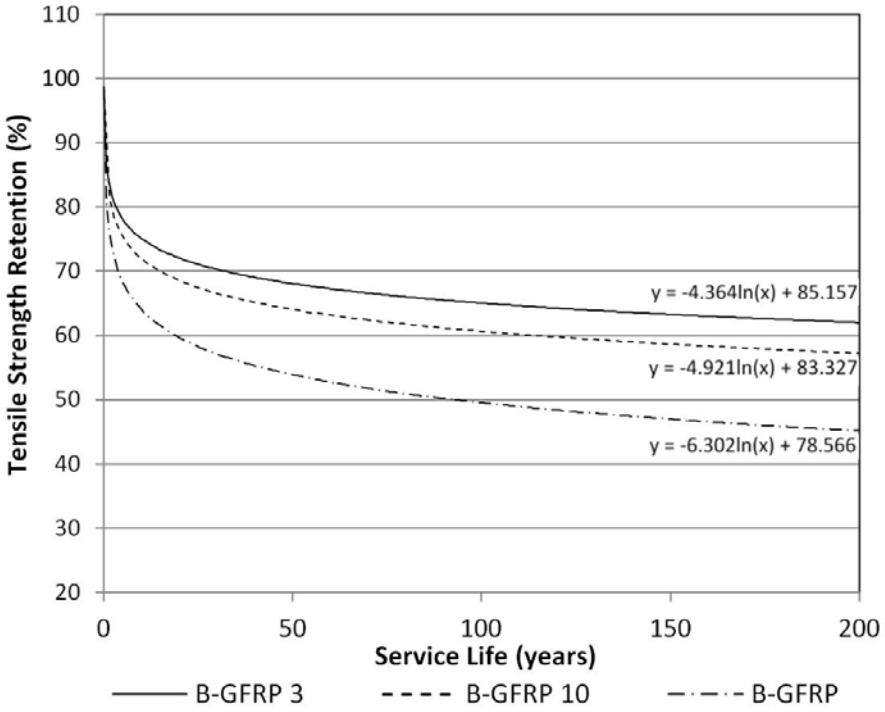


Figure 3-11: Predicted relationship between the retained tensile strength of B-GFRPs and service life at annual mean temperatures of 3°, 10° and 20°C.

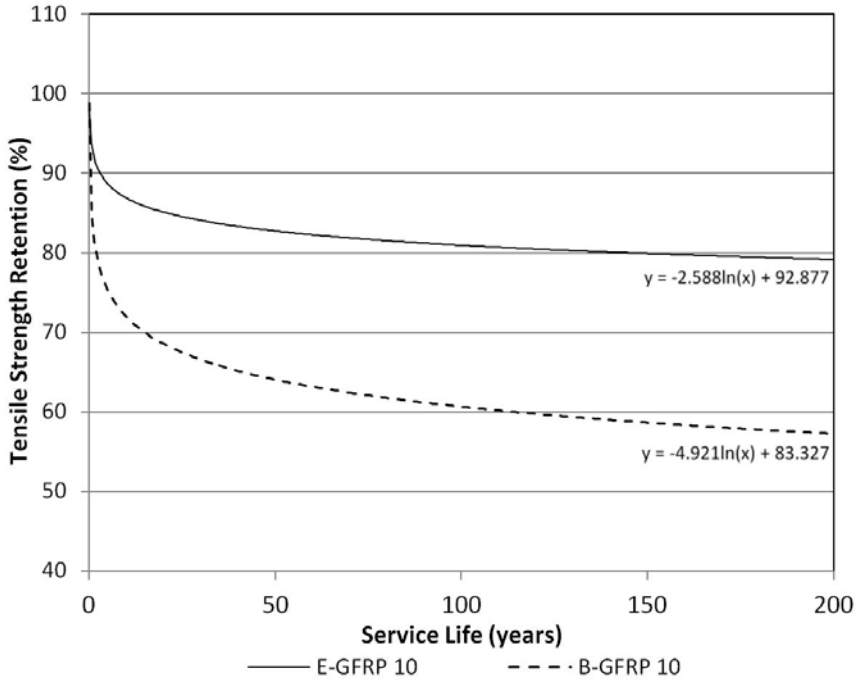


Figure 3-12: Comparison of the relationship between the predicted retained strength of E-GFRPs and B-GFRPs over their service life at an annual mean temperature of 10°C.

Table 3-1: Test Matrix

Type	No. of coupons	Environment condition	Temperature (^{o}C)	Time in tanks (days)
Bio-resin GFRP	5	(control, dry)	23	-
	5	Full immersion in 3% salt water	23	14
	5			29
	5			97
	5			182
	5			300
	5		40	14
	5			29
	5			97
	5			182
	5			300
	5		55	14
	5			29
	5			97
	5			182
	5			300
Epoxy GFRP	5	(control, dry)	23	-
	5	Full immersion in 3% salt water	23	14
	5			29
	5			97
	5			182
	5			300
	5		40	14
	5			29
	5			97
	5			182
	5			300
	5		55	14
	5			29
	5			97
	5			182
	5			300

Table 3-2: Test Results Summary

Specimen ID	Type	No. of coupons to calculate mean	Mean maximum strength (MPa)	Standard deviation (MPa)	% change in strength*	Mean Young's modulus (GPa)	Standard deviation (GPa)
B-Control	Bio-resin (B)-GFRP	5	520	22.4	-	26.58	0.97
B-23-14		5	527	45.3	+1.19	26.40	1.56
B-23-29		5	479	74.5	-7.92	27.39	1.88
B-23-97		5	501	63.9	-3.72	26.67	1.14
B-23-182		5	436	77.7	-16.17	26.23	1.13
B-23-300		5	418	30.6	-19.74	26.72	0.95
B-40-14		5	520	46.7	+0.02	27.08	1.89
B-40-29		5	455	32.2	-12.64	26.20	2.19
B-40-97		5	294	62	-43.58	27.59	0.28
B-40-182		5	251	21.6	-51.81	26.46	0.91
B-40-300		5	231	38.3	-55.69	25.78	1.12
B-55-14		5	491	49.5	-5.55	27.08	2.59
B-55-29		5	463	38.3	-10.93	24.87	1.69
B-55-97		5	243	42.1	-53.34	26.17	1.65
B-55-182		5	229	22.3	-56.02	25.77	2.11
B-55-300		5	203	28.0	-60.93	25.92	2.06
E-Control	Epoxy (E)-GFRP	5	525	17.1	-	26.14	0.98
E-23-14		5	515	42.1	-1.82	25.54	1.16
E-23-29		5	505	22.5	-3.67	28.26	2.24
E-23-97		5	517	54.4	-1.52	25.34	0.97
E-23-182		5	493	33.8	-5.94	27.55	1.31
E-23-300		5	451	25.7	-13.95	26.41	1.23
E-40-14		5	507	30.7	-3.39	25.37	1.66
E-40-29		5	483	64.5	-7.89	26.66	0.72
E-40-97		5	451	27.1	-14.11	26.35	0.73
E-40-182		5	404	16.2	-23.03	26.22	0.54
E-40-300		5	380	23.1	-27.56	26.24	1.21
E-55-14		5	467	7.6	-10.91	26.67	2.29
E-55-29		5	398	6.8	-24.12	25.57	2.14
E-55-97		5	337	18.8	-35.79	27.48	1.52
E-55-182		5	332	16.9	-36.8	25.79	1.47
E-55-300		5	319	7.4	-39.25	26.88	1.87

* a "+" indicates an increase in strength; a "-" indicates a decrease in strength.

Chapter 4: Durability of Concrete Cylinders Wrapped with GFRP made from Furfuryl Alcohol Bio-Resin[3]

4.1 INTRODUCTION

Fibre reinforced polymers (FRP) have been used in many structural retrofitting applications. In particular, numerous research studies have been done on the confinement of concrete columns [Pessiki et al, 2001; Spoelstra and Monti, 1999; and Mirmiran and Shahwy, 1997]. Confinement is provided by wrapping the columns with an FRP sheet, where fibers are oriented primarily in the hoop direction. An increase in the inherent concrete strength is provided by restraining the dilation of the column at high strains, thereby significantly increasing the column's axial strength and strain capacities beyond the traditional crushing strain of concrete. This type of retrofitting is becoming increasingly popular compared to conventional concrete jacketing. The FRP sheets light weight allows workers to wrap columns without the use of heavy machinery, while its corrosion resistance characteristics enhance the durability of the structure significantly.

FRP composites can be composed of a variety of fibre and resin materials, each providing a different set of mechanical and environmental characteristics. Carbon, glass and aramid are among the most widely used fibres. The polymer resins used in FRPs act as a matrix, which allows the stress to be uniformly distributed among the fibres, while at the same time acts as an adhesive in concrete retrofit applications. The most common resins used in practise are epoxy, vinyl ester, and polyester. These resins are

[3] This chapter has been submitted for publication as the following journal paper:
Eldridge, A. and Fam, A. (2013) "Durability of Concrete Cylinders Wrapped with GFRP made from Furfuryl Alcohol Bio-Resin", *ASCE Journal of Composites for Construction*, Under review.

unsustainable, being synthetic chemicals. Due to this concern, “green” resins have been developed in the attempt to reduce the environmental impact associated with producing FRPs [Li et al, 2003; Casado et al, 2009; and O’donnell et al, 2004]. However, durability of bio-materials, particularly bio-resins, is generally a prime concern. For composite materials with conventional resins, many studies have been conducted on environmental aging [Cromwell et al, 2010; Chen et al, 2007; Saenz and Pantelides, 2006; and Robert and Fam, 2012]. Some of the exposure environments include freeze-thaw, wet/dry cycles and alkaline solutions. Kshirsagar et al (2000) studied the effect that alkaline solutions, temperature and freeze/thaw cycles had on the mechanical properties of FRP-wrapped concrete columns with conventional epoxy resin. It was concluded that 66^{o}C water was the most severe environment and it decreased the strength of the wrapped concrete cylinders by 36% over a period of 333 days. Toutanji (1999) investigated the durability of FRP-wrapped concrete cylinders exposed to wet/dry cycles with saltwater. Two various types of glass fibres, carbon fibres and conventional epoxy resins were investigated. The results showed that after 300 cycles the carbon-FRP wrapped cylinders did not experience significant strength loss, whereas the glass-FRP wrapped cylinders decreased in strength by 18%.

Research had also been conducted on procedures and models that will predict long-term reductions in strength [Dejke, 2001; Chen et al, 2006; and Porter et al, 1997]. It is well established that Arrhenius model can be used to predict the property retention over a material’s service life in a given temperature. According to the model, the material must be conditioned in an aqueous environment at no less than three different elevated temperatures [Bank et al, 2003; and Gerritse, 1998]. The property retention must be

measured throughout the aging process. This technique was also verified by Robert and Fam (2012) in a study on the durability of concrete filled FRP tubes in a saltwater environment. The specimens were aged in 23, 40 and 50^{o}C salt water baths with 3% NaCl, and the Arrhenius relationship was used to predict the property retention over extended time.

This study investigates the durability of concrete cylinders wrapped with a bio-resin GFRP, which is furfuryl alcohol based and derived from renewable resources such as corn cobs and sugar canes [PennAKem, 2010]. The short term characteristics of this resin along with those of GFRP coupons made from this resin were evaluated at room temperature to establish the optimal type and dosage of catalyst and the minimum curing time [Fam et al, 2013]. The current study addresses the durability of the bio-resin GFRP-confined concrete cylinders by submerging them in 23, 40 and 55^{o}C water with 3% NaCl. The cylinders were then tested to failure under axial compression after 29, 97, 182 and 300 days of exposure. A parallel investigation was conducted on control epoxy-GFRP confined cylinders for comparison. Based on test results, the long term performance of the bio-resin-GFRP confinement was predicted using the Arrhenius relationship.

4.2 EXPERIMENTAL PROGRAM

The experimental program involved the construction and testing of 81 concrete cylinders. Most of the cylinders were retrofitted with either bio-resin or epoxy GFRP wraps. Conditioned specimens were tested at various time intervals and compared to counterparts kept at room temperature as well as to un-retrofitted control specimens, both conditioned and unconditioned. The following is a detailed description of the experimental program.

4.2.1 Materials

The fibres and resins used in this investigation are described below, along with the concrete properties of the cylinders.

Glass fibres: The unidirectional fibres that were used in this study were commercially available Tyfo® SEH-51A. The tensile strength and elastic modulus, determined by the manufacturer, are 3240 MPa and 72.4 GPa, respectively.

Bio-resin and bio-catalyst: Commercially available QuaCorr1001 was the bio-resin used in this investigation. It is a furfuryl alcohol based, derived from renewable resources such as sugar cane and corn cobs. It has a dark reddish-to-brown color, and a specific gravity of 1.22, a viscosity of 300-600 cps and a gel time of 18-24 minutes at 25^{o}C. It has a flash point of 75.6^{o}C. The commercially available catalyst used is QuaCorr 2001, which is a $C_8H_4O_4Cl_2$ phthaloyl chloride and $C_{10}H_{10}O_4$ dimethyl phthalate, of a light yellow color. A 3% by weight catalyst is used to cure the resin. No specific mechanical properties were reported by manufacturer.

Epoxy-resin: The epoxy-resin used as a comparison to the bio-resin was commercially available Tyfo® S Epoxy resin. The epoxy-resin combination consists of 100 parts of component A to 34.5 parts of component B by weight. The manufacturer reported tensile strength and elastic modulus of 72.4 MPa and 3.18 GPa, respectively.

Concrete: The concrete used in this study has a compressive strength of 41 MPa after three months. The maximum aggregate size was 19 mm, with a slump of 150 mm.

4.2.2 Test Specimens and Parameters

The study investigated the durability of GFRP-wrapped standard size (152x305 mm) concrete cylinders exposed to a saltwater environment at varying temperatures. Axial

compression tests were completed to assess the strength. The text matrix is shown in Table 4-1. A total of 51 confined cylinders and 30 unconfined plain cylinders were tested, including three identical specimens for each parameter. Six of the confined cylinders and three of the unconfined cylinders were not environmentally conditioned and used as reference control specimens kept in dry conditions at room temperature. The remaining cylinders were aged in saltwater solutions for up to 300 days. A total of 36 of the confined and conditioned cylinders were wrapped with bio-resin GFRP, referred to as 'B-GFRP' and the remaining nine were wrapped with epoxy-GFRP 'E-GFRP'. Out of the nine control cylinders, three were confined with B-GFRP, three were confined with E-GFRP and three were unconfined. Three large environmental tanks with varying water temperatures were prepared to condition the cylinders. Each tank had 3% NaCl (salt) concentration by weight and the temperatures were 23^{o}, 40^{o} and 55^{o} C, respectively. Axial loading tests were completed after 29, 97, 182 and 300 days of exposure in the tanks. Each set of tests included three repetitions. The goal of these tests was to examine the long-term durability of concrete cylinders wrapped with bio-resin GFRP in comparison to conventional epoxy-GFRP.

4.2.3 Fabrication of Test Specimens

All cylinders were cast from the same concrete batch in accordance with ASTM C31 (2010). The start of the environmental exposure took place three months after casting. All cylinders were wet cured for one week. The ends of the cylinders were ground down to a smooth surface. For the wrapped cylinder, two layers of GFRP sheets were used. During this process, the glass fibre sheets were cut to the appropriate size, allowing a 200 mm overlap after the GFRP was wrapped around the cylinder twice, as shown in Figure

4-1 (a). The surface of the cylinders was coated first with the resin and the glass fibres were saturated fully with the resin before the wrapping process. The wrapped cylinders were then laid down on a plastic sheet on their seam to cure for a week. The weight of the cylinder on the seam prevented the GFRP from loosening from the concrete cylinder during the curing process. A sample of the B-GFRP and E-GFRP wrapped cylinders is shown in Figure 4-1(b) and (c).

4.2.4 Test Setup and Instrumentation

Three environmental tanks were prepared, each containing saltwater at different temperatures. The conditioning guidelines and procedures specified by Bank et al (2003) were used. Each tank was filled with water and a 3% salt concentration was provided. Two of these tanks were heated to a temperature of 40 and 55^{o}C, while the third was left at a steady room temperature of 23^{o}C. For the heating process, a screw plug heater was installed to reach the specified temperatures and an electronic controller was used to control the system. Insulation was provided around the sides and top of the tank in order to prevent excessive heat escape and reduce the heater duty cycle. The tanks sat on wooden pallets and were operated on separate circuits. A typical environmental ageing tank setup is shown in Figure 4-2(a).

Three B-GFRP wrapped cylinders were removed from each tank after 29, 97, 182 and 300 days. Three unconfined control concrete cylinders were also removed from each tank and tested after 97, 182 and 300 days. The three E-GFRP wrapped cylinders were removed from each tank after the 300 days. The study focused on more time intervals for the new B-GFRP, but for the E-GFRP, it was deemed sufficient to establish the strength at the end of 300 days, for comparison. All removed cylinders were left to dry at room

temperature for one day, then were tested in axial compression in a Forney testing machine with a capacity of 2260 kN. Two linear potentiometers (LPs) were installed to measure the axial strain for all cylinders using a two ring extensometer. One wrapped concrete cylinder in each set of three was also instrumented with three electric resistance strain gauges in the hoop direction. The test set-up is shown in Figure 4-2(b). Each cylinder was tested at a rate of 0.25 MPa/sec, in accordance with ASTM C39 (2010).

4.3 EXPERIMENTAL RESULTS AND DISCUSSION

The following sections present the results of the axial compression tests. A summary of test results is shown in Table 4-2. The average strength, standard deviations, percent reduction in strength and failure modes are reported in the table.

4.3.1 Results of Control Specimens

Three sets of control concrete cylinders were tested in this study; unconfined, bio-resin GFRP (B-GFRP)-wrapped and epoxy-resin GFRP (E-GFRP)-wrapped cylinders. This provided a baseline for comparison of all subsequent tests. The E-GFRP and B-GFRP wrapped concrete cylinders had an average axial strength ($f_{cc}^{'}$) of 94 MPa and 93.9 MPa, respectively, before any degradation. These results reveal that the B-GFRP and E-GFRP systems have very comparable confinement properties. When tested in axial compression, the unconfined unconditioned concrete cylinder had an average strength ($f_c^{'}$) of 41.9 MPa. The bio-resin GFRP confinement increases the strength of the unconfined concrete cylinders by 124%, essentially a 2.24 strengthening ratio ($f_{cc}^{'}/f_c^{'}$). Each environmentally conditioned set of specimens is compared to its respective control set. This is presented later in the form of percent retention, which is the amount of strength retained compared to the unconditioned control specimen.

Comparison of performance between bio-resin- and epoxy-GFRP: As discussed above, the B-GFRP and E-GFRP provide the same amount of confinement to the concrete cylinders, suggesting that the glass fibres govern the axial strength increase independently from the type of resin. The confined concrete axial stress-strain graph comparing the E-GFRP and B-GFRP wrapped cylinders is shown in Figure 4-3. This clearly shows the resemblance between the two types of GFRP. The peak strengths are the same, while the B-GFRP specimen has slightly higher ultimate axial and hoop strains. Both specimens exhibit the same bilinear trend, with the transition occurring at a stress of about 55 MPa.

4.3.2 Results of Environmental Conditioning

Unconfined concrete cylinders: The unconfined concrete cylinders form the baseline for comparison with confined concrete. As such, it was important to identify the aging and conditioning effects on the plain concrete, whether it is a positive or negative effect, to be able to isolate the conditioning effect on the GFRP jacket. For this reason, the plain concrete cylinders were conditioned in the same environments as the GFRP-wrapped ones and tested after 97, 182 and 300 days of exposure. Figure 4-4 shows the average axial strengths of the control and conditioned cylinders, along with the maximum and minimum test results for each set. At the 23 and 40^{o}C, it is interesting to note some gain in strength of about 17% by 182 days, likely due to moisture post-curing and then reduces to 12 and 8% at 300 days. On the other hand, the strength remains stable at the 55^{o}C temperature throughout the 300 days.

Confined concrete cylinders: The axial strength of the wrapped concrete cylinders decreased over the 300 days of exposure as shown in Table 2. Figure 4-5 displays the average axial strength of the B-GFRP wrapped concrete cylinders along with the maximum and minimum test results at 29, 97, 182 and 300 days of exposure, as well as the results for E-GFRP wrapped cylinders at 300 days of exposure. It is clear that the reduction in strength increases as the temperature gets higher, where the maximum reduction of 27.6% occurred at 55^{o}C for the B-GFRP wrapped cylinders at 300 days. The percent retention of axial strength of the B-GFRP concrete cylinders over time for each environmental tank is shown in Figure 4-6(a). The B-GFRP wrapped cylinders had strength retention values, after 300 days, of 83, 78, and 72% while being exposed to 23, 40 and 55^{o}C saltwater, respectively. However, focusing on the change in values of confined concrete strength ($f_{cc}^{'}$) alone may be a bit misleading, since the base unconfined concrete strength ($f_{c}^{'}$) also changes with time as indicated earlier (Figure 4-4). As such, to isolate the confinement effect of the GFRP jacket, it is more appropriate to evaluate the strengthening ratio ($f_{cc}^{'}/f_{c}^{'}$) retention, commonly referred to as confinement effectiveness, as shown in Figure 4-6(b). The figure generally shows that a loss of about 27% occurs at 300 days for all range of temperatures. The discrepancy shown at 182 days where the loss at the 40^{o}C is 32%, higher than that at 300 days, is directly related to the peak increase in unconfined strength at this age, at this temperature (Figure 4-4). It may also relate to the statistical variation among repetitions.

The E-GFRP wrapped cylinders were tested after 300 days of environmental exposure. When compared to the results of the B-GFRP wrapped cylinders after 300 days (Figure 4-5), it can be seen that a slightly less reduction in strength occurred. The E-

GFRP cylinders strength retention values were 91, 82 and 75% after being exposed for 300 days in the 23, 40 and 55^{o}C saltwater, respectively. At the highest temperature, after 300 days, the E-GFRP and B-GFRP wrapped cylinder axial strength retention values were only 3% different.

Stress-strain graphs: The stress-strain plots of the B-GFRP wrapped concrete cylinders after 29, 97, 182 and 300 days of exposure are shown in Figure 4-7(a, b, c and d), in comparison to the control stress-strain curve of wrapped unconditioned cylinders. Similarly, Figure 4-8 shows the stress-strain plots of the E-GFRP wrapped cylinders after 300 days in comparison to the control specimen. Clearly, for both the bio-resin and epoxy GFRP wraps, the ultimate hoop strain of the jacket reduces with time and with the increased temperature, but most noticeably at the 6 and 10 months. This also reduces ductility significantly by shortening the length of the second branch of the bi-linear axial stress-strain curve. For instance, the axial strain at failure after 10 months is less than half that of the control specimens. It is also noticed that the slope of the second branch is reduced, particularly as the temperature increases at the 6 and 10 months. It is important to note that each stress-strain plot represents only one cylinder and not the average of the three cylinders in each set. Therefore, one can only interpret these stress-strain plots with caution.

4.3.3 Failure Modes

The failure of the E-GFRP wrapped cylinders occurred by rupture of the GFRP jacket in the hoop direction, as shown in Figure 4-9(a), and referred to by “R” in Table 2. Similarly, the B-GFRP wrapped cylinders failed by rupture of the GFRP jacket in the hoop direction, as shown in Figure 4-9(b and c). It appears though that, as the time of

exposure and temperature increase, the nature of fracture shifts gradually from a spread fracture (Figure 4-9(b)) to a more localized one (Figure 4-9(c)). In some specimens, the jacket fracture was accompanied by what appears to be opening or slip of the overlap splice, as shown in Figure 4-9(d) and referred to as "RS" in Table 4-2. However, judging from the results in Table 4-2 and the standard deviations, the variability among each three repetitions is relatively small. Also, there was no specific correlation between the axial strength and the type of failure. In fact, in some cases, the specimen with 'RS' type failure showed a higher load than that with 'R' type failure in the same set of three repetitions.

4.3.4 Prediction of Long-Term Behaviour using Arrhenius Relationship

By applying Arrhenius relationship, a prediction of the property retention of a material over its service life for a certain site temperature can be made. The linearized form of Arrhenius equation is given by the following Equation [Meyer et al 1994]:

$$\ln\left(\frac{1}{k}\right) = \frac{E_a}{R}\frac{1}{T} - \ln(A) \qquad (1)$$

where k = degradation rate (1/time); A = constant relative to the material and degradation process; E_a = activation energy; R = universal gas constant; T = Temperature (Kelvin). E_a and A can be determined from an Arrhenius plot. Based on this equation, it can be observed that ln(A) is the intercept of the y-axis of the regression line and (E_a/R) is the slope of the regression line.

Some of the assumptions made in this model are as follows: over the aging process, only one mode of degradation can occur. This mode cannot change with time or temperature; hence, it is important not to use a temperature close to the FRP's glass transition temperature. Also, the FRP must be aged in an aqueous solution, not a dry

environment [Bank et al 2003]. Gerritse (1998) states that at least three elevated temperatures (temperatures that are above the average service temperature being used for the prediction of the longer term) are required to get accurate results from the Arrhenius model. In this current study, the retention in strength of the bio-resin GFRP wrapped concrete cylinders was predicted over an extended service life at an assumed average annual temperature of 10^{o}C, representing southern parts of Canada or Northern United States.

Arrhenius relationship was used to predict the strength retention of the B-GFRP wrapped concrete cylinders over its service life, using the procedure outlined by Bank et al. (2003). The first step in this process is to produce a graph that describes the relationship between the property retention, expressed in percentage of the original strength, over the natural logarithm of time for given temperatures, as shown in Figure 4-10(a). Equations of each regression line are generated, as shown in the figure, which are then used to produce Arrhenius plot that illustrates the relationship of the natural logarithm of time over the inverse of temperature, expressed in 1000/K for given property retentions, as shown in Figure 4-10(b). From this graph, the prediction of property retention for the B-GFRP wrapped concrete cylinders can be made over an extended service life. Figure 4-11 shows the predicted axial strength retentions of B-GFRP wrapped concrete cylinders immersed in saltwater at 10^{o}C. After 5, 50 and 100 years, the property retention is predicted to be 77%, 68%, and 65%, respectively. Results clearly show that the majority of reduction occurs very early in the exposure, with about half of the 100 year's reduction in strength occurring in the first one and half years.

4.4 SUMMARY

Very limited studies exist on durability of 'green' bio-composites, particularly resins, in the context of structural engineering applications. This paper investigates the durability of concrete cylinders wrapped with glass fiber reinforced bio-resin made from furfuryl alcohol extracted from renewable sources such as corn cobs and sugar cane. Conditioning was achieved by immersion of various groups of GFRP-wrapped 153x305 mm cylinders in saline solutions with 3% salt concentration, at 23^{o}, 40^{o} and 55^{o}C, for up to 300 days. The groups included control specimens fabricated with conventional epoxy resin for comparison and plain concrete cylinders. Specimens were then tested in axial compression, periodically, at 29, 97, 182 and 300 days. It was shown that control unconditioned epoxy-GFRP and bio-resin-GFRP wrapped cylinders had the same confined axial compressive strength ($f_{cc}^{'}$), essentially a strengthening ratio ($f_{cc}^{'}/f_{c}^{'}$) of 2.24. After conditioning for 300 days, the ($f_{cc}^{'}/f_{c}^{'}$) ratio retentions for the bio-resin-GFRP was 73% at all temperatures, and were 81, 76 and 76% for the epoxy-GFRP at the 23^{o}, 40^{o} and 55^{o}C, respectively. Using the Arrhenius model, it was estimated that after 5, 50 and 100 years, the bio-resin-GFRP wrapped cylinders immersed in a saltwater environment at 10^{o}C, representing an annual average temperature, would retain 77, 68 and 65%, respectively, of their axial strength.

(a) (b) (c)

Figure 4-1: (a) Schematic of wrapped cylinder; (b) Sample B-GFRP wrapped cylinder; (c) Sample E-GFRP wrapped cylinder

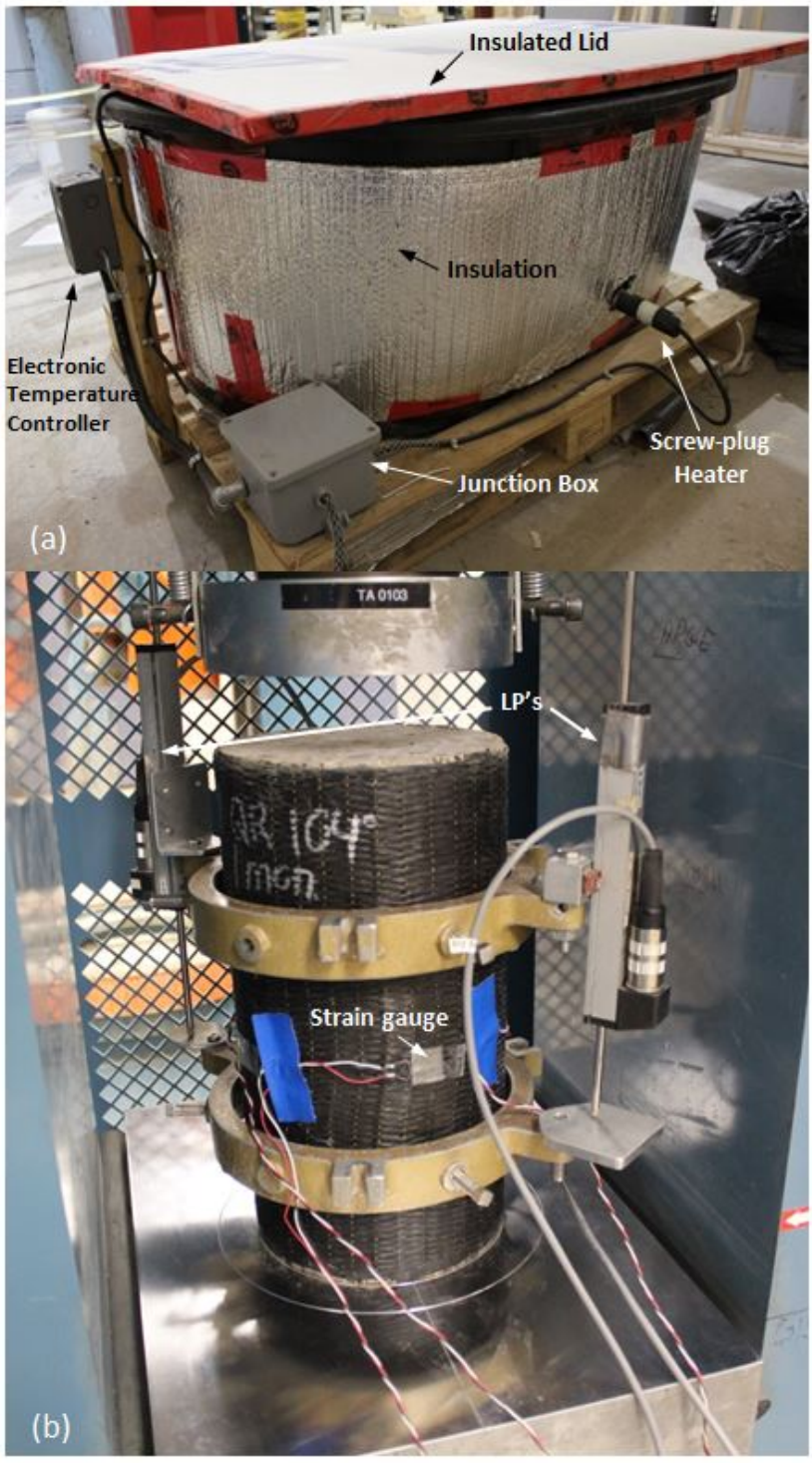


Figure 4-2: (a) Environmental chamber set-up; (b) Test-set-up and instrumentation of the wrapped cylinders

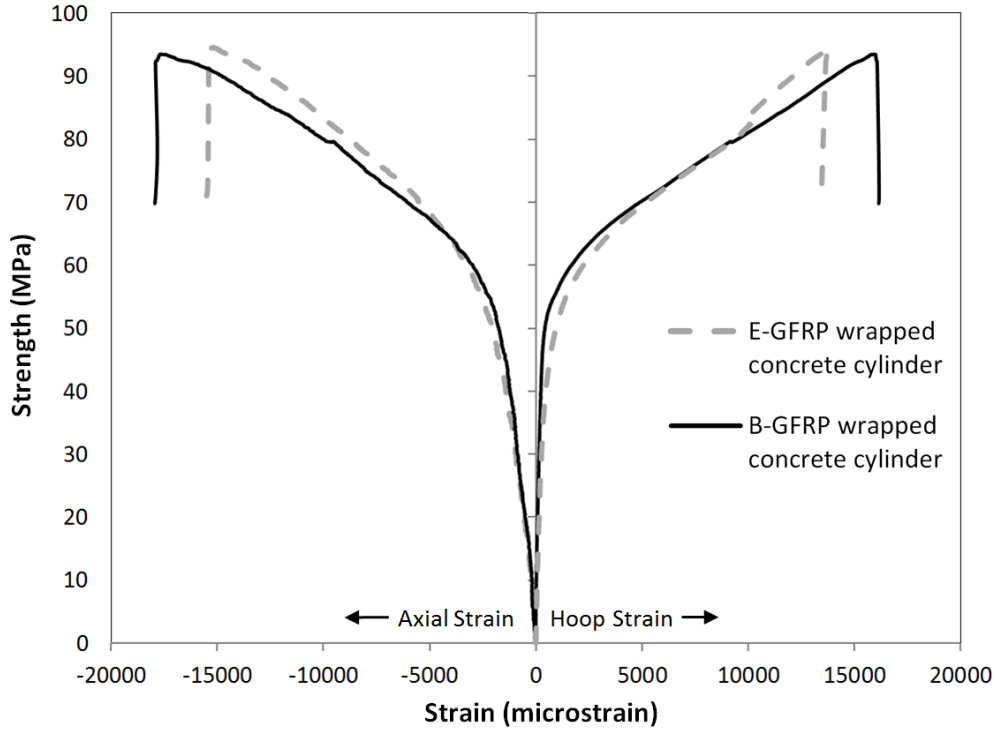


Figure 4-3: Stress-strain curves for control (unconditioned) E-GFRP and B-GFRP wrapped cylinders

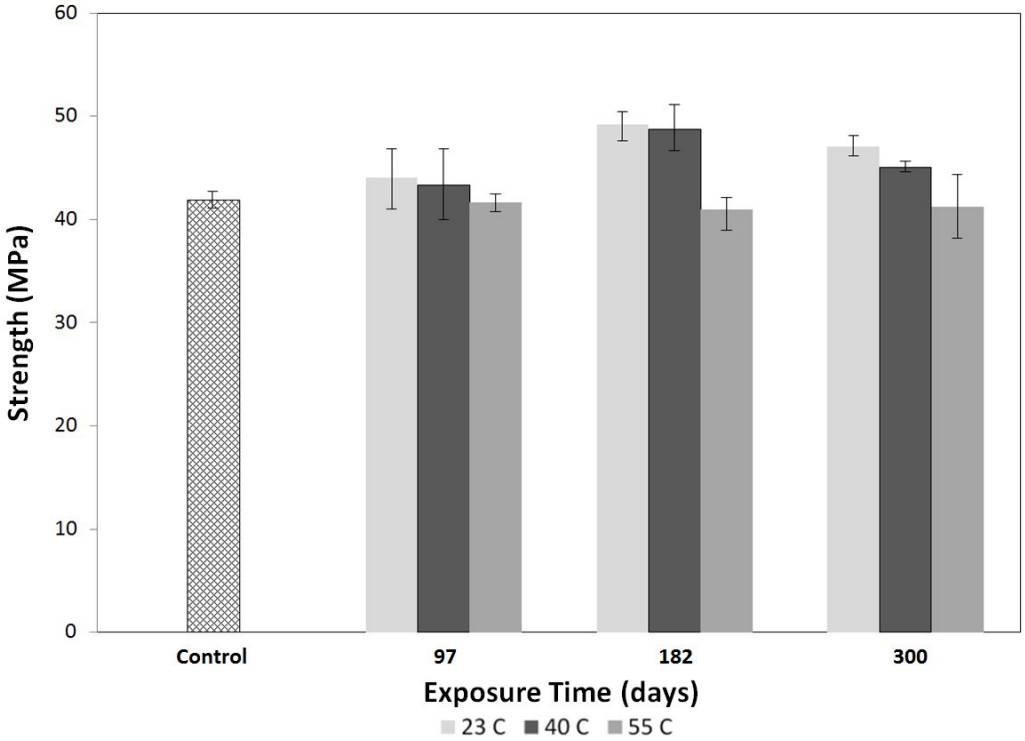


Figure 4-4: Conditioning effect in salt solution at 23°, 40° and 55°C on plain (unconfined) concrete cylinders

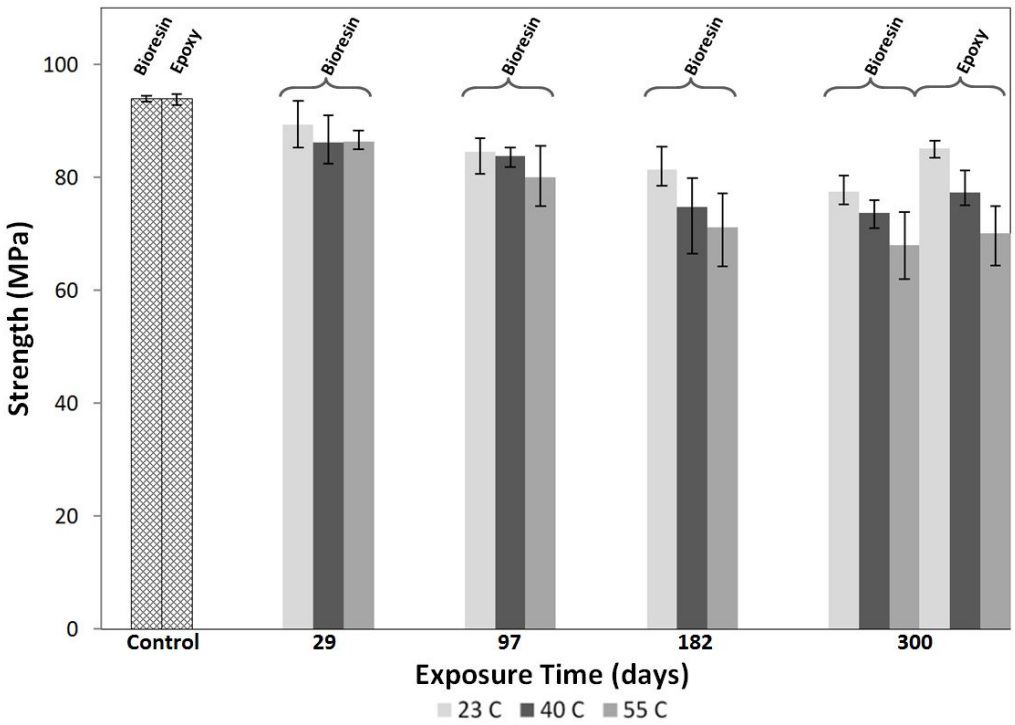
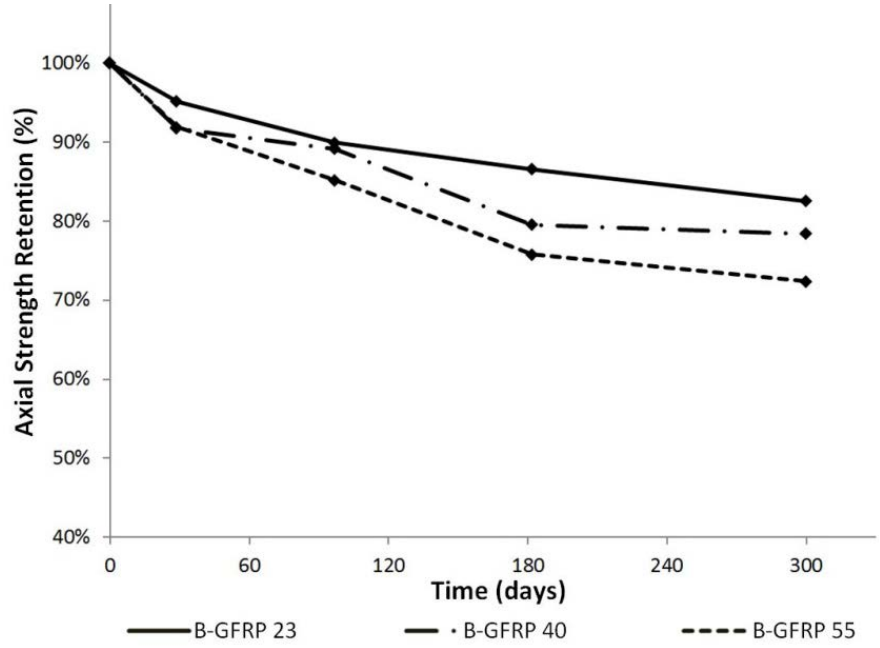
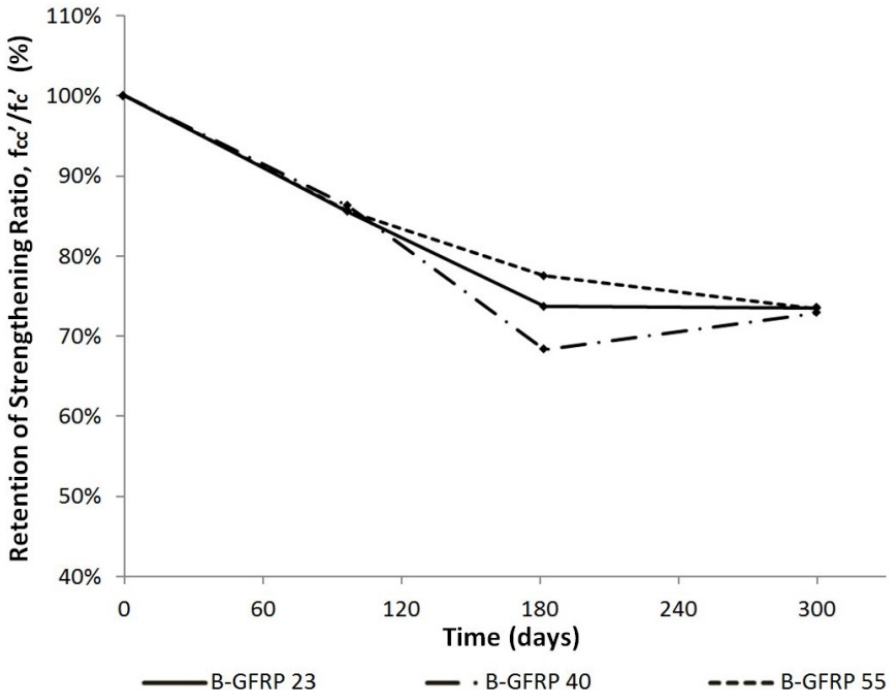


Figure 4-5: Axial strength of E-GFRP and B-GFRP wrapped cylinders conditioned in salt solution at 23^{o}, 40^{o} and 55^{o}C compared to control specimens



(a) Axial compressive strength (f_{cc}')



(b) Strengthening ratio (f_{cc}'/f_c')

Figure 4-6: Percent retention of axial strength and strengthening ratio of B-GFRP wrapped cylinders over 300 days in salt solution at 23°, 40° and 55°C

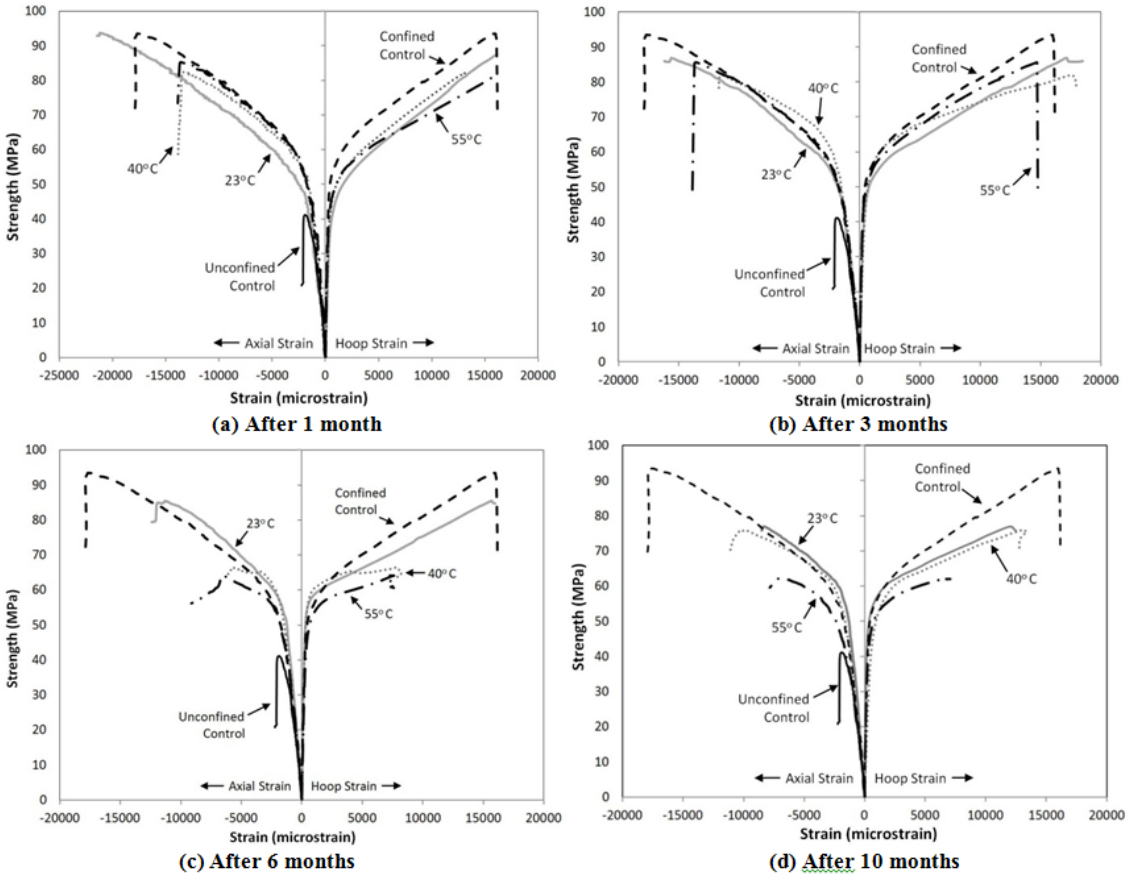


Figure 4-7: Stress-strain curves of conditioned B-GFRP wrapped cylinders in salt solution at 23°, 40° and 55°C

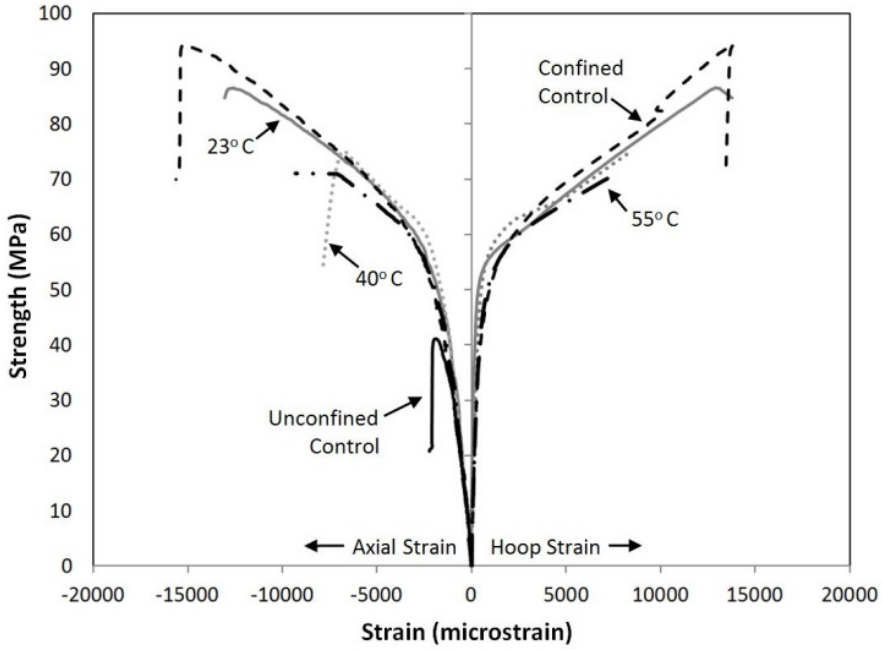


Figure 4-8: Stress-strain curves of conditioned E-GFRP wrapped cylinders after 10 months in salt solution at 23°, 40° and 55°C

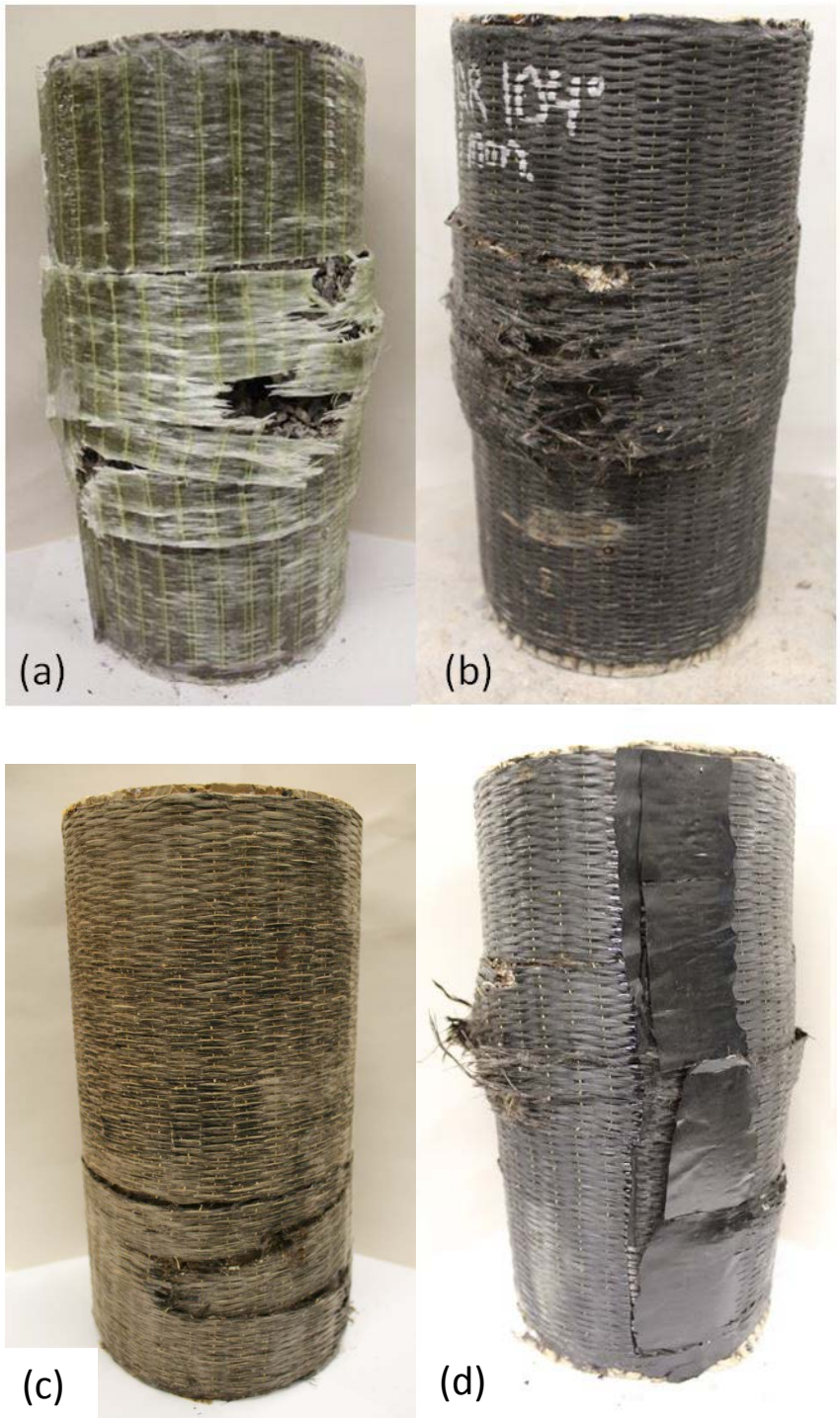
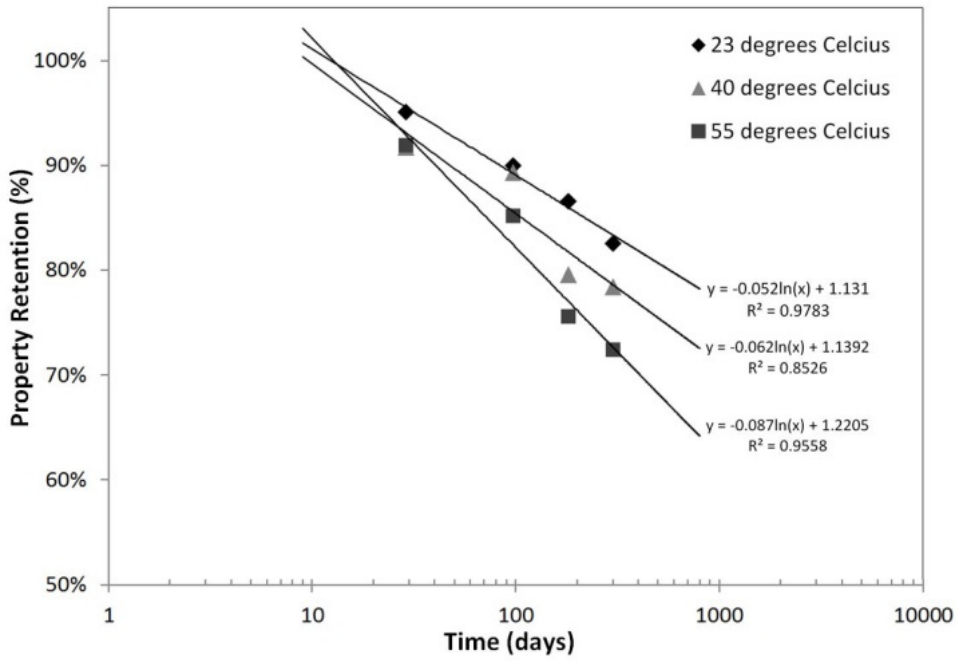
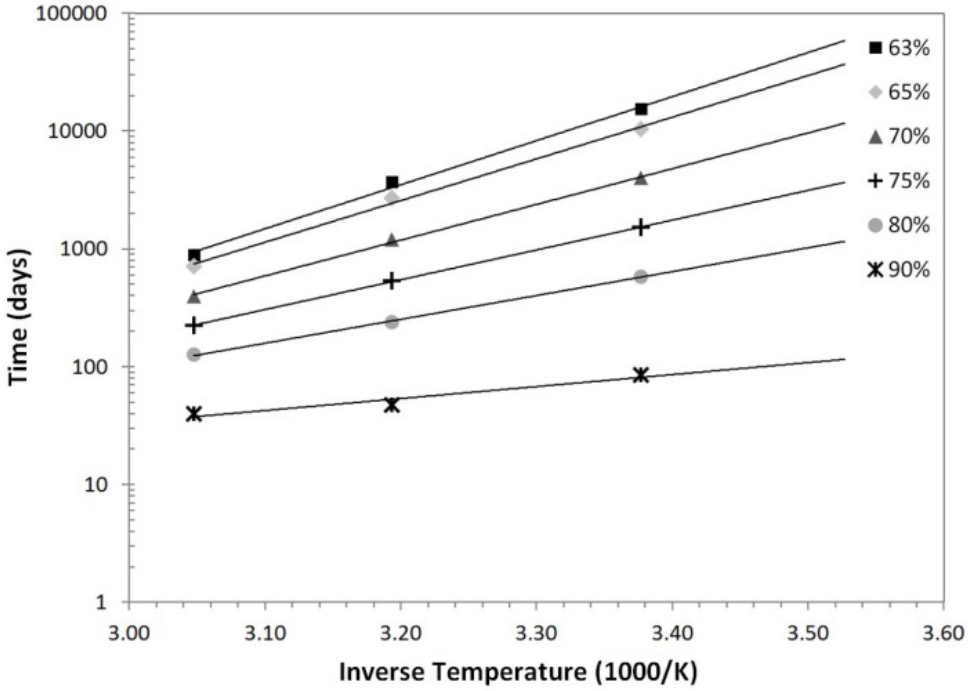


Figure 4-9: Failure modes of GFRP wrapped cylinders: (a) E-GFRP rupture, (b) B-GFRP spread rupture, (c) B-GFRP localized rupture and (d) B-GFRP rupture and splice opening



(a) Variation of property retention with logarithm of time



(b) Arrhenius plot

Figure 4-10: Process for generating a generalized form of axial strength retention with time

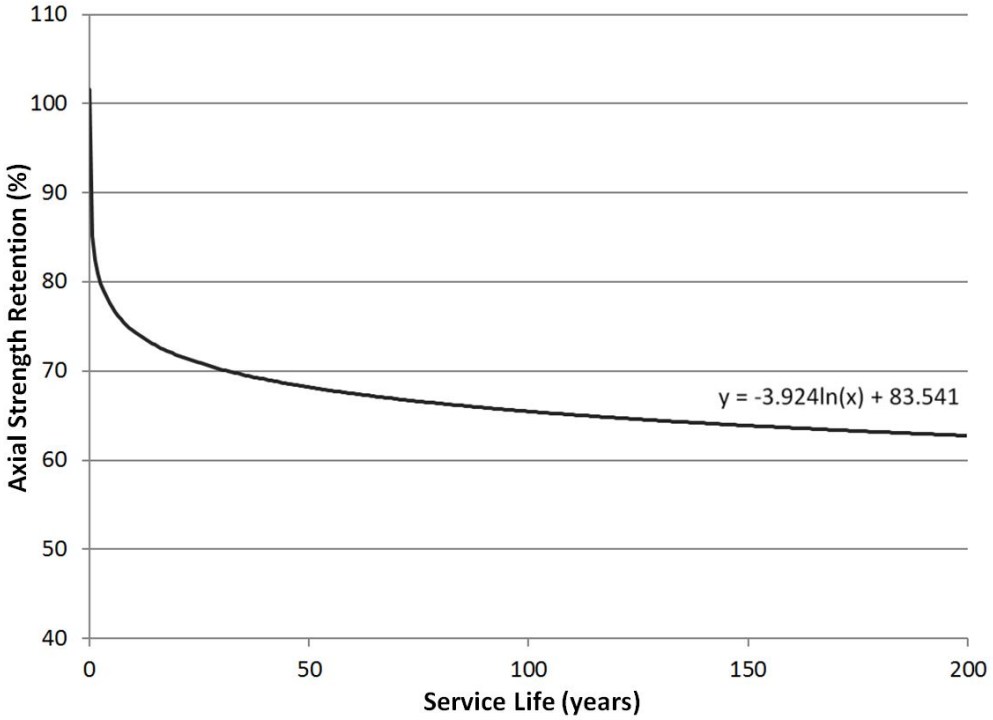


Figure 4-11: Prediction of axial strength retention over the service life of the B-GFRP wrapped concrete cylinders

Table 4-1: Test Matrix

Type of Cylinder	No. of cylinders	Environment Condition	Temperature (^{o}C)	Time in tanks (days)
Bio-resin GFRP wrapped	3	(control, dry)	23	0
	3	Full Immersion 3% Salt Water	23	29
	3	Full Immersion 3%SW	23	97
	3	Full Immersion 3%SW	23	182
	3	Full Immersion 3%SW	23	300
	3	Full Immersion 3%SW	40	29
	3	Full Immersion 3%SW	40	97
	3	Full Immersion 3%SW	40	182
	3	Full Immersion 3%SW	40	300
	3	Full Immersion 3%SW	55	29
	3	Full Immersion 3%SW	55	97
	3	Full Immersion 3%SW	55	182
	3	Full Immersion 3%SW	55	300
Epoxy GFRP wrapped	3	(control, dry)	23	0
	3	Full Immersion 3%SW	23	300
	3	Full Immersion 3%SW	40	300
	3	Full Immersion 3%SW	55	300
Unconfined	3	(control, dry)	23	0
	3	Full Immersion 3%SW	23	97
	3	Full Immersion 3%SW	23	182
	3	Full Immersion 3%SW	23	300
	3	Full Immersion 3%SW	40	97
	3	Full Immersion 3%SW	40	182
	3	Full Immersion 3%SW	40	300
	3	Full Immersion 3%SW	55	97
	3	Full Immersion 3%SW	55	182
	3	Full Immersion 3%SW	55	300

Table 4-2: Test Results Summary

Specimen ID	Type	No. of cylinders used to calculate mean	Mean axial strengths (MPa)	Standard deviation (MPa)	% Reduction in Strength	Failure Mode R: rupture, SR: rupture & splice opening
B-Control	Bio-resin-GFRP wrapped cylinders	3	93.9	0.53	-	R, R, RS
B-23-29		3	89.4	4.16	-4.86	R, R, RS
B-23-97		3	84.5	3.36	-10.06	R, R, RS
B-23-182		3	81.3	3.69	-13.41	R, R, RS
B-23-300		3	77.5	2.59	-17.46	RS, RS, RS
B-40-29		3	86.2	4.37	-8.25	R, RS, RS
B-40-97		3	83.8	1.75	-10.82	RS, RS, RS
B-40-182		3	74.7	7.25	-20.46	RS, RS, RS
B-40-300		3	73.7	2.53	-21.59	R, R, RS
B-55-29		3	86.3	1.76	-8.12	RS, RS, RS
B-55-97		3	80.0	5.32	-14.83	RS, RS, RS
B-55-182		3	71.2	6.55	-24.24	R, R, RS
B-55-300		3	68.0	5.89	-27.63	R, R, R
E-Control	Epoxy-GFRP wrapped cylinders	3	94.0	1.06	-	R, R, R
E-23-300		3	85.2	1.58	-9.43	R, R, R
E-40-300		3	77.3	3.44	-17.84	R, R, R
E-55-300		3	70.1	5.36	-25.45	R, R, R
U-Control	Unconfined plain cylinders	3	41.9	0.79	-	-
U-23-97		3	44.0	2.95	+5.14	-
U-23-182		3	49.2	1.44	+17.51	-
U-23-300		3	47.0	1.03	+12.26	-
U-40-97		3	43.3	3.45	+3.41	-
U-40-182		3	48.7	2.28	+16.34	-
U-40-300		3	45.0	0.53	+7.56	-
U-55-97		3	41.7	0.88	-0.52	-
U-55-182		3	40.9	1.74	-2.26	-
U-55-300		3	41.3	3.07	-1.49	-

Chapter 5: Conclusions

5.1 Mechanical Characteristics of Glass Fibre Reinforced Polymer made of Furfuryl Alcohol Bio-resin

In this study, the mechanical properties of glass fiber reinforced polymer (GFRP) laminates fabricated using two types of furfuryl alcohol bio-resin extracted from corncob. The study assessed the composite behavior in terms of tensile strength and Young's modulus and compared the properties to control GFRP specimens with conventional epoxy resin. The study examined different catalysts along with the effects of the dosage of the catalyst and the curing time on mechanical properties. The study also established the length of the overlap splice necessary to achieve the optimal strength of the composite. This novel bio-resin GFRP can be used in rehabilitation efforts as an externally bonded composite and provide a more sustainable option than traditional epoxy resins. The following conclusions are drawn from this study:

1. Careful selection of the types of bio-resin and catalyst along with the dosage of catalyst and curing time can indeed lead to mechanical properties quite similar to those obtained by epoxy resins in GFRP laminates, in terms of tensile strength and modulus.
2. Two days after fabrication, the bio-resin GFRP composite (3-Q2001-Q1 system) reached 84% of its maximum tensile strength. After four days, 93% was reached and full strength was reached at about 13 days.
3. The low-viscosity type bio-resin (3-Q2001-Q1 system) was the most successful in that it resulted in a similar tensile strength to epoxy-GFRP coupons. It also proven

to be the most suitable for the hand layup fabrication technique, unlike the higher viscosity system (3-pTam-Q3) which could not saturate the glass fibres completely.

4. The optimal catalyst proportion was studied for the higher viscosity (3-pTam-Q3 system) and was found to be 2.5% by weight. This dosage will produce the highest tensile strength of the composite, but it remains 17% lower than epoxy-GFRP coupons. For the lower viscosity bio-resin (3-Q2001-Q1 system), a 3% catalyst resulted in tensile strength equal to that of epoxy-GFRP coupons.
5. Generally, various parameters studied, namely type of resin and type and dosage of catalyst and curing time have little effect on Young's modulus but significant effect on tensile strength.
6. The lap splice length required to produce the maximum strength of the bio-resin GFRP composite (3-Q2001-Q1 system) was 200 mm. Longer splices will not lead to any further gain in strength and failure continues to be governed by bond. However, this maximum strength is only 68% of the full ultimate tensile strength based on fiber rupture.

5.2 Environmental Aging Effect on Tensile Properties of GFRP made of Furfuryl Alcohol Bio-Resin Compared to Epoxy

The durability of bio-resin GFRP composites was determined through environmental aging in saltwater. Standard tension coupons were subjected to three different water temperatures of 23^{o}, 40^{o} and 55^{o}C, with 3% salt concentration by weight and tested at five time intervals, up to 300 days. The durability of these coupons was assessed through standard tension tests and compared to the control un-aged bio (B)-GFRPs and epoxy (E)-GFRPs. The following conclusions were made:

1. The tensile strength retentions of the bio-resin GFRP after aging for 300 days at 23, 40 and 55^{o}C were 80, 44 and 39%, respectively.
2. The bio-resin GFRP is more vulnerable to the saltwater environment than the epoxy GFRP. Although their control un-aged tensile strengths were virtually identical, their residual strengths after 300 days were 7, 39 and 36% lower than epoxy GFRP, at 23^{o}, 40^{o} and 55^{o}C, respectively.
3. No degradation was observed in Young's modulus as it remain relatively stable for both the epoxy GFRP and bio-resin GFRP over 300 days of exposure at various temperatures.
4. The failure mode of the bio-resin GFRP specimens changed from a wide-spread explosive tensile rupture failure at early stages of exposure to a localized non-explosive one towards the end of aging. Epoxy GFRP coupons failed in the same manner throughout the history of aging.
5. By applying the Arrhenius relationship, it was estimated that after 100 years of the bio-resin GFRP being immersed in a saltwater environment at an average annual temperature of 10^{o}C, it will retain 61% of its tensile strength. The majority of loss occurs initially as the 5 years retention is 75%.
6. The estimated 100 years tensile strength retention of the epoxy GFRP is 81% at 10^{o}C, 33% higher retention than the bio-resin GFRP under the same condition.

5.3 Durability of Concrete Cylinders Wrapped with GFRP made from Furfuryl Alcohol Bio-Resin

Environmental tests were conducted to assess the durability of bio-resin- and epoxy-GFRP-wrapped concrete cylinders, as well as unconfined cylinders. These specimens

were conditioned in a saltwater bath at 23°, 40° and 55°C temperatures. Axial compression tests were completed after 29, 97, 182 and 300 days of exposure. The following conclusions were made:

1. The control unconditioned epoxy-GFRP and bio-resin-GFRP wrapped cylinders had the same confined axial compressive strength (f_{cc}'), essentially producing a strengthening ratio (f_{cc}'/f_c') of 2.24.
2. After 300 days submersion in salt water at 23°, 40° and 55°C, the bio-resin-GFRP confined cylinders lost 18, 22 and 28%, respectively, of their strength f_{cc}'.
3. As the unconfined concrete strength (f_c') also changed with time, the loss in (f_{cc}'/f_c') ratio at 300 days was 27% at all temperatures for the bio-resin-GFRP and 19, 24 and 24% for the epoxy-GFRP at the 23°, 40° and 55°C, respectively.
4. It follows from previous point that the bio-resin-GFRP examined appears to be only slightly more vulnerable to environmental degradation than the conventional epoxy-GFRP used. After 300 days in 23°, 40° and 55°C saltwater, the bio-resin-GFRP provided 9%, 5% and 3% lower f_{cc}' than the epoxy-GFRP in the same conditions.
5. The bio-resin-GFRP wraps failed by rupture in the hoop direction, which in some cases was combined with some opening or slip at lap splice. However, the latter did not result in any reduction in strength. Epoxy-GFRP wraps failed consistently by hoop rupture.
6. Using Arrhenius relationship, it was estimated that after 5, 50 and 100 years, the bio-resin GFRP wrapped cylinders immersed in a saltwater environment at an

average temperature of 10^{o}C, would retain 77, 68 and 65%, respectively, of their axial strength.

5.4 Recommendations and Future Work

Some areas of study that can be researched in the future are as follows:

1. Determine the mechanical behaviour of this bio-resin combined with bio-fibres.

2. Expose the bio-resin GFRP to different environments, such as freeze/thaw, alkaline exposure and UV radiation. This would allow for a greater understanding of the long-term performance of this material.

3. Determine the behaviour of this bio-resin GFRP in a bond critical application rather than a contact critical application as seen in this thesis. For example, flexural rehabilitation of beams.

4. Experiment with different types of bio-resin and glass fibres.

REFERENCES

Adekunle, Kayode, et al. "Impact and flexural properties of flax fabrics and Lyocell fiber-reinforced bio-based thermoset." *Journal of Reinforced Plastics and Composites* 30.8 (2011): 685-697.

Al-Zahrani, M.M., S.U. Al-Dulaijan, A. Sharif, M. Maslehuddin. 2002. "Durability performance of glass fiber reinforced plastic reinforcement in harsh environments," presented at the 6th Saudi Engineering Conference, December 2002.

ASTM C39. 2010. " Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens." *American Society for Testing and Materials.*

ASTM C31. 2010. " Standard Practice for Making and Curing Concrete Test Specimens in the Field." *American Society for Testing and Materials.*

ASTM D 3039. "Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials." *American Society for Testing and Materials.* (2007)

ASTM D7616. "Standard Test Method for Determining Apparent Overlap Splice Shear Strength Properties of Wet Lay-Up Fiber-Reinforced Polymer Matrix Composites Used for Strengthening Civil Structures," *American Society for Testing and Materials.* (2011)

Bank, L.C., T.R. Gentry, B.P. Thompson, J.S. Russell. 2003. "A model specification for FRP composites for civil engineering structures," *Const. & Bldg. Matls.*, 17:405-437.

Casado, U., N.E. Marcovich, M.I. Aranguren, M.A. Mosiewicki. 2009. "High-strength composites based on tung oil polyurethane and wood flour: Effect of the filler concentration on the mechanical properties."*Polymer Engineering & Science*, 49(4):713-721.

Chen, Y., J.F. Davalos, I. Ray, H. Kim. 2007. “Accelerated aging tests for evaluations of durability performance of FRP reinforcing bars for concrete structures,” *Composite Structures*, 78:101-111.

Chen, Y., J. F. Davalos, and I. Ray. 2006. “Durability prediction for GFRP bars using short-term data of accelerated aging tests.” *J. Compos. Constr.*, 10(4): 279–286.

Cromwell, J.R., K.A. Harries, B.M. Shahrooz. 2010. “Environmental durability of externally bonded FRP materials intended for repair of concrete structures,” *Const. & Bldg. Matls.*, 25:2528-2539.

Dejke, V. 2001. “Durability of FRP reinforcement in concrete-literature review and experiments.” Tekn. Lic. thesis, Depart. of Builiding Materials, Chalmers, Univ. of Technology, Göteborg, Sweden.

Fam, A. and Eldridge, A. Misra, M. (2013) “Mechanical characteristics of glass fibre reinforced polymer made of furfuryl alcohol bio-resin.” *Journal of Materials and Structures.*

Gerritse, A. 1998. “Assessment of long term performance of FRP bars in concrete structures.” *Durability of Fiber Reinforced Polymers (FRP) Composites for Construction*, Sherbrooke, Québec, Canada, 285–297.

JAFFE, F. "Furfuryl alcohol resins." U.S. Patent No. 3,055,844. 25 Sep. 1962.

Kajorncheappunngam, S., R. K. Gupta, H. V. S. GangaRao. 2002. “Effect of Aging Environment on Degradation of Glass-Reinforced Epoxy,” *Journal of Composites for Construction*, 6(1):61-69.

Karbhari, Vistasp M. "Materials considerations in FRP rehabilitation of concrete structures." *Journal of materials in civil engineering*, 13.2 (2001): 90-97.

Khot, Shrikant N., et al. "Development and application of triglyceride-based polymers and composites." *Journal of applied polymer science* 82.3 (2001): 703-723.

Kshirsagar, S., R.A. Lopez-Anido, and R.K. Gupta. 2000. “Environmental Aging of Fiber-Reinforced Polymer-Wrapped Concrete Cylinders,” ACI Materials Journal, 97(6):703-712

Li, Fengkui, and Richard C. Larock. "New soybean oil–styrene–divinylbenzene thermosetting copolymers. v. shape memory effect." *Journal of applied polymer science* 84.8 (2002): 1533-1543.

Li, F., J. Hasjim, and R.C. Larock. 2003. "Synthesis, structure, and thermophysical and mechanical properties of new polymers prepared by the cationic copolymerization of corn oil, styrene, and divinylbenzene." *Journal of applied polymer science*, 90(7):1830-1838.

Lu, Jue, Shrikant Khot, and Richard P. Wool. "New sheet molding compound resins from soybean oil. I. Synthesis and characterization." *Polymer* 46.1 (2005): 71-80.

Meyer, M.R., R.J. Friedman, H.D. Schutte Jr., R.A. Latour, Jr. 1994. “Long-term durability of the interface in FRP composites after I. exposure to simulated physiologic saline environments.” *Journal of Biomedical Materials Research*, 28:1221-1231.

Mirmiran, A. and M. Shahawy. 1997. “Behavior of Concrete Columns Confined by Fiber Composites.” *J. Struct. Eng.*, 123(5): 583–590.

Miyagawa, Hiroaki, et al. "Fracture toughness and impact strength of anhydride-cured biobased epoxy." *Polymer Engineering & Science* 45.4 (2005): 487-495.

Miyagawa, Hiroaki, et al. "Biobased epoxy/clay nanocomposites as a new matrix for CFRP." *Composites Part A: Applied Science and Manufacturing* 37.1 (2006): 54-62.

Mosiewicki, M., M. I. Aranguren, and J. Borrajo. "Mechanical properties of linseed oil monoglyceride maleate/styrene copolymers." *Journal of applied polymer science* 97.3 (2005): 825-836.

O'donnell, A., M. A. Dweib, and R. P. Wool. 2004. "Natural fiber composites with plant oil-based resin." *Composites Science and Technology,* 64(9):1135-1145.

PennAKem. *QuaCorr Resins and Catalysts.* Tennessee. <http://www.pennakem.com/products/QuaCorr.html> (2010) (November 2012).

Pessiki, S., K. Harries, J. Kestner, R. Sause, and J. Ricles. 2001. "Axial Behavior of Reinforced Concrete Columns Confined with FRP Jackets." *J. Compos. Constr.,* 5(4): 237–245.

Petrović, Zoran S., et al. "Soy-oil-based segmented polyurethanes." *Journal of Polymer Science Part B: Polymer Physics* 43.22 (2005): 3178-3190.

Porter, M. L., J. Mehus, K. A. Young, E. F. O'Neil, and B. A. Barnes. 1997. "Aging for fiber reinforcement in concrete." *Proc. of the Third Int. Symp. on Non-Metallic (FRP) Reinforcement for Concrete Structures,* Japan Concrete Institute, Sapporo, Japan, 2:59–66.

Rivera, J., V.M. Karbhari. 2002. "Cold-temperature and simultaneous aqueous environment related degradation of carbon vinylester composites," *Composites: Part B,* 33:17-24.

Robert, M., R. Roy, B. Benmokrane. 2010. "Environmental Effects on Glass Fiber Reinforced Polypropylene Thermoplastic Composite Laminate for Structural Applications," *Polymer Composites,* 604-611.

Robert, M., A. Fam. 2012. “Long-Term Performance of GFRP Tubes Filled with Concrete and Subjected to Salt Solution,” *J. Compos. Constr.,* 16(2):217-224.

Saenz, N. and C.P. Pantelides. 2006. “Short and Medium Term Durability Evaluation of FRP-Confined Circular Concrete,” *J. of Composites for Construction,* 10(3): 244-253.

Spoelstra, M. and G. Monti. 1999. “FRP-Confined Concrete Model.” *J. Compos. Constr.,* 3(3): 143–150.

Toutanji, H.A. 1999. “Durability characteristics of concrete columns confined with advanced composite materials,” *Composite Structures,* 44: 155-161.

Vroman, Isabelle, and Lan Tighzert. "Biodegradable polymers." *Materials* 2.2 (2009): 307-344.

Wambua, Paul, Jan Ivens, and Ignaas Verpoest. "Natural fibres: can they replace glass in fibre reinforced plastics?" *Composites Science and Technology* 63.9 (2003): 1259-1264.

Williams, George I., and Richard P. Wool. "Composites from natural fibers and soy oil resins." *Applied Composite Materials* 7.5 (2000): 421-432.

Wollerdorfer, Martina, and Herbert Bader. "Influence of natural fibres on the mechanical properties of biodegradable polymers." *Industrial Crops and Products* 8.2 (1998): 105-112.