



UNIVERSITY OF NAIROBI
SCHOOL OF ENGINEERING DEPARTMENT OF
ENVIRONMENTAL AND BIOSYSTEMS ENGINEERING

***INVESTIGATING THE MECHANICAL PROPERTIES OF GLASS
REINFORCED POLYMER AS MATERIAL FOR SOLAR HOT WATER
TANKS IN COASTAL AREAS.***

A research thesis submitted in partial fulfillment of the requirements for the award of Degree of Master of Science (in Environmental and Biosystems Engineering), in the school of Engineering, University of Nairobi.

By AMOS ABALA WAMBURA,
B. Tech. Mechanical and Production Engineering,
Moi University,
P.O. Box 41762-00100, Nairobi

DATE: 10/11/2015

Declaration

I declare that this thesis is my original work and has not been presented for a degree in any other University

Approval

This thesis has been submitted for examination with my/our approval as University supervisor(s).

Eng. Dr. DUNCAN ONYANGO MBUGE,

University of Nairobi,

P.O Box 30197, Nairobi

SIGNATURE:.....

DATE: 10/11/2015

DECLARATION OF ORIGINALITY

| | |
|---------------------------|---|
| Name of student: | Amos Abala Wambura |
| Registration: | F56 /68967/2011 |
| College: | College of Architecture and Engineering |
| Faculty/School/Institute: | School of Engineering |

- 1) I declare that this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other works or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.
- 2) I have not sought or used the services of any professional agencies to produce this work
- 3) I have not allowed , and shall not allow anyone to copy my work with the intention of passing it off as his/her work
- 4) I understand that any false claim in respect of this work shall result in disciplinary action in accordance with University of Nairobi anti-plagiarism policy

Signature:

Date: 20th July 2015

Dedication

This work is dedicated to my wife Mary, mother Janet and my daughter Margaret Giovanna, for their support and understanding.

Acknowledgement

First and foremost, I give thanks and honour to God through whom everything is possible. The completion of this work has also been the consequence of voluntary investment of resources by many dedicated people. For those who spent their time and mental resources on this project, I would like to say a special thank you.

I would like to thank my supervisor Eng. Dr. Duncan Onyango Mbuge for his willingness to assist me with ideas, critique and encouragement necessary to undertake this work. It is impossible to thank him enough in a few paragraphs.

I am grateful to the Department of Environmental and Biosystems Engineering, particularly the Chairman Eng. Dr. Ayub Gitau for his encouragement and for accepting to host me. Special thanks also go to the Department of Mechanical Engineering and Manufacturing Technology where I carried out most of the lab work. I would like to single out Mr. Kahiro, and Macharia from the Department of Mechanical and Manufacturing Engineering without whom I may not have obtained any data.

TABLE OF CONTENTS

| | |
|--|------|
| APPROVAL | II |
| DEDICATION | II |
| ACKNOWLEDGEMENT | III |
| TABLE OF CONTENTS..... | IV |
| ACRONYMS | VI |
| LIST OF TABLES | VII |
| LIST OF FIGURES | VIII |
| ABSTRACT..... | X |
| CHAPTER ONE..... | 1 |
| 1.0 INTRODUCTION | 1 |
| 1.1 Background Information..... | 1 |
| 1.2 Problem Statement..... | 5 |
| 1.3 Justification | 6 |
| 1.4 Objective | 6 |
| CHAPTER TWO | 7 |
| 2.0 LITERATURE REVIEW | 7 |
| 2.1 Properties of Glass Fibre and Polymer | 7 |
| 2.2 Glass Fibre | 8 |
| 2.3 Chemistry of Fiber / Matrix Interface..... | 9 |
| 2.4 Production of Fiber | 10 |
| 2.5 Resins..... | 13 |
| 2.6 Polyester Resins | 14 |
| 2.7 Polymer Matrix Selection | 18 |
| 2.8 Mechanical Properties..... | 20 |
| 2.9 Hand Lay-Up | 22 |
| 2.10 Mechanical Properties of Glass Reinforced Polymer | 23 |
| 2.11 Glass Reinforced Polymer Chemical Corrosion Resistance..... | 24 |
| 2.12 Solar Hot Water Systems | 25 |
| 2.18 Summary of Literature Review..... | 41 |

| | |
|--|-----------|
| CHAPTER THREE | 42 |
| 3.0 MATERIALS AND METHODS..... | 42 |
| 3.1 Scope of Work | 42 |
| 3.2 Materials | 42 |
| 3.3 Apparatus..... | 46 |
| 3.4 Experimental Setup..... | 49 |
| 3.5 Experiments. | 50 |
| CHAPTER FOUR..... | 55 |
| 4.0 RESULTS AND DISCUSSION..... | 55 |
| 4.1 Water Absorption..... | 55 |
| 4.2 Tensile Strength Tests..... | 56 |
| 4.3 Prototype Testing..... | 66 |
| 4.4 The Hygrothermal Impact on GRP | 67 |
| CHAPTER FIVE | 69 |
| 5.0 CONCLUSIONS AND FUTURE WORK..... | 69 |
| 5.1 Conclusions..... | 69 |
| 5.2 Future Work..... | 70 |
| REFERENCE | 71 |
| APPENDIX 1.0..... | 77 |

Acronyms

| | |
|------|--|
| AFM | Atomic force microscopy |
| ASTM | America Society for Testing and Materials |
| BPA | Bisphenol-A |
| CSM | Chopped Strand Mat |
| DCPD | Dicyclopentadiene |
| DHW | Domestic Hot Water |
| DMTA | Dynamic Mechanical Thermal Analysis |
| DSC | Differential Scanning Calorimetry |
| D&S | Davis & Shirliff Ltd |
| ERC | Energy Regulation Commission |
| ERC | Energy Regulation Commission of Kenya |
| ESC | Environmental Stress Cracking |
| FRP | Fibre Reinforced Plastic |
| GRP | Glass Reinforced Plastic |
| GSM | Grams per Square Meter |
| MEKP | Methyl Ethyl Ketone Peroxide |
| PET | Polyethylene Terephthalic |
| PMC | Polymer Matrix Composites |
| PSB | Persistent Slip Bands |
| RTM | Resin Transfer Molding |
| UPE | Unsaturated Polyester |
| UTS | Ultimate Tensile Strength |
| UV | Ultraviolet Radiation |
| XPS | X-ray photoelectron spectroscopy |
| W-O | Woven mat-Orthopolyester composite |
| C-O | Chopped Strands mat-Orthopolyester composite |
| W-I | Woven mat-Isoopolyester composite |
| C-I | Chopped Strands mat-Isoopolyester composite |

List of Tables

Table 2-1: E-glass compositions (wt. %)...9

Table 2-2: Comparison of Polyesters, Vinyl esters and Epoxies... 17

Table 2-3: ASTM test methods for characterizing mechanical properties of polyester resins.20

Table 2-4: Mechanical properties of clear-cast (unreinforced) polyester resins.21

Table 2-5: Mechanical properties of fiberglass-polyester composites (glass content,40wt %)...21

Table 2-6: Effect of glass content on mechanical properties of fibreglass reinforced polyester.21

Table 2-7: Mechanical properties of FRP (polyester) composites.....24

Table 3-1: Moisture Effect Data Collection Table51

Tables 3-2: Tensile Test Stress-Strain Data Collection Summary Sheet.....53

Tables 4-1; summary of Young’s Modulus for the dry control samples57

Tables 4-2; summary of Young’s Modulus for the chopped mat - ortho resin samples58

Tables 4-3; summary of Young’s Modulus for the chopped mat-Iso resin samples59

Tables 4-4; summary of Young’s Modulus for the Woven mat-Iso resin samples60

Tables 4-5; summary of Young’s Modulus for the Woven mat-ortho resin samples62

Tables 4-6; summary of Young’s Modulus for the 65 deg. Samples63

Tables 4-7; summary of Young’s Modulus for the 95 deg. Samples64

Tables 4-8; summary of Young’s Modulus for the test at 65⁰C and 95⁰C salty samples65

List of Figures

| | |
|---|----|
| Figure:1.1:Galvanized Uninsulated Tank | 1 |
| Figure 1.2: Galvanized Tank inside GRP Barrel Being Insulated | 2 |
| Figure 1.3: Galvanized Insulated Tank and Solar Collector..... | 2 |
| Figure 1.4:Images of a Corroded Tank..... | 3 |
| Figure 2.1: Specific strength vs specific stiffness for a range of materials. | 7 |
| Figure 2.2: Strength per volume cost vs stiffness per volume cost | 8 |
| Figure 2.3: Diagrammatic sketch of Glass Fibre Manufacturing | 11 |
| Figure 2.4: E-Glass Surface tissue | 12 |
| Figure 2.5: E-Glass chopped strands mat 450 GSM,..... | 12 |
| Figure 2.6: E-Glass woven..... | 13 |
| Figure 2.7:E-Glass Rovings..... | 13 |
| Figure 2.8: shows the idealised chemical structure of typical polyester..... | 15 |
| Figure 2.9: Schematic Representation of Polyester Resin (Uncured)..... | 16 |
| Figure 2.10: Schematic Representation of Polyester Resin (Cured)..... | 16 |
| Figure 2.11: Hand lay-up technique..... | 22 |
| Figure 2.12: Transformation of a craze nuclei into a craze | 33 |
| Figure 2.13: Glass transition temperature of F922 as a function of moisture content | 37 |
| Figure 2.14: Schematic of the osmotic process–leading to delaminations/blistering..... | 39 |
| Figure 3.1: Specimen Geometry | 43 |
| Figure 3.2: GRP production process..... | 44 |
| Figure 3.3: GPR-Orthophthalic polyester sample molded sheets..... | 44 |
| Figure 3.4: GPR- Isophthalic polyester sample molded sheets | 45 |
| Figure 3.5: Different Types of Specimens..... | 45 |
| Figure 3.6: Bundles of GRP specimens | 45 |
| Figure 3.7: Pictorial drawing of Solution Heating Can | 46 |
| Figure 3.8: Pictures of Solution Heating Can | 47 |
| Figure 3.9: Ashton Meyers Weighing Balance..... | 48 |

| | |
|---|----|
| Figure 3.12: Tensile test with difference moisture content..... | 51 |
| Figure 3.13: Hygrothermal Tensile Tests in the UoN Mechanical lab..... | 52 |
| Figure 3.14: UV Chamber..... | 54 |
| Figure 4.1: Physical look before and after water absorption | 55 |
| Figure 4.2: The specimens after tensile tests failure modes | 56 |
| Figure 4.3; Comparison of various dry composite specimens under tensile tests | 57 |
| Figure 4.4: Comparison of various chopped mat-Ortho resin composite specimens under tensile tests..... | 58 |
| Figure 4.5: comparison of toughness of various chopped mat-Iso resin composite specimens under tensile tests | 59 |
| Figure 4.6: Comparison of various Woven mat-Iso resin composite specimens under tensile tests..... | 60 |
| Figure 4.7: Comparison of toughness for various Woven mat - Ortho resin composite specimens under tensile test..... | 61 |
| Figure 4.8: Comparison of effect of temperature on toughness for various composite specimens under tensile test at 65 ⁰ C and 95 ⁰ C. | 63 |
| Figure 4.9: Comparison of effect of salinity on toughness for various composite specimens under tensile test at 65 ⁰ C and 95 ⁰ C..... | 65 |
| Figure 4.10: the hot water tank made from GRP-iso-polyester resin. | 67 |
| Figure 4.11: GRP Hot Water Tank under test for water under both high..... | 67 |

Abstract: Over the years solar water heater storage tanks have been made of galvanized steel or coated with enamel to prevent rusting due to corrosion. Current designs and fabrications of solar heater storage tanks do not last long due to corrosion of the tanks accelerated by high temperatures and saline water they handle at the coastal regions. The objective of this research was to investigate the performance of Glass Reinforced Plastic as a material for the tanks in the saline coastal waters. The research was done from June 2012 to April 2014 in a laboratory setup by looking at the effect on the physical and mechanical properties due to heat, water and saline solution diffusion, on the Glass Reinforced Plastic as well as the physical failures due to hygrothermic and ultraviolet radiation influence.

The composite of Isophthalic and Orthophthalic polyester resin matrix together with woven and chopped strands powder mat of 450g/m² E-Glass fibers were used in the study. Strips of the composite sheet samples were exposed to ultraviolet radiation, hygrothermic, and saline conditions by varying the intensity of each parameter. Ultraviolet lamp chamber was used for detecting ultraviolet radiation effects while the strength, viscoelastic response and thermal loading properties were evaluated through Universal Test Machine.

The tensile strength decreased as temperature increases while the ultraviolet radiation exposure effect was insignificant. Isopolyester had higher strength under pressure than orthopolyester due to its stronger chemical properties. It was envisaged that polyester resin E-glass composite performed better than galvanized steel as solar hot water tank material. The result showed that Glass Reinforced Polyester can be used for saline hot water storage tanks and perform better.

Keywords: E-glass, polyester, corrosion, hydrothermic, tensile strength.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information

The use of solar water heaters has been on the increase owing to the fact that solar energy is cheap and available in most parts of the world. In Kenya the adaptation of this technology is gaining momentum and the government of Kenya through the Energy Regulatory Commission (ERC) enacted legal policies as well as time deadlines to promote the use of the systems as indicated by Energy Regulatory Commission, (2010) regulations.

Davis & Shirliff Ltd, one of the leading major solar water heater importer and manufacturer in Kenya, has been facing the challenge of high failure rate of the tanks at the coastal areas on both locally manufactured (thermally insulated galvanized mild steel) and imported (thermally insulated enamel coated steel), due to tanks corrosion. The tanks are fabricated from 3mm mild steel sheet material and then galvanized. The galvanized tanks are then insulated using iso/blended polyol mixture enclosed in GRP sheet in form of a barrel. These are shown in *Figure:1.1*, *Figure 1.2* and *Figure 1.3*.



*Figure:1.1:Galvanized Uninsulated Tank
(Courtesy: D&S, 2014)*



*Figure 1.2: Galvanized Tank inside GRP Barrel Being Insulated
(Courtesy: D&S, 2014).*



*Figure 1.3: Galvanized Insulated Tank and Solar Collector
(Courtesy: D&S, 2014)*

The corrosion of the tanks is so rapid according to Davis & Shirliff Ltd at the coast with more than 50% of the company's tanks never operating to their expected lifespan of at least five years in operation. The galvanization and enamel coating aim at preventing the corrosion of the underlying layer of steel

but this is short-lived as the tanks corrode after a very short while, within two years of service in the coastal environment.

This is because of the aggressive ions in the environment. For instance, sea water will expose higher salts concentration as compared to dry land soft water. According to Min, (2008), it is difficult to predict the effect of higher salt concentrations. In generally, sections of steel exposed to higher salt concentrations become anodic and corrode, shown in Figure 1.4.



*Figure 1.4: Images of a Corroded Tank
(Courtesy: D&S 2012)*

Glassfiber Reinforced Polymer (GRP)

A composite material is a non-uniform solid consisting of two or more different materials that are mechanically bonded together. Each of the various components retains its identity in the composite and maintains its characteristic structure and properties. Generally, the structure of a composite consists of two phases, matrix and reinforcement.

The matrix is a continuous phase and the reinforcement is a discontinuous one. The duty of reinforcements is attaining strength of the composite and the matrix has the responsibility of bonding of the reinforcements. There are recognizable interfaces between the materials of matrix and reinforcements. The composite materials, however, generally possess combination of properties such as

stiffness, strength, weight, high temperature performance, corrosion resistance, hardness and conductivity which are not possible with the individual components. Indeed, composites are produced when two or more materials or phases are used together to give a combination of properties that cannot be achieved otherwise.

Composite materials especially the fiber reinforced polyester (FRP) kind highlight how different materials can work in synergy. Analysis of these properties shows that they depend on:

- (1) The properties of the individual components;
- (2) The relative amount of different phases;
- (3) The orientation of various components; the degree of bonding between the matrix and the reinforcements and
- (4) The size, shape and distribution of the discontinuous phase.

The material involved can be organics, metals or ceramics. Therefore, a wide range of freedom exists, and composite materials can often be designed to meet a desired set of engineering properties and characteristics, (Askland *et al*, 2003).

Fiber Reinforced Polymer (FRP) composites can be considered a new class of structural material when compared with classical materials such as steel, concrete, timber and masonry. The relatively recent and growing interest in FRP in the domain of structural engineering can be traced to its advantageous properties ranging from a very high strength-to-weight ratio, electromagnetic neutrality, excellent fatigue behaviour, to superior durability including corrosion resistance. These properties have, in turn, lead to a broad spectrum of application that can be divided into two general categories: all-FRP members or structures in new construction or in the replacement of existing structural

elements, and FRP components in the repair and rehabilitation of damaged or deteriorating structures.

The GRPs that are well-designed can perform well in water environment and even handle sea saline waters. These properties are well utilized in marine vessels like hulls, boats and undersea pipes. In the water treatment sector, the rapid sand filters and underground waste water tanks are generally made of GRP mainly the polyester resin which is relatively cheaper.

Considering these advantages that GRP offers, their application into the solar heater storage tanks would be worthwhile investigating to solve the problem of corrosion and other degradation failures experienced with steel tanks. The GRP tanks under study will be expected to withstand corrosion, water seepage, salinity, UV rays, and high temperatures experienced and handled by the solar water systems in the coastal region.

There is a need to reduce and prevent the high rate of failure due to corrosion of solar hot water tanks operated in the coastal areas as a result of the saline and humid environment they operate in. This research investigated the use of GRP as an alternative structural material for hot water storage in areas where other materials cannot withstand high levels of corrosion.

1.2 Problem Statement

The use of galvanized steel for solar hot water tank material has not performed well and does not achieve the intended service period due to accelerated corrosion under higher temperatures and saline water environment. This problem called for research into an alternative material that could be used under such environments. It was for this reason that this research investigated the performance of glass reinforced polyester composite as a better material for the hot water storage tanks.

1.3 Justification

Because there was high rate of failure due to corrosion in galvanized steel tanks, this research evaluated the use of GRP as alternative structural component material to be used in solar hot water tank to solve the failure due to corrosion in galvanized mild steel tanks. Polyester resin GRP has low weight, high specific rigidity, corrosion-resistance, high specific strength and long life fatigue resistance; properties that can be exploited for solar hot water tank application. This made it viable to be considered for this application.

1.4 Objective

Overall Objective

To investigate the performance of polyester based Glass Reinforced Plastic as material for solar hot water storage tanks for the coastal areas.

Specific Objectives

- To determine the tensile strength properties (ultimate strength, toughness and maximum strains) of GRP.
- To determine the effect of diffusion of water and salinity on the mechanical strength properties of GRP.
- To evaluate the effect of UV radiation on strength properties of GRP.
- To evaluate the effect of hydrothermal condition on strength properties of GRP.
- To conduct a real life test on the prototypes made with the composites to determine their behavior under typical working conditions

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Properties of Glass Fibre and Polymer

A major hindrance to the acceptance of polymer composites in mechanical engineering applications is the susceptibility of the polymeric matrix to weathering. The polymer matrix is prone to degradation initiated by ultraviolet (UV) radiation, moisture, temperature, and high pH environments according to Astrom (1997).

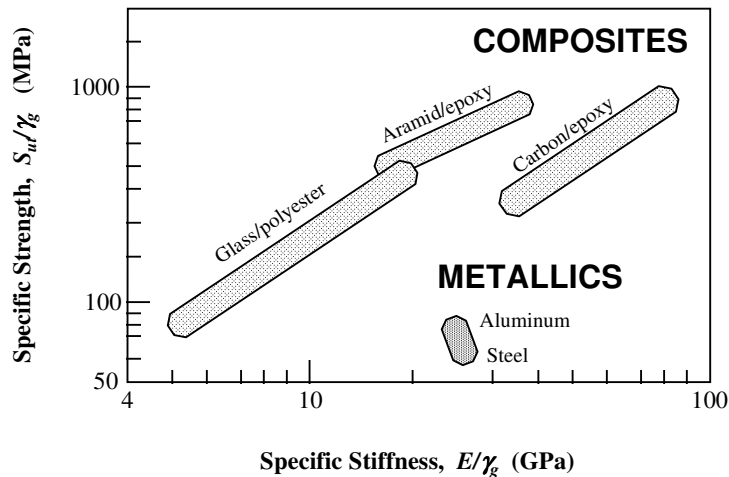


Figure 2.1: Specific strength vs specific stiffness for a range of materials.(
Astrom (1997)

According to Gibson, (1993) specific strength is defined as the ratio of the ultimate tensile strength (UTS) to specific gravity (γ_g) and specific stiffness as the ratio of Young's modulus (E) to specific gravity.

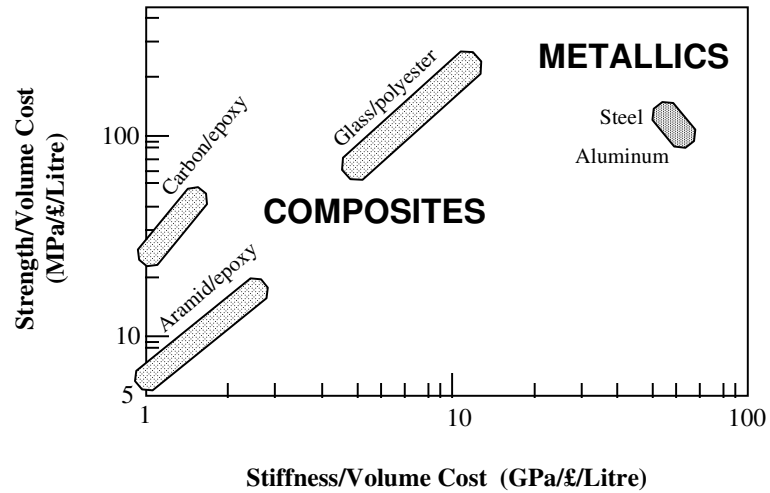


Figure 2.2: Strength per volume cost vs stiffness per volume cost

2.2 Glass Fibre

E-glass fibers can be obtained from E-glass which is a family of glasses with a calcium aluminoboro silicate composition and a maximum alkali content of 2%. The composition of E-glass is shown in Table 2-1.

At present, E-glass fibers have been widely used in fiber reinforced plastics not only because they have the advantage of low price, availability, ease of processing and high strength, but also because they have good resistance to moisture. Moisture does produce the well-known static fatigue effect in E-glass, with a loss in strength of about 4% for each factor of ten in time under tensile stress.

Table 2-1: E-glass compositions (wt. %)

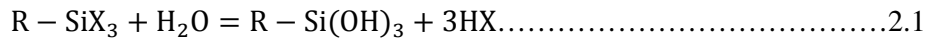
Courtesy of ASM International, (1987)

| COMPONENTS | E-GLASS RANGE (wt. %) |
|----------------------------------|------------------------------|
| Silicon Dioxide | 52-56 |
| Aluminium Oxide | 12-16 |
| Boric Oxide | 5-10 |
| Sodium Oxide and Potassium Oxide | 0-2 |
| Magnesium Oxide | 0-5 |
| Calcium Oxide | 16-25 |
| Titanium Dioxide | 0-1.5 |
| Iron Oxide | 0-0.8 |
| Iron | 0-1 |

2.3 Chemistry of Fiber / Matrix Interface

The interface plays an important role in composite materials. Composite materials with weak interfaces have relatively low strength and stiffness but can have high resistance to fracture. On the contrary, composite materials with strong interfaces have relatively high strength and stiffness but may be brittle. The nature of the interface depends on the atomic arrangement and chemical properties of the fiber and on the molecular conformation and chemical constitution of the polymer matrix according to Parvatareddy *et al*, (1997). Usually a silane coupling agent which are used to provide a stable bond between two otherwise nonbonding and incompatible surfaces, in aqueous solution is applied on the surface of glass fibers to provide protection from the water

degradation and to improve the bonding between the glass and the resin. The general formula for the silane coupling agent is R-SiX₃. The X units represent hydrolysable group. They can be hydrolysed according to Parvatareddy *et al*, (1997), to get the corresponding silanol as shown in equation 2.1.



The trihydroxysilanols can form hydrogen bonds with hydroxyl groups on the glass surface. When the coupling agents are dried, a reversible condensation reaction occurs between the silanol and the surface, and between adjacent silanol molecules on the surface. The result is a polysiloxane layer bonded to the glass surface, which provides the chemical link with the glass fibers. The R-unit represents a compatible organo-functional group, which can react with the matrix resin during the curing process. The R-unit needs to be chosen for different kinds of polymer matrix to get the optimum interfacial property and good environmental resistance. Besides chemical adhesion at the interface, adsorption and mechanical adhesion also contribute to the interfacial bonding.

In composites there are a lot of internal stresses induced in the processing operations. For example, resin shrinkage and the differential thermal coefficient of fibers and matrix can bring tensile, compressive or shear stresses which will affect the fiber / matrix interfacial strength.

2.4 Production of Fiber

Glass fibre filaments are produced by mechanically drawing molten glass streams. Next, the filaments are usually gathered into bundles called strands or rovings. The strands may be used in continuous form for filament winding; chopped into short lengths for incorporation into moulding compounds or use in spray-up processes; or formed into fabrics and mats of various types for use in hand coatings with a material known as a coupling agent, which serves to promote adhesion of the glass to the specific resin being used. The filament

diameter ranges from 3 to 19 micrometers. Figure 2.3 illustrates the manufacture process of the glass fibres.

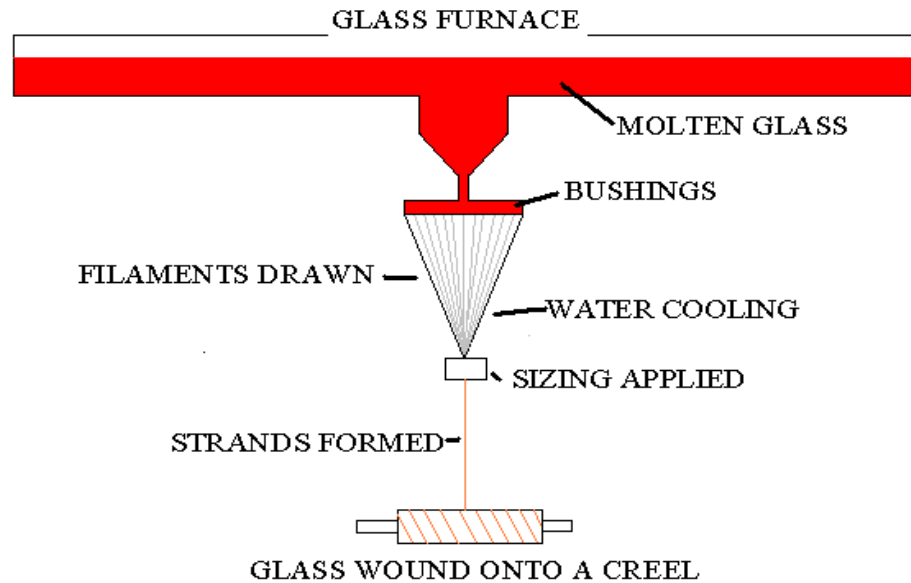


Figure 2.3: Diagrammatic sketch of Glass Fibre Manufacturing

Glass fibre is the most common reinforcing material used in polymer matrix composites. These have high tensile strength but low modulus compared with other fibres. Glass fiber reinforcements are classified according to their properties. At present there are five major types of glass used to make fibers. The letter designation is taken from a characteristic property:

- 1) A-glass is a high-alkali glass containing 25% soda and lime, which offers very good resistance to chemicals, but lower electrical properties.
- 2) C-glass is chemical glass, a special mixture with extremely high chemical resistance.
- 3) E-glass is electrical grade with low alkali content. It manifests better electrical insulation and strongly resists attack by water. More than 50% of the glass fibers used for reinforcement is E-glass.

4) S-glass is a high-strength glass with a 33% higher tensile strength than E-glass.

5) D-glass has a low dielectric constant with superior electrical properties. However, its mechanical properties are not so good as E-or S-glass. It is available in limited quantities.

These variations of glass are supplied in several different forms as indicated in the Figure 2.4 to Figure 2.5



*Figure 2.4: E-Glass Surface tissue
(Courtesy: D&S 2012)*



*Figure 2.5: E-Glass chopped strands
mat 450 GSM,
(Courtesy: D&S 2012)*



*Figure 2.6: E-Glass woven
(Courtesy:D&S2012)*



*Figure 2.7:E-Glass Rovings
(Courtesy: D&S 2012)*

Of the above fibers, the E-glass is the most common reinforcement material used in civil and industrial structures. It is produced from lime-alumina-borosilicate which can be easily obtained from abundance of raw materials like sand. The fibers are drawn into very fine filaments with diameters ranging from 2 to 13 X 10⁻⁶m.

2.5 Resins

The resins that are used in fibre reinforced composites are sometimes referred to as ‘polymers’. All polymers exhibit an important common property in that they are composed of long chain-like molecules consisting of many simple repeating units. Man made polymers are generally called ‘synthetic resins’ or simply ‘resins’. Polymers can be classified under two types, ‘**thermoplastic**’ and ‘**thermosetting**’, according to the effect of heat on their properties.

Thermoplastics, like metals, soften when heated and eventually melt, hardening again on cooling. This process of crossing the softening or melting point on the temperature scale can be repeated as often as desired without any appreciable effect on the material properties in either state. Typical thermoplastics include

nylon and polypropylene, and these can be reinforced, although usually only with short chopped fibres such as glass.

Thermosetting materials or ‘thermosets’ are formed from a chemical reaction in situ, where the resin and hardener or resin and catalyst are mixed and then undergo a nonreversible chemical reaction to form a hard, infusible product. This characteristic makes the thermoset resin composites very desirable for structural applications.

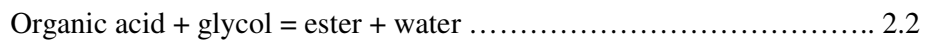
Other thermosetting resins such as polyester and epoxy cure by mechanisms that do not produce any volatile by products and thus are much easier to process. Once cured, thermosets will not become liquid again if heated, although above a certain temperature their mechanical properties will change significantly. This temperature is known as the Glass Transition Temperature (T_g), and varies widely according to the particular resin system used, its degree of cure and whether it was mixed correctly. Above the T_g , the molecular structure of the thermoset changes from that of a rigid crystalline polymer to a more flexible, amorphous polymer. This change is reversible on cooling back below the T_g . Above the T_g properties such as resin modulus (stiffness) drop sharply and as a result the compressive and shear strength of the composite decreases. Other properties such as water resistance and colour stability also reduce considerably above the resin’s T_g .

Although there are many different types of resin in use in the composite industry, the majority of structural parts are made with three main types, namely polyester, vinylester and epoxy; the least common ones are the polyurethanes and phenolics.

2.6 Polyester Resins

Polyester resins are the most widely used resin systems, particularly in the marine industry. By far the majority of dinghies, yachts and work-boats built in composites make use of this resin system. Polyester resins such as these are of

the 'unsaturated' type. The reaction of an alcohol with an organic acid produces an ester and water. By using special alcohols such as glycol in a reaction with di-basic acids, a polyester and water will be produced. This reaction, together with the addition of compounds such as saturated di-basic acids and cross-linking monomers, forms the basic process of polyester manufacture. As a result there is a whole range of polyesters made from different acids, glycols and monomers, all having varying properties. By varying the acid and alcohol, a range of polyester resins can be made. Orthophthalic polyesters are made by phthalic anhydride with either maleic anhydride or fumaric acid. Isophthalic polyesters, however, are made from isophthalic acid or terephthalic acid as shown in equation 2.2 and illustrated in *Figure 2.8*.



The esters so formed are joined together to form long chain molecules known as polyester

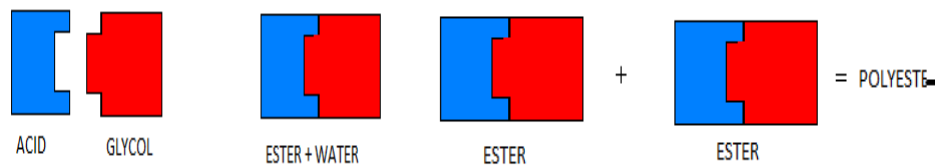


Figure 2.8: shows the idealised chemical structure of typical polyester.

For use in moulding, as mentioned above, polyester resin requires the addition of several ancillary products. These products are:

- Catalyst (Methyl Ethyl Ketone Peroxide MEKP)
- Accelerator
- Additives: Thixotropic, Pigment and Filler

Since accelerators have little influence on the resin in the absence of a catalyst they are sometimes added to the resin by the polyester manufacturer to create a 'pre-accelerated' resin.

The molecular chains of the polyester can be represented as shown in Figure 2.9, where 'B' indicates the reactive sites in the molecule.

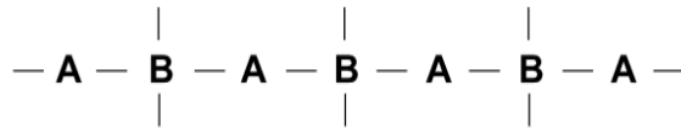


Figure 2.9: Schematic Representation of Polyester Resin (Uncured)

With the addition of styrene 'S', and in the presence of a catalyst, the styrene cross links the polymer chains at each of the reactive sites to form a highly complex three dimensional network as shown in Figure 2.10.

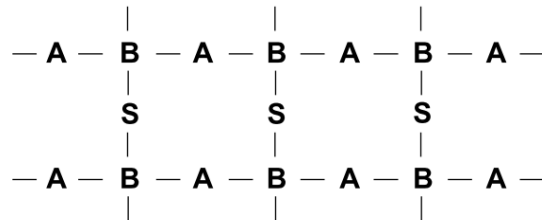


Figure 2.10: Schematic Representation of Polyester Resin (Cured)

The polyester resin is then said to be 'cured'. It is now a chemically resistant (and usually) hard solid. The cross-linking or curing process is called 'polymerisation'. It is a non-reversible chemical reaction. The 'side-by-side' nature of this cross-linking of the molecular chains tends to mean that polyester laminates suffer from brittleness when shock loadings are applied.

Great care is needed in the preparation of the resin mix prior to moulding. The resin and any additives must be carefully stirred to disperse all the components evenly before the catalyst is added.

The properties of the polyester resin are affected by the type and amount of reactant, catalyst and monomers as well as the curing temperature. The higher the molecular weight of polyester and the more points of unsaturation in molecules, the higher is the strength of the cured resins. Orthophthalic polyesters are environmentally sensitive and have limited mechanical properties. They have been replaced in some applications by isophthalic polyesters due to the excellent environment resistance and improved mechanical properties of the latter as noted by Mathews et al, (1994).

Table 2-2: Comparison of Polyesters, Vinyl esters and Epoxies

| Resin | Advantages | Disadvantages |
|---------------------|--|---|
| Polyesters | <ul style="list-style-type: none"> Easy to use Lowest cost of resins available Electrical and chemical stability Better mould release Good thixotropy | <ul style="list-style-type: none"> Only moderate mechanical properties High styrene emissions in open moulds High cure shrinkage Limited range of working times |
| Vinyl esters | <ul style="list-style-type: none"> Very high chemical/environmental resistance Higher mechanical properties than polyesters | <ul style="list-style-type: none"> Post cure generally required for high properties High styrene content Higher cost than polyesters High cure shrinkage |
| Epoxies | <ul style="list-style-type: none"> High mechanical and thermal properties High water resistance Long working times available Temperature resistance of 140 °C wet/ 220°C dry Low cure shrinkage | <ul style="list-style-type: none"> More expensive than vinyl esters Critical mixing Corrosive handling |

2.7 Polymer Matrix Selection

The matrix of a composite works as a binder transferring the loads through the fiber network. It maintains the fiber orientation and protects the fibers from environmental effects, redistributing the load to surrounding fibers when an individual fiber breaks. The selection of a resin involves several factors. Chemical characteristics such as resin viscosity, glass transition temperature, gel time, cure cycle, injection pressure, thermal stability, shelf life, environmental resistance, and volatile emissions during processing, are some of the parameters that need to be considered in order to determine operating and processing conditions for a specific resin. Mechanical properties such as strength and elastic modulus in certain directions, interlaminar fracture toughness, and environmental resistance are major composite properties to which the matrix must contribute according to Astrom, 1997).

The most common thermoset resins used as composite matrices are unsaturated polyesters, epoxies, and vinylesters. The nature of the process and the requirements of the solar hot water storage tank applications demand that the resin system should meet these target requirements:

- Low cost
- Resin elastic modulus of 2.75 GPa or higher
- Resin viscosity from 100 to 500 cps
- Glass transition temperature of 70 °C or higher
- Low moisture absorption
- Gel time of at least 20 minutes
- Room temperature cure preferable
- Tough resin preferable

Of these, the resin modulus is important in maintaining composite compressive strength, particularly under hot, wet conditions. Currently, unsaturated polyester resins are the most common systems used in composites by the water

and chemical industries for the manufacture of containers and vessels. They are the most affordable, are easily processed, and possess adequate mechanical properties. However, most polyester are brittle resins and have a low temperature resistance and significant moisture sensitivity.

The resin must be compatible with the processing method. Hand lay-up is the main process of concern in this study. The advantages of epoxies and vinyl esters are not considered sufficient to offset the disadvantages of epoxies and vinyl esters, particularly with regard to cost. Therefore I choose polyester resin.

There are two principle types of polyester resins used as standard laminating systems in the composites industry, these are: Isophthalic polyester resins and Orthophthalic polyester resins.

Orthophthalic polyester resin is the basic polyester resin. It is based on Orthophthalic acid. It is called general purpose polyester resin and has a type of molecular structure that is considered to be standard in the industry. Orthophthalic resins tend to be low-molecular-weight resins. In spite of their poor thermal stability, Orthophthalic polyester resins perform well in moderate-to low-temperature applications and are often preferred in such applications because of their low cost.

Isophthalic polyester resins are based on Isophthalic acid and maleic anhydride. The incorporation of Isophthalic acid creates a high-molecular-weight resin with good chemical and thermal resistance and good mechanical properties. Isophthalic polyester resins are conducive for mildly corrosive applications. The use of nonpolar glycols contributes to improved aqueous resistance which is required to protect the fibre-glass.

Isophthalic polyester resins tend to show higher tensile and flexural properties than orthophthalic polyester resins. This may be because isophthalics usually form more linear, higher- molecular-weight polymers than orthophthalics.

Isophthalic polyester resins perform well in both mild aqueous and mild organic environments. The ortho structure is rigid and the iso is flexible. The benzene ring in the latter allowing stretch by distorting. This does not occur with ortho structure. This is because iso resins have higher elongation of break than ortho resins made with the same formulation substituting the one acid with the other.

2.8 Mechanical Properties

Mechanical properties are often the critical factor in selecting a polyester resin for a specific application.

Table 2-3 lists the common test methods of the American Society for Testing and Materials (ASTM) that are used to characterize the mechanical properties of polyester resin composites.

Table 2-3: ASTM test methods for characterizing mechanical properties of polyester resins.

| Properties | ASTM Test Method |
|---|-------------------------|
| Tensile strength, modulus, and % elongation | D 638 |
| Flexural strength and modulus | D 790 |
| Compressive strength, modulus, and % compression on break | D 695 |
| Izod impact | D 256 |
| Heat distortion | D 648 |
| Barcol hardness | D 2583 |

Figure 2.4 highlights the differences among isophthalic and orthophthalic resins. Isophthalic resins tend to show higher tensile and flexural properties than orthophthalic resins. This may be because isophthalics usually form more linear, higher- molecular-weight polymers than orthophthalics.

Although the glass creeps under a sustained load, it can be designed to perform satisfactorily. The fiber itself is regarded as an isotropic material and has a lower thermal expansion coefficient than that of steel.

Table 2-4: Mechanical properties of clear-cast (unreinforced) polyester resins.
 Courty of Astrom, (1997)

| Material | Barcol hardness | Tensile Strength | | Tensile Modulus | | Elongation % | Flexural Strength | | Flexural Modulus | | Compressive Strength | | Heat-deflection temperature °C |
|---------------|-----------------|------------------|-----|-----------------|---------------------|--------------|-------------------|-----|------------------|---------------------|----------------------|-------|--------------------------------|
| | | Mpa | ksi | Gpa | 10 ⁶ psi | | Mpa | ksi | Gpa | 10 ⁶ psi | Mpa | ksi | |
| Isophthalic | 40 | 75 | 11 | 3.38 | 0.49 | 3.3 | 130 | 19 | 3.59 | 0.52 | 120 | 17 | 90 |
| Orthophthalic | | 55 | 8 | 3.45 | 0.50 | 2.1 | 80 | 12 | 3.45 | 0.50 | | | 80 |

Table 2-5: Mechanical properties of fiberglass-polyester composites (glass content,40wt %)
 Astrom, (1997)

| Material | Barcol hardness | Tensile Strength | Tensile Modulus | Elongation % | Flexural Strength | Flexural Modulus | Compressive Strength | Izod impact |
|---------------|-----------------|------------------|-----------------|--------------|-------------------|------------------|----------------------|-------------|
| | | Mpa | Gpa | | Mpa | Gpa | Mpa | J/mm |
| Isophthalic | 45 | 190 | 11.7 | 2.0 | 240 | 7.6 | 210 | |
| Orthophthalic | | 150 | 5.5 | 1.7 | 220 | 6.9 | | 0.57 |

Table 2-6: Effect of glass content on mechanical properties of fibreglass reinforced polyester.
 Astrom, (1997)

| Material | Glass content, wt% | Flexural Strength | Flexural Modulus | Tensile Strength | Tensile Modulus | Compressive Strength |
|---------------|--------------------|-------------------|------------------|------------------|-----------------|----------------------|
| | | Mpa | Gpa | Mpa | Gpa | Mpa |
| Isophthalic | 30 | 190 | 5.5 | 150 | 8.27 | |
| | 40 | 240 | 7.58 | 190 | 11.7 | 210 |
| Orthophthalic | 30 | 170 | 5.5 | 140 | 4.8 | |
| | 40 | 220 | 6.9 | 150 | 5.5 | |

2.9 Hand Lay-Up

Hand lay-up is the oldest and simplest method for producing glass-reinforced structures from polyester resins. To make an article (moulding) a mould is used and a laminate is built up from layers of fibreglass, usually in the form of chopped fibreglass mat or woven roving mat, which are impregnated with suitably accelerated and catalyzed polyester resin. The hand lay-up process as sketched *Figure 2.11* can be successfully adapted to either small or large articles ranging from a few centimeters to tens of meters long, with very good physical properties.

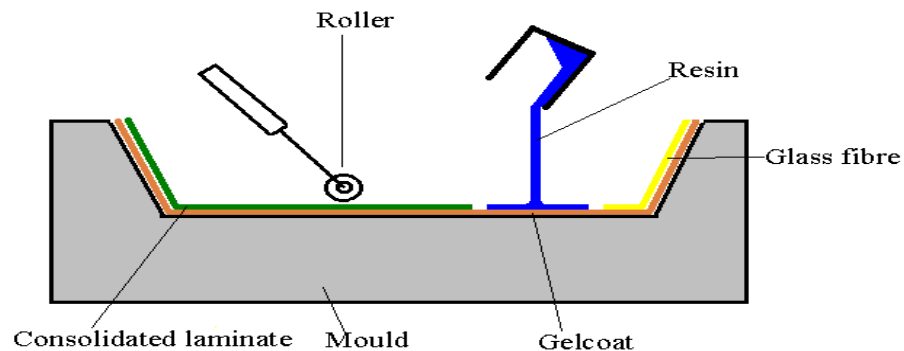


Figure 2.11: Hand lay-up technique

With this technique, the quality of the moulding produced can vary somewhat, depending on the skill of the particular operator. Once the gelcoat has sufficiently cured, a coat of laminating resin system is applied by brush, roller or spray followed by the first layer of chopped strand mat. Sufficient resin should be applied to wet out completely this first layer of reinforcement so that all trapped air can be forced out by rolling with a laminating roller. The resin to glass ratio at this stage should be about 2:1 according to resin manufacturer NCS.

The resin, catalyzed so as to give an adequate pot life (e.g. 30 minutes) is applied generously to the back of the cured gelcoat and the first layer of previously tailored glass mat is laid over the resin.

When the first layer of glass mat has been fully impregnated, further layers of resin and reinforcement are successively applied using the same technique, but for thick mouldings it is necessary to proceed in stages, allowing the resin to cure after each stage.

To obtain a homogeneous laminate free from air bubbles, sufficient resin system should always be placed in the mould to completely wet out the glass mat prior to placing the mat in the mould. Rolling will then displace the air outwards. If, on the other hand, resin is applied to non-impregnated glass mat there is every probability that air bubbles will be trapped in the laminate. These trapped air bubbles will then almost certainly result in the failure of the moulding in service, particularly if the moulding comes into contact with liquids.

2.10 Mechanical Properties of Glass Reinforced Polymer

Improved strength, fatigue resistance, Young's modulus, and strength to weight ratio are provided in most fiber reinforced composites by incorporating strong, stiff, but brittle fibers into a softer, more ductile matrix. The matrix material transmits the force to the fibers, which carry most of the applied force. The matrix also provides protection for the fiber surface and minimizes diffusion of species such as oxygen or moisture that can degrade the mechanical properties of fibers. The strength of the composite may be high at both room temperature and elevated temperatures.

The application of composite materials to primary structure to reduce structural weight is forcing structural designers and materials engineers to look for new, toughened resin systems. Thermosets, elastomers, and thermoplastics are the three main polymer categories. Thermoset polymers dominate as matrices in structural composite applications for reasons of good mechanical and thermal properties, good bonding to reinforcement, low cost, low viscosity and ease of processing. Thermoplastics are raising interest for their advantages in areas such as: toughness, potential processing advantages, recyclability and low volatile emissions; their high viscosity and poor bonding to reinforcement are disadvantages according to Astrom, (1997). Tough resins are generally

formulated by adding elastomeric or thermoplastic compounds to the more brittle thermoset resin base. Elastomers generally have too low of an elastic modulus to serve as a matrix for rigid structural composites.

Table 2-7: Mechanical properties of FRP (polyester) composites. Astrom, (1997).

| Type of glass fibre reinforcement | Glass content, wt% | Density g/cm ³ | Tensile strength Mpa | Tensile modulus GPa | Elongation % | Flexural strength MPa | Flexural modulus Gpa |
|-----------------------------------|--------------------|---------------------------|----------------------|---------------------|--------------|-----------------------|----------------------|
| Neat cured resin | 0 | 1.22 | 59 | 5.4 | 2 | 88 | 3.9 |
| Chopped-strand mat | 30 | 1.5 | 117 | 10.8 | 3.5 | 197 | 9.784 |
| | 50 | 1.7 | 288 | 16.7 | 3.5 | 197 | 14.49 |
| Roving fabric | 60 | 1.76 | 314 | 19.5 | 3.6 | 317 | 15 |
| Woven glass fabric | 70 | 1.88 | 331 | 25.86 | 3.4 | 403 | 17.38 |
| Unidirectional roving fabric | 70 | 1.96 | 611 | 32.54 | 2.8 | 403 | 29.44 |

2.11 Glass Reinforced Polymer Chemical Corrosion Resistance

Polymer matrix composite has been used for many years as a cost-effective material for chemical containers. However, all polymers are permeable to water, and a number of other liquids to a certain extent. The material selection depends on the severity of the environment. For weak acids, chlorinated or long chain iso-polyester would be suitable. For aggressive environments such as caustics and solvents vinyl esters with their increased chemical would be preferred. Although epoxies have a greater solvent and thermal resistance than vinyl esters, they are more difficult to process and more expensive as Rapra,(2012) put it.

Polymer matrix composites can be designed for excellent corrosion resistance i.e. resistance to specific hostile environments. Although the selection of polymer matrix is paramount, attention to the details of design is needed to

ensure that optimum performance is achieved. The whole manufacturing process, installation and service life, needs to be optimised to achieve corrosion resistance. Once the details of fluid environment have been established the appropriate polymer can be selected. Manufacturer guides for corrosion resistant polymers are available and should be consulted. Within each generic polymer family, there are particular grades with optimised performance.

2.12 Solar Hot Water Systems

Hot water storage tanks (solar applications, conventional heating by electric heaters or other means) are designed considering pressure requirements. Corrosion protection is the other important design parameters. It is to be noted that the capacity of the tanks for simple (thermosiphon) solar domestic hot water is usually in the range from 120 liters to 320 liters.

Mild steel is the most commonly used material for the storage tanks, because it has the strength for the pressure requirements (6 bars or more) for wall thickness of 2mm-3mm. Corrosion protection, in the water side of the tank, is achieved by appropriate coatings like: Glass enameling, galvanizing, thermosetting resin-bonded lining materials, thermoplastic coating materials, cement coating, or by the use of an internal tank from corrosion resistant material such as thin copper sheet, polymer and others as in ASM International, (1987).

Materials, that have been used for tank construction are stainless steel and copper (interest has been diminished for copper due to high prices). It is necessary to point out that the water temperature in the solar storage tank can easily reach, 70°C-80°C, during regular use of the system or as high as 100°C when it is not used. The hot water temperatures of solar domestic hot water systems are higher than those of conventional water heaters. In electric water heaters, for example, maximum temperature is controlled by a thermostat, which is usually set at 60°C ASM International, (1987).

The higher temperatures in solar domestic hot water systems require special attention to the design of the storage tank against corrosion. Standards, in

different countries, cover the construction of the tank and also methods for corrosion protection in the water side. References DIN 4753.1, are relevant German standards. Final details of tank design depend on the corrosion protection method.

One important item in tank design is that the corrosion protection coatings should satisfy the requirements with regard to physiological suitability according to the current state of the art.

In the standards, shown in references ISO 9459-2 and EN 12976-2, a special testing is foreseen for determining the mixing conditions during the draw off of hot water from the tank. This test can be conducted by the solar producer relatively easily. Storage tank manufacturers have established business in many countries. The tanks are sold either for electric or solar applications. The corresponding buyer (solar manufacturer) fits insulation, outer cover, and other accessories to the tanks and adapts them to his product line.

i. Glass Enameled Hot Water Storage Tanks

Enameling has been a valuable protection against corrosion for steel. The enameling process includes pickling, which is the metal surface pre-treatment in order to accept the enameling. The enamel is deposited by pouring “slurry” (ground enamel frit, other additives and water) on the inside walls of the vessel (largely an automated process). The “biscuit” (after drying) is brushed off the sealing and threaded areas. Firing at a temperature of approximately 850°C is the last step in enamel coating on steel tanks as indicated in ASM International, (1987).

Many years of established experience has shown that properly constructed and enameled storage tanks with a magnesium anode (it protects areas that might not be covered with enamel) represent reliable products with long life (decades). It is only necessary to inspect regularly (especially in the beginning) the function of the anode. Enameling facilities require high investment in the ASM International, (1987).

ii. Galvanized Hot Water Storage Tanks

Zinc has been utilized to extend the life of steel by galvanizing. Galvanized steel has been used for many years for electric hot water storage tanks. Its main drawback is the fact that the zinc coating loses its protective action at the temperature range of 60°C-85°C. In the middle of this range the rate of zinc loss is very high (more than 100 times at lower temperatures). This temperature range can easily be achieved in solar DHW systems and so there are obvious restrictions in its use. Electric hot water heaters with a thermostat setting at 55°C-60°C, made of galvanized steel, have been used for many years and are considered reliable as in ASM International, (1987).

Galvanized tanks can be used in solar DHW systems in the cases that hot water temperature in the tank can be kept below 60°C (continuous use of hot water, low efficiency collectors). The recommended procedure is to construct the tank from mild steel and then galvanize it by hot dipping.

iii. Use of Thermosetting Resin-Bonded Lining Materials

The lining material, used for corrosion protection of the water side of steel hot water storage tanks, is thermosetting resin-bonded products especially developed for this purpose. Application and heat treatment of these linings are to be performed as suggested by the lining material manufacturer. The water side vessel surface preparation includes a compressed air sand blasting (use of metallic particles). Irregularities within the zone of welds should be smoothed by grinding before blasting. The lining is applied continuously and uniformly by spraying, brushing, dipping or flooding. Usually, several layers are required that are applied and post treated separately (temperatures of 150°C-200°C have been reported). Relevant German standard is DIN 4753.4

Lining has a minimum thickness of 0.250mm and it can sustain temperature exceeding 95°C (no specific temperature has been reported by solar product manufacturers). Actually one of the tests in DIN 4753.4 requires the vessel to be subjected to 1000 periodical temperature changes between approx. 15°C and

a maximum water temperature of approx. 95°C. The relevant investment is not very high and the method can be applied to relatively moderate production rates.

Other methods are: Internal Tank from Corrosion Resistant Material, Use Of Thermoplastic Coating Materials, Stainless Steel Storage Tanks and Use of Cement Coating these are processes that are considered sophisticated and special equipment and experience are necessary hence expensive (DIN 4753.4)

The Ageing Mechanisms in Polymer Composites Materials

This section reviews failure mechanisms commonly experienced in polymeric materials and the techniques that can be used to predict their useful service life.

The review consists of the following according to Maxwell et al, (2005):

- A summary of the main degradation mechanisms present in polymeric materials.
- A review of techniques for predicting the life expectancy of plastics and polymer composites.
- Standards for accelerated testing.

i. Thermal Ageing

Thermal degradation refers to the chemical and physical processes in polymers that occur at elevated temperatures. Increased temperature accelerates most of the degradation processes that occur in polymers such as oxidation, chemical attack and mechanical creep. Oxidation is generally considered to be the most serious problem when using polymers at elevated temperatures according to Wright, (2001). The influence of temperature on the oxidation processes will depend on the chemical structure of the polymer. Thermo-oxidation is initiated by the reaction of free radicals P with oxygen to form peroxide radicals:



All polymers contain these free radicals due to their polymerisation and processing history. However, the concentration of free radicals can be

significantly increased by interaction with light, ionising radiation or the presence of transition metals.

Once formed the peroxide radicals undergo slower propagation reactions that breakdown the polymer chains. The overall degradation process will normally involve a relatively long induction period during which little degradation is observed according to Wright, (2001). At the end of this period there is a rapid increase in degradation leading to a significant reduction in the mechanical properties of the polymer. This induction period is temperature sensitive and is reduced significantly at elevated temperatures. The induction period of the degradation process can normally be regarded as the serviceable lifetime of the polymer.

Prolonged or even short term, exposure to elevated temperatures will often produce irreversible chemical and physical changes within PMCs (Polymer Matrix Composites). As the temperature increases, the stiffness and strength decreases. All resin systems degrade at elevated temperatures.

Oxidation is the primary degradation process at elevated temperatures. The rate of degradation increases with the amount of oxygen present. PMCs are permeable to atmospheric gases. Oxidation can lead to a change of colour, with severe heating or long term use at temperature; oxidation may lead to microcracks Rapra, (2012).

The use of anti-oxidant additives in resin systems slows the degradation process by scavenging any free radicals. Elevated temperatures also depolymerise resins and degrade the fibre-matrix interface.

Other physical changes can occur in a polymer at elevated temperatures, one of the most common being thermal expansion, Brown, Kockott *et al*, (1995). Differences in thermal expansivity between fibre and matrix can induce residual stresses, thereby reducing fibre-matrix bond efficiency. Thermal expansion is reversible and in general does not significantly affect the life expectancy of a polymer. However, in polymer composites the mismatch between the thermal

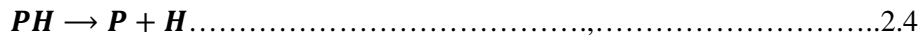
expansion of the polymermatrix and the fibres may cause thermo-mechanical degradation during thermal cycling. Similar mechanisms may also occur in adhesive joints. A sudden brief exposure to high temperatures can result in a phenomenon known as thermal spiking.

ii. Weathering

Weathering also referred to photo-oxidation of polymers is the chemical and physical changes that occur when radiation is absorbed by a polymer Brown, Kockott *et al.*, (1995) and Greewood, (1997).

Photo-degradation is initiated by solar radiation, which results in the absorption of UV radiation by chromophores and in the activation of excited states in macromolecules. However, according to White and Turnbull, (1994), other climatic quantities such as heat, moisture and air-born pollution all influence the mechanisms of degradation and the subsequent results of ageing.

When a polymer is exposed to solar radiation the energy absorbed by the polymer results in the formation of free radicals within the polymer by the dissociation of the C-H bonds in the polymer chains.



The extent of this chemical reaction depends on the radiation exposure that is the quantity of ultraviolet light (<350nm) to which it is exposed. According to Wypych, (2003) once free radicals have been produced, reaction with oxygen generates hydroperoxides (POOH). These hydroperoxides can dissociate further to produce a series of decomposition products including aldehydes and ketones.



The formation and propagation of free radicals in itself does not serious affect the mechanical properties of the polymer, as they do not significantly alter the long-chain nature of the polymer molecules. Degradation of the mechanical

properties occurs because the free radicals produced are highly unstable and readily undergo chain scission reactions. This results in the formation of two smaller polymer chains, one of which is a free radical and capable of further reactions according to Wypych, (2003).

The intensity of the UV radiation decreases with increasing depth in the material, so that the reaction tends to be a near surface process. Since oxygen is involved in the reaction process, there is an important balance between UV radiation and oxygen diffusion, and of course temperature since that will also determine the kinetics of reaction and the transport of reactive species.

Under natural exposure conditions there will be wetting and drying cycles and dark periods. The significance of the latter is that some recovery of the oxygen concentration in the material can occur, which otherwise is confined to the very near surface due to consumption by reaction with the polymer radicals. Since the concentration of these radicals diminishes by termination reaction during the dark period, oxygen ingress can extend to greater depth.

iii. Environmental Stress Cracking

Environmental stress cracking (ESC) remains one of the most common causes of failure in polymers according to Maxwell et al, (2005). The main reason for this is the complexity of the phenomenon, with aspects such as chemical compatibility, liquid diffusion, craze formation and crack development all playing their part. While crystalline and amorphous polymers are both susceptible to ESC, amorphous polymers are particularly susceptible due to their relatively open structure that leads to easy fluid penetration. Once the fluid has penetrated the polymer it becomes locally dissolved promoting cracking and crazing in the polymer. Cracking is normally preceded by the formation of crazes initiated at sites of stress concentration or at regions of local micro-structural inhomogeneity.

Crazes are voids that are held together by highly drawn fibrils, which bridge the void allowing the craze to transmit stress and prevent the craze from

propagating. The mechanism of crazing in chemical environments is generally considered to be identical to that in air according to Wypych, (2003) and Arnold, (1996). In general terms, Wellinghoff and Baer indicated that craze initiation is considered to evolve from micro-deformation processes in localised regions about 30 nm in diameter as shown in

Figure 2.12. As the deformation region develops, further localised deformation is induced. The growth and coalescence of such deformed nuclei create a narrow plasticzone. In the presence of dilatational stress, voids develop. This voided structure is considered the precursor of the fibrillated craze structure that ultimately leads to failure according to Kausch and Oudet, (1988).

According to Maxwell et al, (2005) stress concentration can be important not only for the development of local deformation zones (although this is not necessarily dependent on stress concentration) but also for concentrating absorbed molecules in response to the presence of dilatational stress.

According to Arnold, (1996) and Wright et al, the rapid growth of the craze precursor to a visible crazes is believed to occur at a critical level of the inelastic strain which is independent of the environment and temperature. This has significant implications for assessing the durability of a polymer. For example, in polymer-fluid combinations that lead to plasticisation-induced toughening, simultaneous exposure may delay the development of crazes.

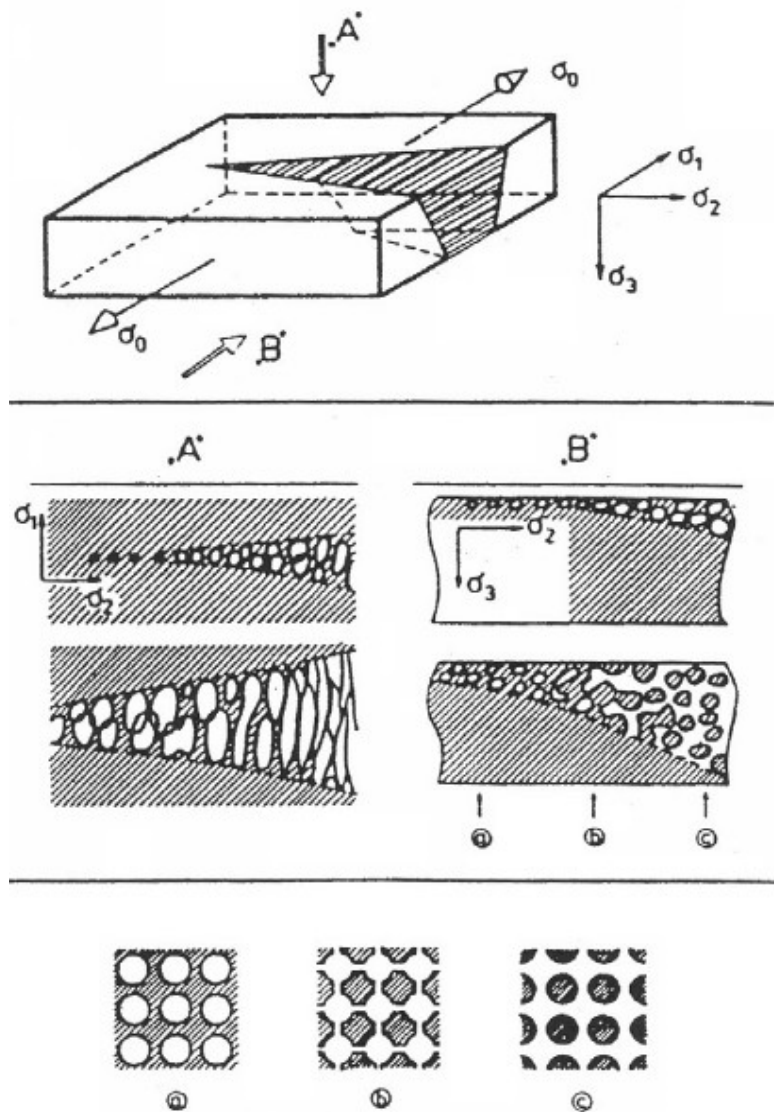


Figure 2.12: Transformation of a craze nuclei into a craze
Maxwel et al, (2005).

ii. Ionising Radiation

Ionising radiation covers a wide range of different forms of radiation including x-rays, gamma rays, neutrons, alpha particles and beta particles. When a polymer is irradiated the ionising radiation induces degradation by the formation of free radicals or ions in the polymer. These reactive intermediates

are capable of initiating chemical reactions which occur by free radical or ionic mechanisms and which result in scission as well as in cross-linking reactions. Free radicals with a long lifetime, which are present in the bulk of the material after irradiation, are responsible for changes in properties even a long time after exposure as noted by Carfago and Gibson, (1980) and Gueguen *et al*, (1994). The intensity of ionising radiation on the earth's surface is not normally high enough to significantly affect most plastics.

iii. Fatigue

Polymers will suffer failure when they are exposed to cyclic loads at stresses well below those they can sustain under static load. This phenomenon is known as fatigue and is responsible for approximately 1 in 5 of all polymer failures. The general approach to fatigue is to develop curves of applied stress (S) against the number of cycles before failure (N). As noted by Brown *et al*, (2002) Greenwood, these are known as S-N curves and have a characteristic sigmoidal shape, often flattening out when N is large suggesting a fatigue limit. Unlike metals the S-N curves for plastics are extremely frequency dependent. This is due to increases in the temperature of the plastic caused by mechanical hysteresis that results in thermal softening. This means that failure under cyclic loading can be either ductile or brittle. Fatigue failures are particularly serious as there is often little visual warning that failure is imminent.

iv. Moisture and Water

The absorption of moisture by the polymer matrix as a result of environmental exposure can have detrimental effects on the overall mechanical properties of the composite structure. The moisture diffuses into the matrix, which leads to delamination expansion and also chemical changes such as plasticization and hydrolysis by Niu, (1992) and Nakamura, (2006). These effects frequently include alterations in coefficients of thermal expansion, stress relaxation and crack and delamination propagation.

Most PMCs will absorb small, but potentially damaging amounts of moisture from the surrounding environments with the degree of degradation that occurs being linked directly with the amount of moisture absorbed. The absorbed water may adversely affect the material in a number of ways:

- Dimensional changes (swelling);
- Reduction in the glass transition temperature T_g of the resin; and
- Reduction in mechanical and physical properties (i.e. stiffness, strength and hardness).

In many instances, water reacts with the matrix and causes irreversible chemical changes and diminished performance. Capillary action along the fibres can account for a significant proportion of initial moisture uptake, although a chemically resistant matrix may encapsulate the fibres and this is according to Ehrenstein *et al*, (1990). Shrinkage of the resin away from the fibres during curing is a contributing factor to the capillary effect. The effect of moisture is to cause hydrolytic breakdown of the fibre-matrix interface resulting in a loss in the efficiency of load transfer between the matrix and the fibre reinforcement.

In degradation by moisture ingress, the controlling factor is the diffusion constant of water vapor. As water is a very polar molecule, the diffusion mechanism involves hydrogen bonding with polar sites in the polymer molecule.

Moisture desorption gradients may induce microcracking as the surface desorbs and shrinks, putting the surface in tension. If the residual tension stress at the surface is beyond the strength of the matrix, cracks occur. Additionally, moisture wicking along the fiber-matrix interface can degrade the fiber-matrix bond, resulting in loss of microstructural integrity Niu, (1992), Hoskin, 1986 and Nakamura, (2006).

All of these factors manifest in a decrease in matrix-dominated properties such as compressive strength, interlaminar shear strength, fatigue, and impact tolerance. Moisture is absorbed into the composite until a saturation point is

reached. This has been described as a non-Fickian process, meaning the rate of relaxation in the material due to water absorption is comparable to the diffusion rate of water. As the material properties change, such as decrease in glass transition temperature, the diffusion process changes. The mechanical properties degrade in relation to the amount of moisture absorbed, with no further deterioration after saturation is reached. Strength reductions in polyester laminates have been found to be 10-15% while epoxy resins are less vulnerable. (M10.1)

Water acts as a plasticiser when absorbed by the matrix, softening the material and reducing some properties of the laminate. Moisture may also migrate along the fibre-matrix interface thereby affecting the adhesion. Moisture in composites reduces matrix dominated properties such as transverse strength, fracture toughness and impact resistance.

Lowering of the glass transition temperature may also occur in epoxy and polyimide resins with an increase in absorbed moisture (as shown in Appendix-Figure M10.3.1). Debonding can occur due to formation of discontinuous bubbles and cracking in the matrix. Mechanical properties can be reduced even further if heat is present or if the composite is under-cured or has a large amount of voids.

The glass transition temperature for a typical polyester resin decreases by approximately 15-20°C for a 2% moisture weight gain. This reduction in T_g is induced by plasticisation (softening) of the polymer matrix and in some cases by loss of organic additives through leaching to the surrounding media. Broughton et al, (2000) illustrated on a graph that it is advisable when using GRP products to ensure that the maximum operating temperature is at least 30-40°C below the T_g of the material (taking into account moisture effects). Figure 2.13 shows the effect of moisture content on T_g for E-glass/F922 that has been immersed in distilled/deionised water for prolonged periods of time at three different temperatures.

Although the process of moisture absorption and desorption within the surface layers occurs almost immediately on contact with the environment, moisture diffusion into the bulk material is usually a slow process. It may take weeks to months before a substantial amount of moisture has been absorbed by the composite, and considerably longer periods (i.e. 1-2 years) before the material is saturated. The rate of moisture uptake by a composite laminate is dependent on the temperature, relative humidity, exposure time and mechanical load. At elevated temperatures, the rate of moisture uptake and material property degradation is accelerated as noted by Maxwell et al, (2005).

The presence of tensile loads accelerates moisture uptake by opening existing internal cavities or voids, and by contributing to micro-crack formation. A laminate containing micro-cracks will absorb considerably more moisture than an undamaged laminate.

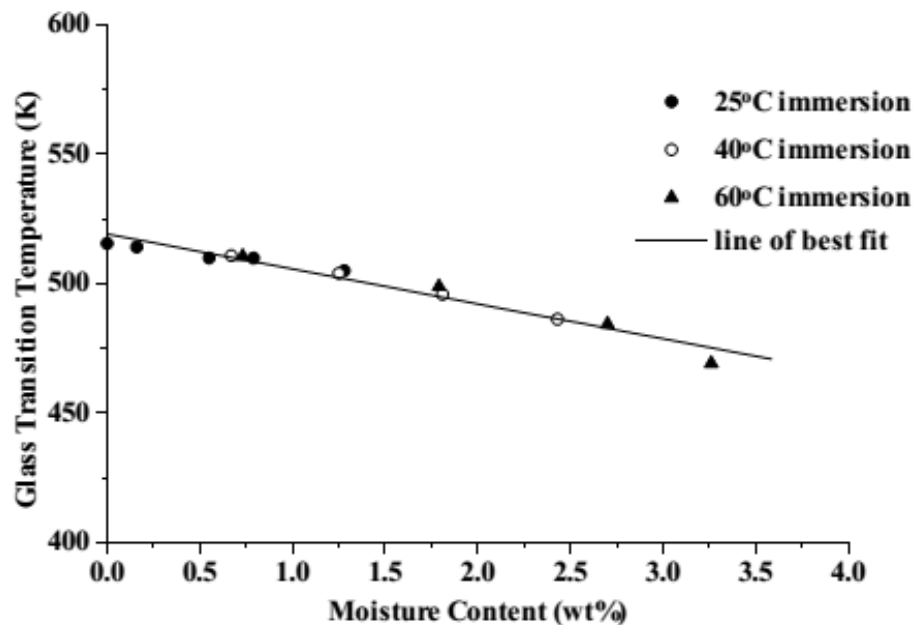


Figure 2.13: Glass transition temperature of F922 as a function of moisture content. Broughton et al, (2000).

v. The Effect of Saline Solution on GRP

Fiber-reinforced polymer composites are increasingly used in offshore and civil engineering structures. In these applications, composite materials are often exposed to aqueous environments. In a technical report presented by Arsenio *et al*, (2012) a testing program for accelerating aging in GFRP was conducted under salt-fog exposure. The resulting high degradation raises serious questions about the durability of composites under this simulated marine exposure. The degradation experienced by these specimens did not allow for a long-term evaluation of their behavior. However, the short-term behavior was significant enough to report and to warrant further research into the effect of salt water on composites.

From their laboratory results and the time-temperature superposition technique they applied, more specific conclusions could be drawn:

i. In the short test time, the degradations experienced by most of the materials were significant enough to compromise their long-term flexural strength (losses of 35% or more in less than five years in all cases), Jamond *et al*, (2012) and Bank *et al*, (1997).

ii. Salt-fog exposure seemed to affect the flexural strengths of the composites to a much larger degree than they affected the moduli.

iii. Glass-reinforced vinylester seems to be the most convenient material for this exposure given the lesser degradation (~35%) over a five-year period. The superior performance of vinylester relative to polyester resin in typical industrial corrosive environments had been well documented Gentry, (2002) and Bank, (1993).

All laminates when exposed to marine environments will allow water vapour to permeate the structure. As the water diffuses into the composite it reacts with any hydrolysable components (e.g. ester groups) inside the laminate to form tiny cells of concentrated solution. Under this osmotic process according to

Pritchard, (1995) in the schematic in Figure 2.14, more water is drawn through the semi-permeable membrane of the laminate in an attempt to dilute the solution. The water can increase the fluid pressure of the cell by 50 atmospheres, which eventually distorts or bursts the laminate or gel coat and can lead to a blistering of the surface. Damage can be very extensive requiring major repair or the replacement of the structure.

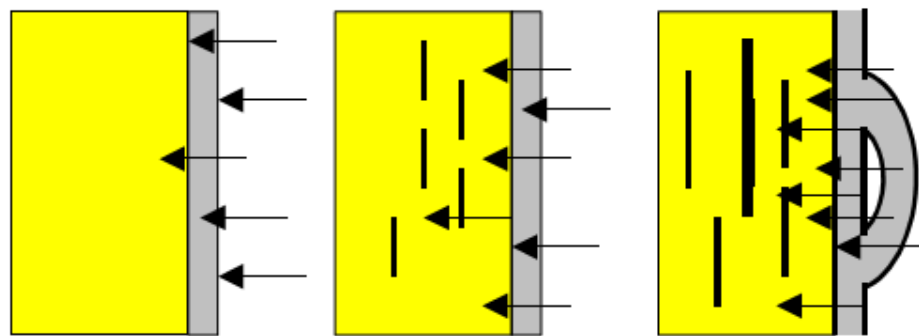


Figure 2.14: Schematic of the osmotic process—leading to delaminations/blistering. Maxwell et al, (2005).

Smith, (1990) noted that osmosis blistering is a very common problem that occurs in GRP laminated structures that have been immersed for long periods in aqueous solutions and is often observed in GRP boats, water tanks and swimming pools. A resin rich layer (e.g. gel coat) is often applied to the composite surface where the material is to be exposed for long periods to aqueous solutions. This protective layer acts as a barrier to moisture ingress, thereby protecting glass fibres from moisture degradation. Other protective measures against natural weathering include marine paint and polyurethane, which also shield the composite substrate from ultraviolet damage and weathering erosion.

The Effect of UV on GRP

The earth's surface is exposed to UV radiation which has a wavelength range of 290-400nm which matches the bond dissociation energy of most polymers. The UV degradation of polymers is caused by a series of complex processes. UV radiation is absorbed by the polymer and bond dissociation is initiated leading to polymer chain scission and/or crosslinking. In addition the presence of oxygen can lead to the formation of some functional groups such as: carbonyl (C=O), carboxyl (COOH) or peroxide (O-O). UV degradation only affects the surface of a composite, however, the resultant embrittlement and flaws in the surface layer can provide a point of initiation for fracture Rapra, (2012).

The energy of these UV photons is comparable to the dissociation energies of polymer covalent bonds, which are typically 290-460 kJ/mole. Therefore, the interactions between this UV light and the electrons are strong, often resulting in excitation of the electrons and a resultant breaking of the bond. Hence, UV light can degrade polymers Kumar *et al*, (2002) and Strong,(2008).

The nature of the atoms in polymermatrix has some effect on the tendency of the electrons to become excited by the UV light and degrade. Generally, aromatic polymers are more easily degraded by UV light than are aliphatic polymers. All resins containing aromatic groups can absorb sufficient UV radiation to cause bond dissociation. Of the typical resins used in composite structures, phenolics are most sensitive, followed by epoxy resins. The high aromatic content common to most high-performance epoxies makes them particularly susceptible to UV radiation induced degradation Hoskin, (1986) and Strong, (2008).

The UV photons absorbed by polymers result in photo-oxidative reactions that alter the chemical structure resulting in material deterioration. The chemical reactions typically cause molecular chain scission and/or chain cross-linking. Chain scission lowers the molecular weight of the polymer, giving rise to reduced heat and strength resistance. Chain cross-linking leads to excessive

brittleness and can result in microcracking. Previous research discovered that exposure of a carbon/epoxy laminate to UV radiation for as little as 500 hrs results in the formation of microcracks, which lead to a reduction in matrix-dominated properties. This was likely caused by embrittlement of the polymer matrix due to increased crosslinking resulting from photo-oxidation reactions induced by UV exposure Kumar *et al*, (2002). In addition to inducing chain scission and increasing crosslink density, photo-oxidative reactions can also result in the production of chromophoric chemical species. Chromophores are simply molecules that transmit and absorb light. These chromophores, may impart discoloration to the polymer, if they absorb visible wavelengths. Furthermore, an autocatalytic degradation process may be established if chromophores produced also absorb UV radiation Kumar *et al*, (2002).

2.18 Summary of Literature Review

Most polymers take up several percent of water by mass, depending on their chemical composition and this influences both thermophysical and viscoelastic response of polymer composites. As discussed in other sections above, extensive studies in this area by a number of researchers had indicated that salinity, moisture, temperature and ultraviolet radiation play a critical role in affecting the material properties of GRP. The literature reviews therefore indicated that some work have been done in this area and can assist to setup study criteria for this thesis.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Scope of Work

The primary focus of this research was to study the synergetic effect of heat, water, saline solution and UV radiation on glass/polyester composite material. Additionally the effectiveness of the two polyester-based (Isopolyester and Orthopolyester) glassfibre composites in mitigating degradation of the solar hot water storage tanks was examined.

The tests were carried out at the Material Testing Laboratory –University of Nairobi Mechanical & Manufacturing Engineering workshop. The more fundamental reason for carrying out the tensile test was to compare the change in the tensile strength and strain as the test material ages under different conditions like temperature changes, UV radiation, moisture content and salt concentrations effect. Then analysis was carried out to make deductions accordingly.

3.2 Materials

Description of Test Specimens

Representative commercial mat and resin systems studied included Isophthalic polyester (NCS 991PA, is thixotropic) and Orthophthalic polyester (general purpose resin) both supplied by NCS of South Africa and the fibre was E-Glass woven and E-Glass chopped strands powder mat of 450 grams per square meter (GSM) with 1040mm thickness, these are commonly used in general molding applications and readily available. In addition the MEKP catalyst was used to cure the polyester resins.

Specimen Preparation

As recommended in ASTM D 638, the Type I specimen geometry, or something very similar, was preferred, and is most commonly used when testing the high performance composite matrix materials. The geometry recommended for testing specimens 0.28 in. (7.0 mm) or less in thickness, which is usually the case, this 6.50 in. (165 mm) long specimen is 0.75 in. (19 mm) wide.

The specimens were hand moulded in Davis & Shirliff Ltd's fiberglass workshop. Both polyesters were used for both one layer of 450GSM woven and chopped strands fibre mats. These produced four different sheets of GRP specimens.

The sheets were then cut according to ASTM D 638. The Type I specimen geometry sizes were 165mm long and 19mm wide. The Figure 3.1 to Figure 3.6 captured the whole process.

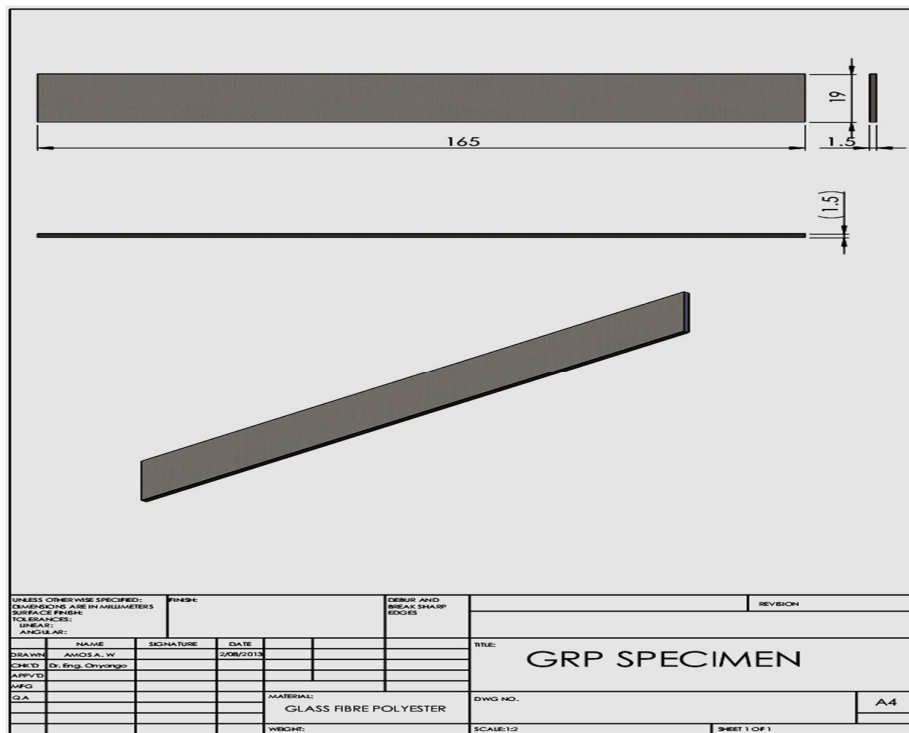


Figure 3.1: Specimen Geometry

The production process of GRP in Figure 3.2 is where glass fibre mat is prepared according the surface are of the mold and layers needed. The weight of the mat will determine the quantity by weight of the resin to be applied. The resin has to be catalysed by adding 2% by weight of the catalyst. During application of the catalysed resin, air bubbles are removed by continuously rolling out air as mat layers are added to achieve the designed number of layers. The wet mat is left to cure and dry for about two hours to achieve the desired strength of the composite which will be trimmed of the extra overlaps.

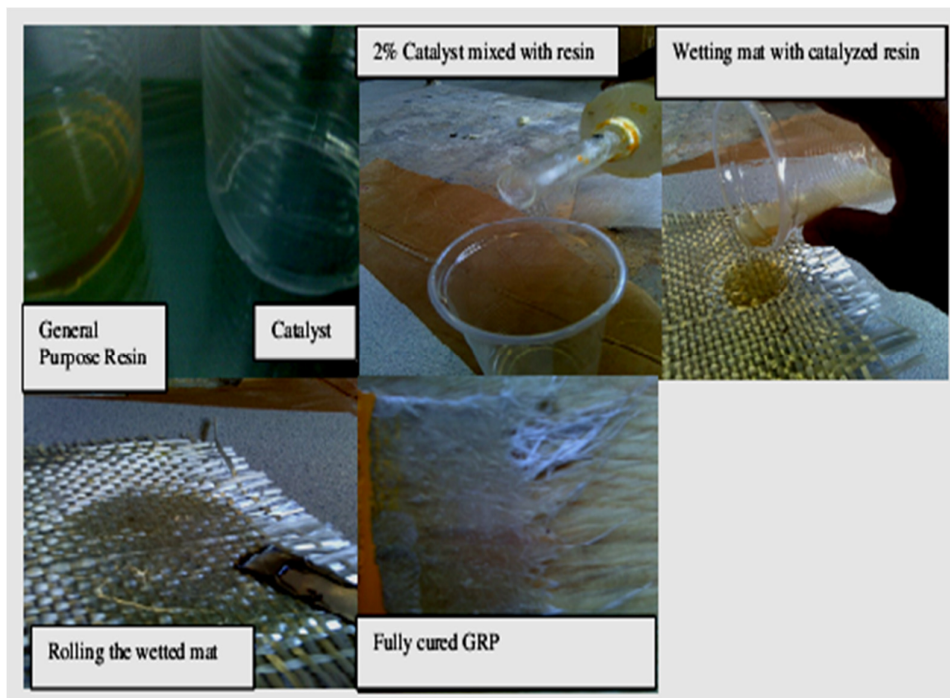


Figure 3.2: GRP production process

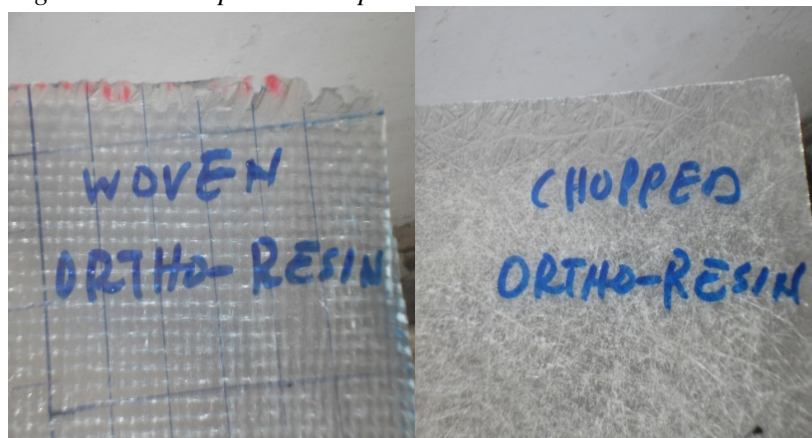


Figure 3.3: GPR-Orthophthalic polyester sample molded sheets

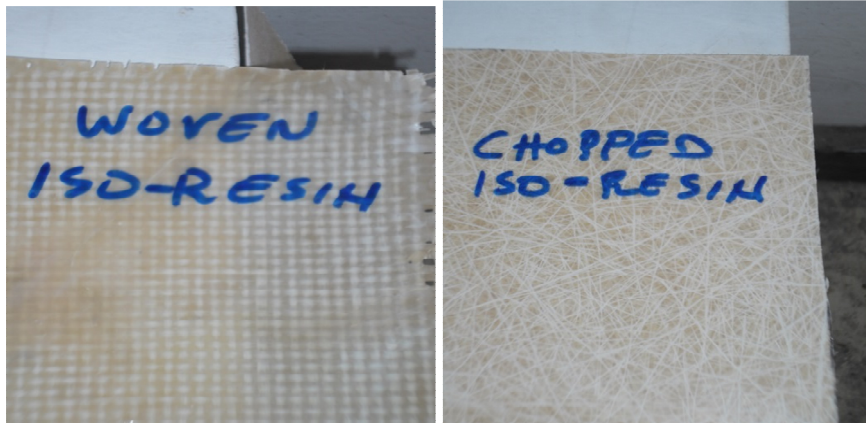


Figure 3.4: GPR- Isophthalic polyester sample molded sheets

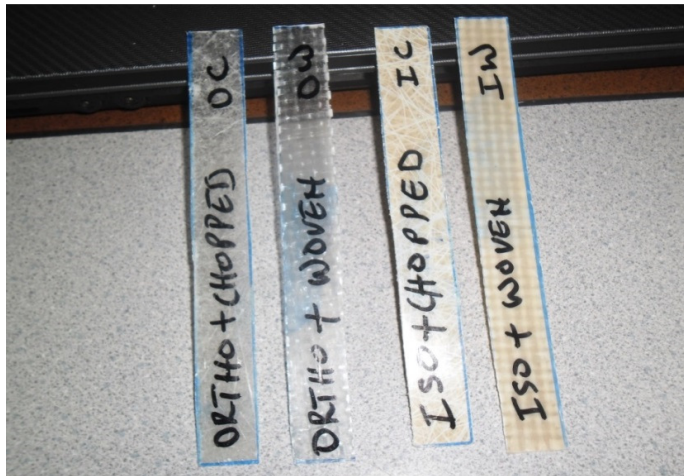


Figure 3.5: Different Types of Specimens



Figure 3.6: Bundles of GRP specimens

3.3 Apparatus

i. Heating Container

A mild steel metallic container was fabricated in D&S manufacturing workshop to the specifications as shown in the Figure 3.7 and

Figure 3.8. It was fitted with 3kW emersion electric heater complete with thermostat for heating the water solution to various specified temperatures.

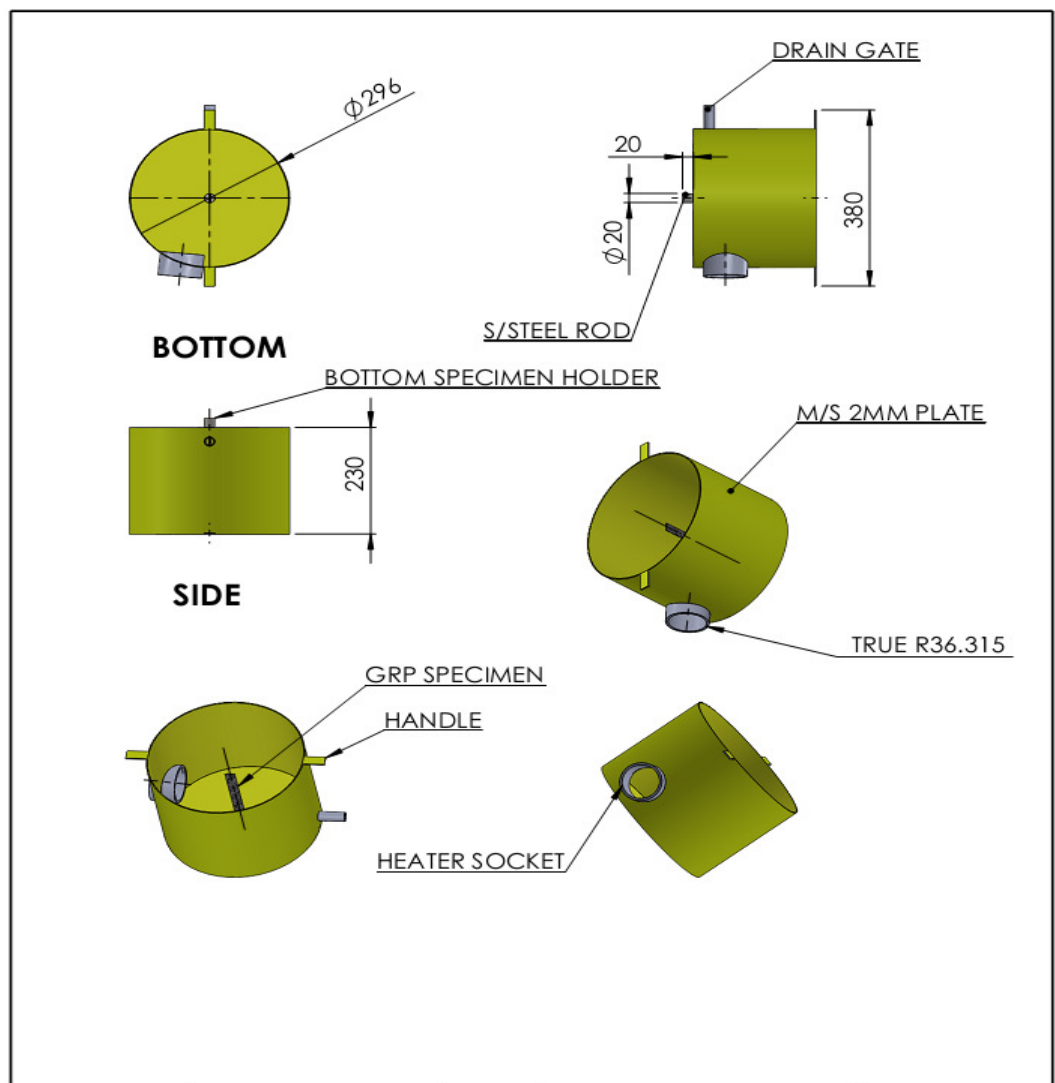


Figure 3.7: Pictorial drawing of Solution Heating Can

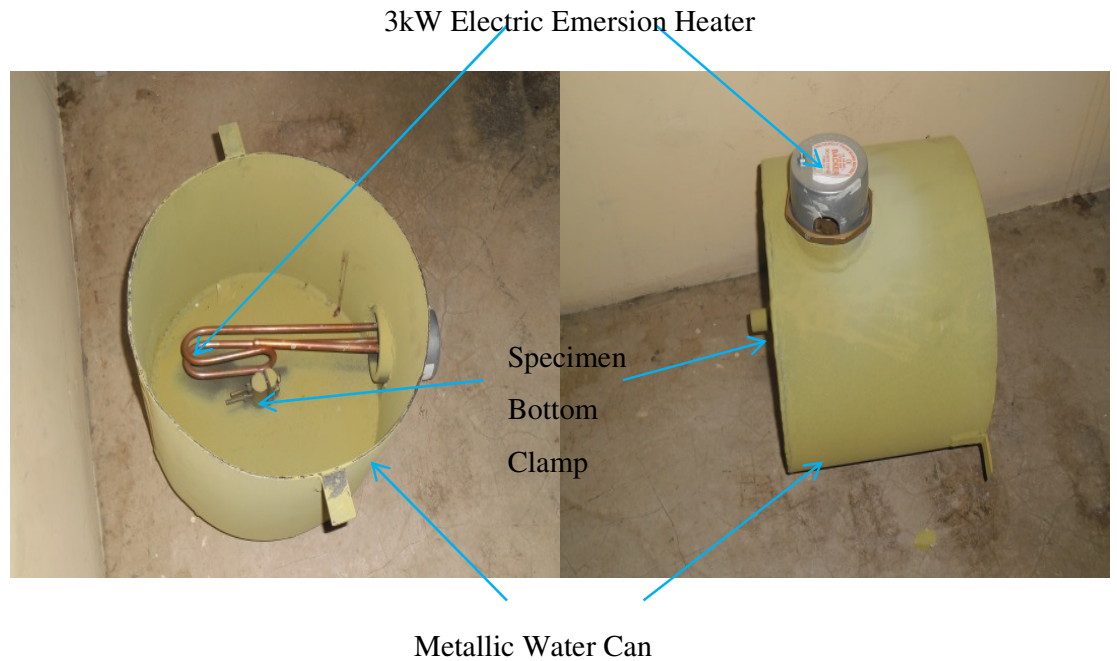


Figure 3.8: Pictures of Solution Heating Can

ii. Ashton Meyers Weighing Balance

The weighing balance in Figure 3.9 was used to determine the amount of water absorbed under specified conditions. The data shed light on the amount of water the specimen could absorb and the subsequent effect of the absorbed amount of water or moisture.



Figure 3.9: Ashton Meyers Weighing Balance (Courtesy: D&S, 2014)

iii. Ultra Violet Chamber



Figure 3.10: UV Chamber (Courtesy: Mag Utility Co. Ltd, 2014)

The UV chamber has UV bulb enclosed inside stainless steel casing. The hot water line is also connected for temperature regulation.

iv. Universal Test Machine

Universal Test Machine from University of Nairobi Tensile Material Mechanical workshop was used. The Figure 3.11 show the Universal Testing Machine TORSEE, 10 TON made by Senstar, Tokyo.



Figure 3.11: *Universal Test Machine (Courtesy: University of Nairobi, 2013)*

3.4 Experimental Setup

The specimens were categorized into four groups:

- i. Iso polyester - Chopped strand mat GRP (*labeled as C-I*)
- ii. Iso polyester – woven mat GRP (*labeled as W-I*)
- iii. Ortho polyester - Chopped strand mat GRP (*labeled as O-C*)
- iv. Ortho polyester – woven mat GRP (*labeled as O-W*)

Each specimen group was subjected to the following accelerated weathering conditions:

- i. Incremental temperatures of soft clean water; from ambient temperature to 100°C at 10°C intervals. This was to simulate offshore water.
- ii. Incremental temperatures of salty water solution; from ambient temperature to 100°C at 10°C intervals. This was to simulate sea waters. The salty water solution was composed of a mass fraction of 3.5% by mass NaCl in distilled water.
- iii. Water absorption levels for each temperature were recorded by weighing the specimen under condition 1 and 2 above.

iv. Ultra violet light exposure.

The following tests were then carried out for the above variables:

- i. As reference point, tensile tests were done at ambient temperature for the four species.
- ii. Visual inspection for any physical change in the appearance.
- iii. Tensile tests for any change in the mechanical strength.

To get representative results, each test was repeated three times and average value recorded by eliminating out of range results where applicable, tensile tests curves were obtained while holding the stress levels constant.

Finally, two prototypes were built with two polyester resins and woven mat and subjected to elevated hygrothermal conditions for both pure and salty waters.

3.5 Experiments.

Water Absorption ASTM D570

Scope: Hygrothermal chamber was installed on a Universal Test Machine filled with clean water then salty water and heated to incremental temperatures from 25°C to 100°C.

Procedure: The specimens were weighed before and then immersion into the water at a specific water temperature for 30min then removed and whipped with a dry cloth then weighed again. Tensile tests were then done with various moisture contents in the specimen at a fixed room temperature.

Water absorption was used to determine the amount of water absorbed under specified conditions. The data on amount of water absorbed by various specimens at various temperatures was collected for analysis. The data shed light on the effect of absorbed moisture and the performance of the materials in water or humid environments.



Figure 3.12: Tensile test with difference moisture content.

Water absorption was expressed as increase in weight percent.

Table 3-1: Moisture Effect Data Collection Table

| SPECIM EN NO. | TEMPERATURE INFLUENCE ON MOISTURE ABSORBILITY | | | | MOISTURE EFFECT ON STRENGTH | | |
|------------------|--|--------------------------|-------------------------|--------------------------------|---------------------------------------|------------------------------------|----------------------|
| | TEMP. °C | Weight Before (mg) | Weight After (mg) | Water Absorb ed (mg). | Length at room temp. (mm) | Extension at room temp. (mm) | Strain (moisture) |
| | | | | | | | |
| | | | | | | | |

Temperature and salt effect test procedure

The standard specimen was used for ASTM D5083 that had a constant rectangular cross section, 19 mm wide and at least 165 mm long. Thickness was between 1.65 mm and 1.5 mm. Hygrothermal chamber was installed on a Universal Test Machine. Testing was conducted inside the controlled thermal

environment. The chamber had immersion electric heater for heating the water and fitted with thermostat to regulate temperature as required.

ASTM D-3518 test procedure:

GRP specimens were immersed in clean soft water and later in salt water. After immersion, the water was heated to 50, 60, 70, 80, 90 and maintained at that temperature for 30 minutes. Tensile tests were then carried out at that temperature and tensile test curves obtained while holding the stress levels constant for three similar samples to get average for the loading and corresponding extensions.

Test specimens were placed in the grips of a universal tester at a specified grip separation and pulled until failure. The test specimens and test protocol were as called out in ASTM D-3039 for Tensile Properties of Composite Materials ^ typical test speed for standard test specimens was 2 mm/min.



Figure 3.13: Hygrothermal Tensile Tests in the UoN Mechanical lab.

The following parameters were determined from Tables 3-2 which was used to collect data for tensile test results:

- Tensile Strength (MPa)
- Modulus of Elasticity (MPA)
- Elongation (%)

- Shear Response ASTM D3518

Tables 3-2: Tensile Test Stress-Strain Data Collection Summary Sheet

| Isophthalic polyester / Orthophthalic (general purpose resin) polyester | | | | | | | |
|---|---------------|----------------|----|--|---------------|----------------|----|
| CHOPPED | | | | | WOVEN | | |
| TEMPERATURE (°C) | PURE WATER | SALTY WATER | UV | | PURE WATER | SALTY WATER | UV |
| Ambient temp. | | | | | | | |
| 65 | | | | | | | |
| 95 | | | | | | | |

Ultraviolet Irradiation Effect Test

Polymer films of 19mm by 165mm with an approximate thickness of 1.5mm were exposed to UV light. The temperature in the specimen chamber during the exposure period was maintained at 30°C by passing 30°C water through. The UV chamber as in Figure 3.14 intensity of 254 nm wavelength mercury vapour quartz lamp output was used.



Figure 3.14: UV Chamber (Courtesy: D&S, 2014)

The specimens were inserted inside the UV housing and left for 30 min. The specimens were then tested through visual inspection followed by tensile tests. The UV effect was investigated by comparing the strength change and physical surface change on irradiated and non-irradiated similar specimens.

| UV EFFECT ON STRENGHT | | |
|---------------------------------------|---------------------------------|--------------|
| Original Length at ambient temp. (mm) | Extension at ambient temp. (mm) | Strain- (UV) |
| | | |
| | | |

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Water Absorption

The physical appearances of the specimens after absorbing water were as shown in Figure 4.1. The samples had differences in physical appearances where the samples that had absorbed water had a dull appearance compared its respective dry samples. The first sample in each set other samples were dry and the second sample had absorbed water. This showed that water had physical effect on the samples. This effect was tested under tensile strength as indicated in the next section.

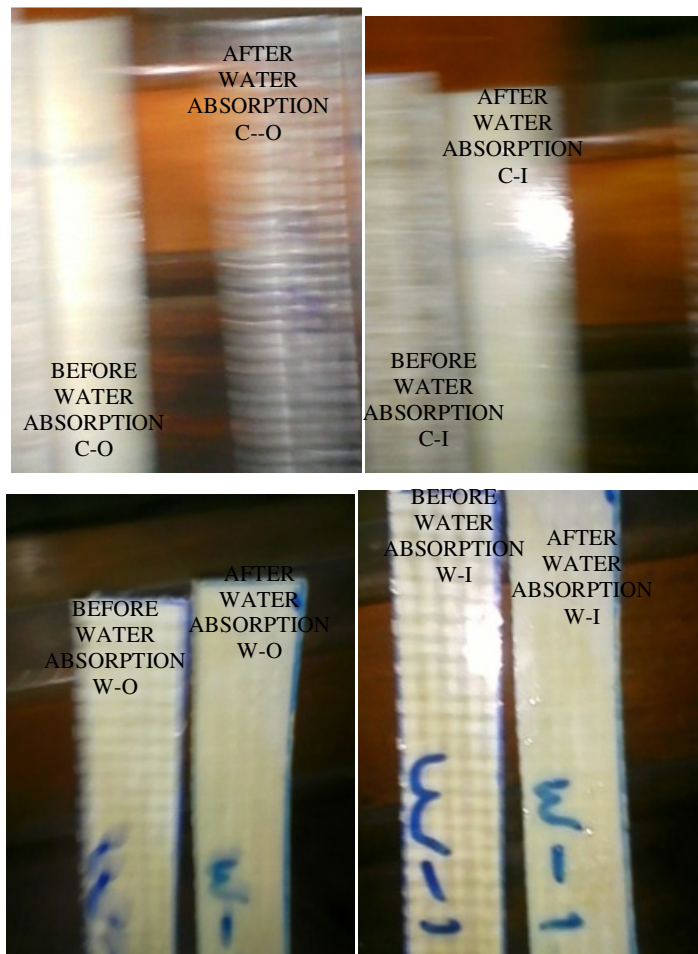


Figure 4.1: Physical look before and after water absorption

4.2 Tensile Strength Tests

After various samples were subjected to the hydrothermal conditions, UV radiations and moisture absorptions as indicated in the procedure above and tensile tests carried out. The data collected were then plotted for various groups as shown in the Figure 4.2.

The tensile tests results from UV radiation and temperatures below 65°C never gave significant difference results from the dry specimens. Therefore, the results that showed significant change were presented in the graphical data for further analysis: dry specimens, water at 65°C and at 95°C on both clean and salty waters.



Figure 4.2: The specimens after tensile tests failure modes

Dry Composite Samples

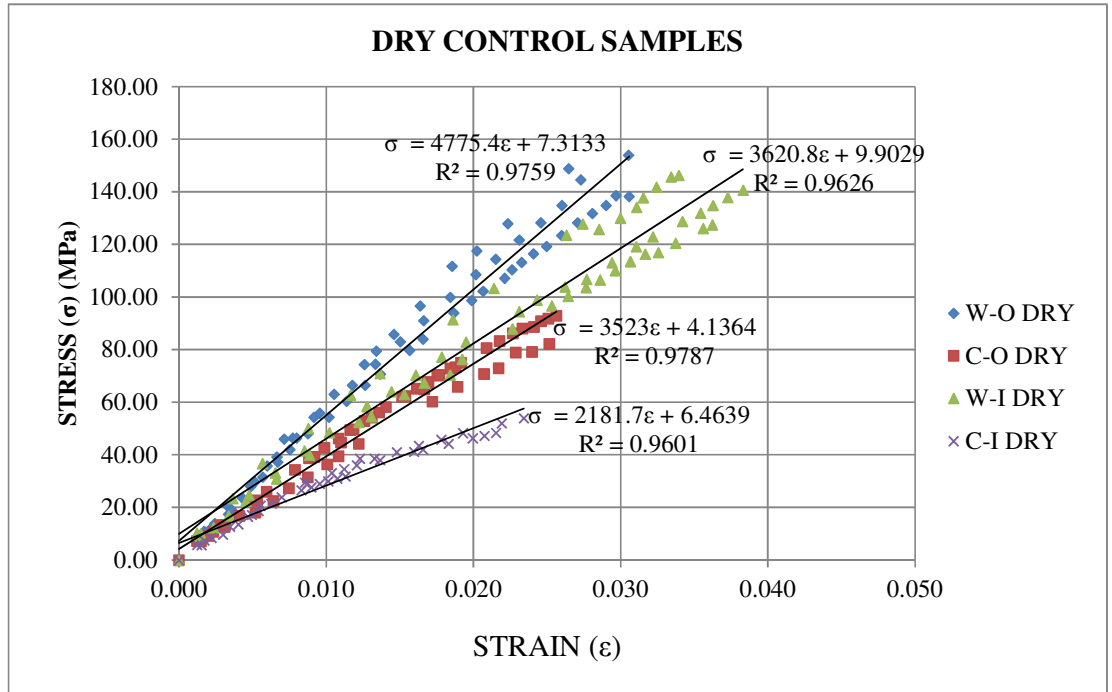


Figure 4.3; Comparison of various dry composite specimens under tensile tests

Tables 4-1; summary of Young's Modulus for the dry control samples

| SAMPLE | R^2 | Young's Modulus, (E) (MPa) |
|---------|--------|----------------------------|
| W-O DRY | 0.9759 | 4775.4 |
| C-O DRY | 0.9787 | 3526 |
| W-I DRY | 0.9626 | 3620.8 |
| C-I DRY | 0.9601 | 2181.7 |

The dry samples represented in Figure 4.3 acted as control tests for comparison purposes. The Young's Modulus for the specimens following environmental exposure are shown in Tables 4-1. The tests were conducted at a room temperature of 25°C. Woven-ortho composites had the highest strength

followed by woven-iso. This confirms that woven mat performs better than chopped mat and this was expected from the literature reviews done.

Chopped Strands Mat

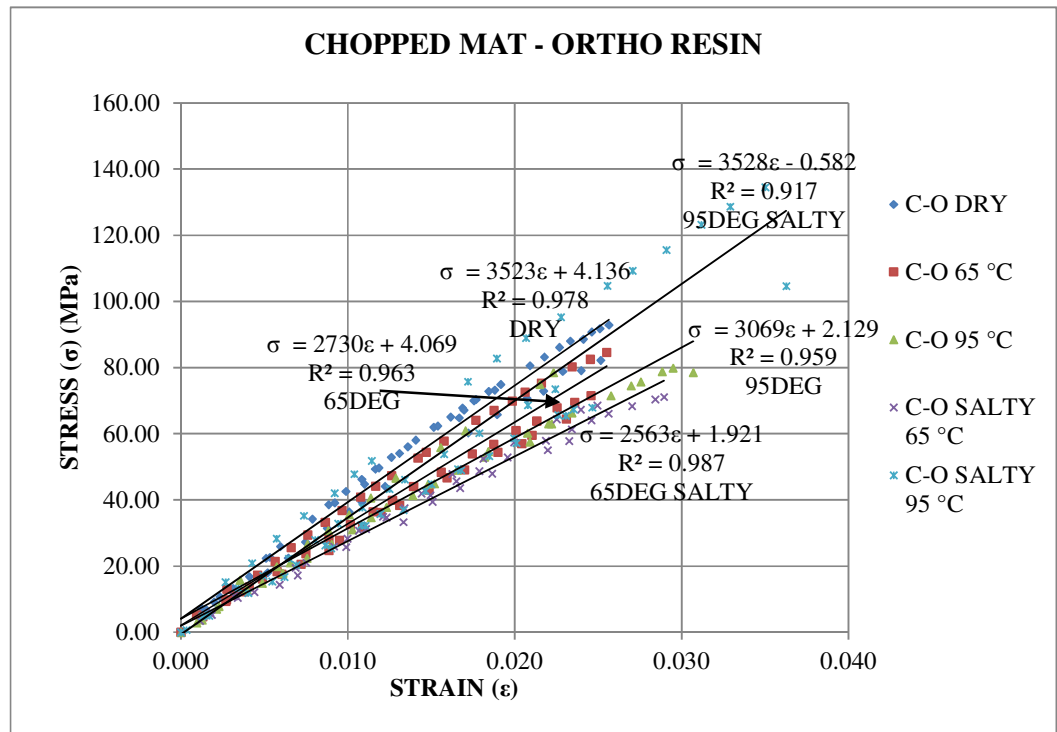


Figure 4.4: Comparison of various chopped mat-Ortho resin composite specimens under tensile tests.

Tables 4-2; summary of Young's Modulus for the chopped mat - ortho resin samples

| SAMPLE | R ² | Young's Modulus, (MPa) | Young's Modulus, (E) Control sample C-O DRY |
|-----------------------------|----------------|------------------------|---|
| C-O 65 ⁰ C | 0.963 | 2730 | 3526 |
| C-O 95 ⁰ C | 0.959 | 3069 | 3526 |
| C-O 65 ⁰ C SALTY | 0.987 | 2563 | 3526 |
| C-O 95 ⁰ C SALTY | 0.917 | 3528 | 3526 |

Isolating and analysing the performance of chopped mat-ortho resin and varying the temperatures and salt, it is seen Young's Modulus decreased from the control sample for both temperature increase and salt additions. As the results showed, a combination of both temperature and salt had greatest effect.

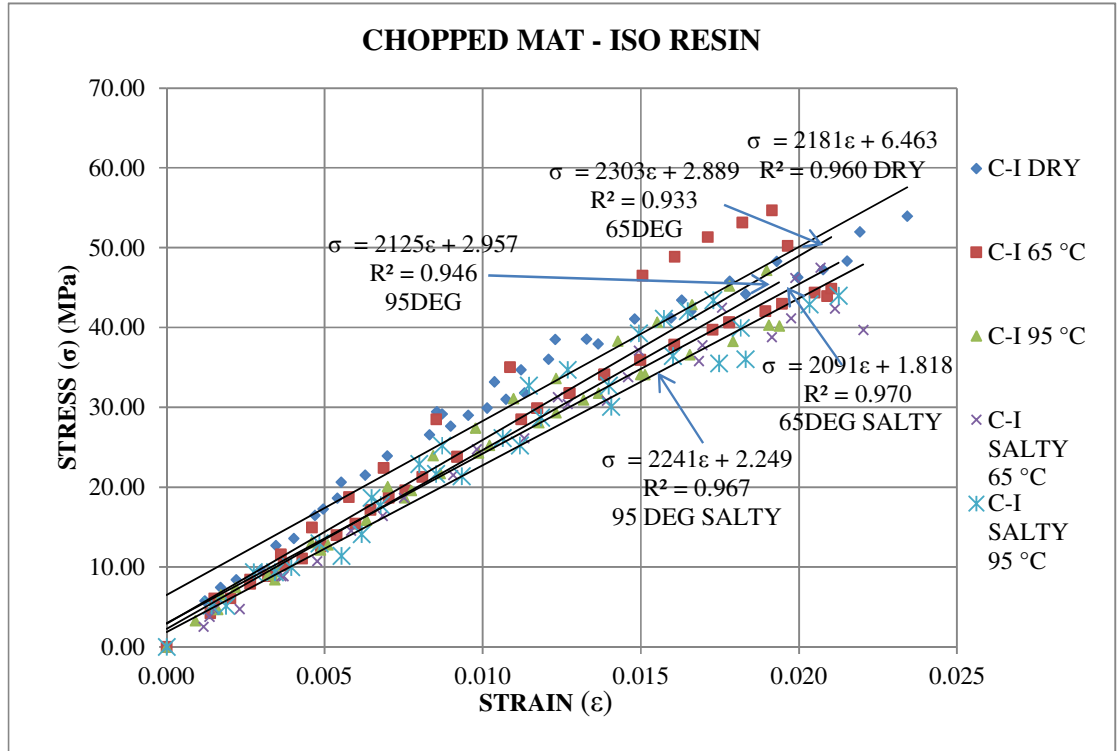


Figure 4.5: comparison of toughness of various chopped mat-Iso resin composite specimens under tensile tests

Tables 4-3; summary of Young's Modulus for the chopped mat-Iso resin samples

| SAMPLE | R ² | Young's Modulus, (E) (MPa) | Young's Modulus, (E) Control sample C-I DRY |
|----------------|----------------|----------------------------|---|
| C-I 65°C | 0.933 | 2303 | 3526 |
| C-I 95°C | 0.946 | 2125 | 3526 |
| C-I 65°C SALTY | 0.970 | 2091 | 3526 |
| C-I 95°C SALTY | 0.967 | 2241 | 3526 |

Isolating and analysing the performance of chopped mat-iso resin and varying the temperatures and salt, again it is seen Young's Modulus decreased from the control sample for both temperature increase and salt additions. As the results showed, a combination of both temperature and salt had greatest effect.

Woven Strands Mat

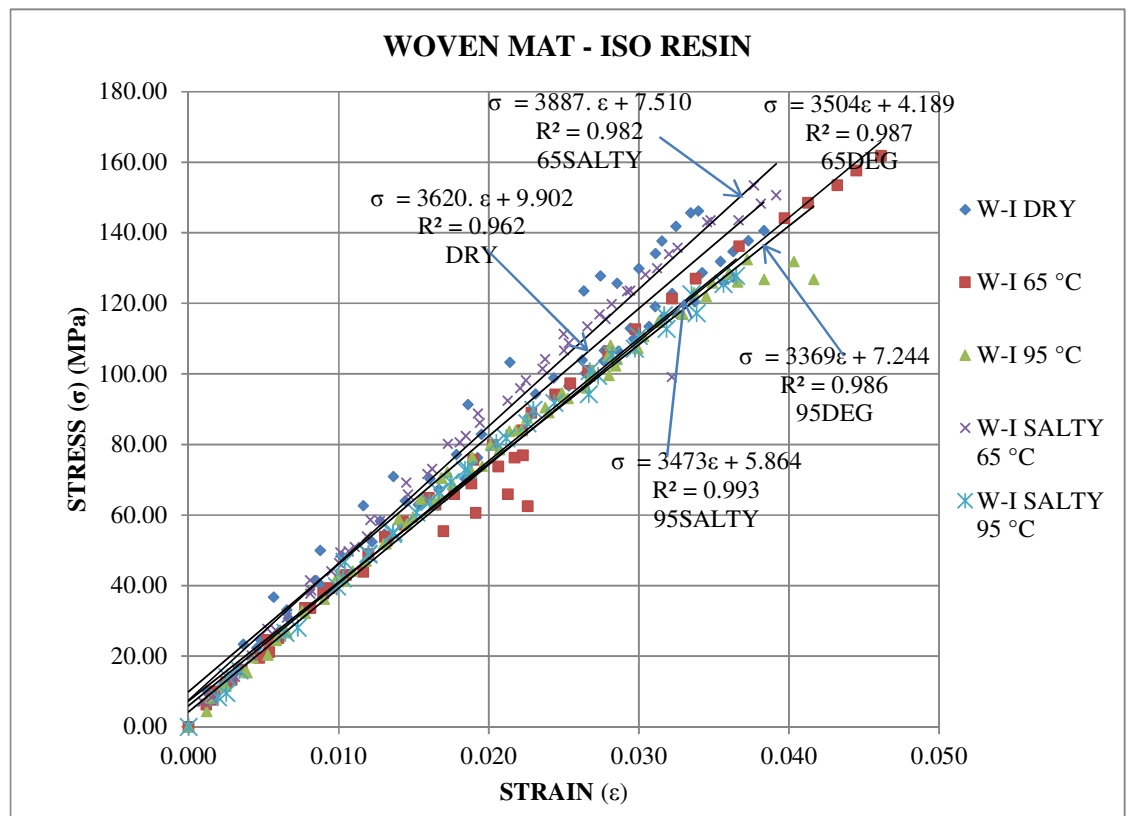


Figure 4.6: Comparison of various Woven mat-Iso resin composite specimens under tensile tests.

Tables 4-4; summary of Young's Modulus for the Woven mat-Iso resin samples

| SAMPLE | R ² | Young's Modulus,(E) (MPa) | Young's Modulus, (E) Control sample W-I DRY |
|-----------------------------|----------------|---------------------------|---|
| W-I 65 ⁰ C | 0.933 | 2303 | 3620.8 |
| W-I 95 ⁰ C | 0.946 | 2125 | 3620.8 |
| W-I 65 ⁰ C SALTY | 0.970 | 2091 | 3620.8 |
| W-I 95 ⁰ C SALTY | 0.967 | 2241 | 3620.8 |

Isolating and analysing the performance of woven mat-iso resin and varying the temperatures and salt, again it is seen Young's Modulus decreased from the control sample for both temperature increase and salt additions. As the results showed, a combination of both temperature and salt had greatest effect.

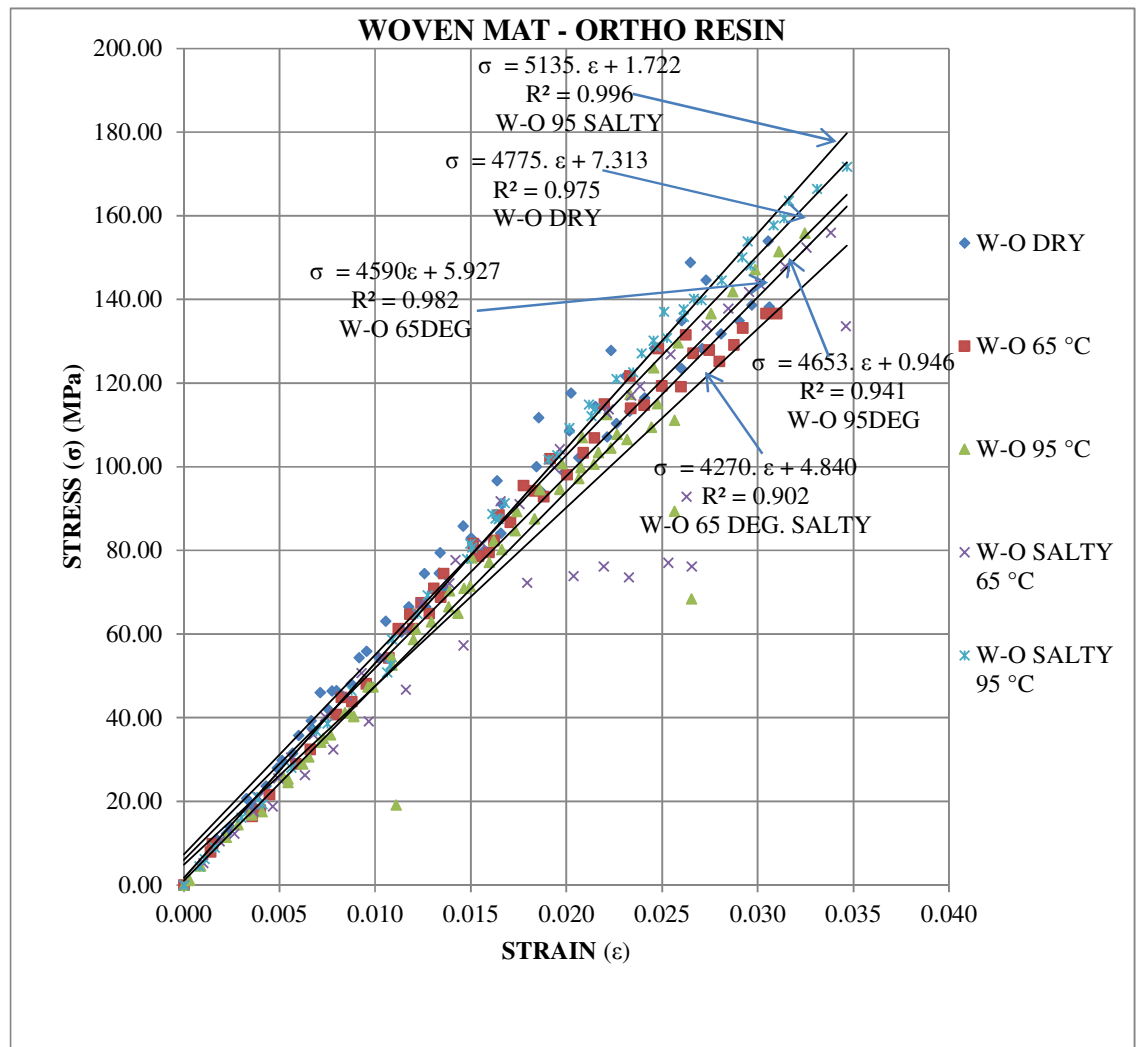


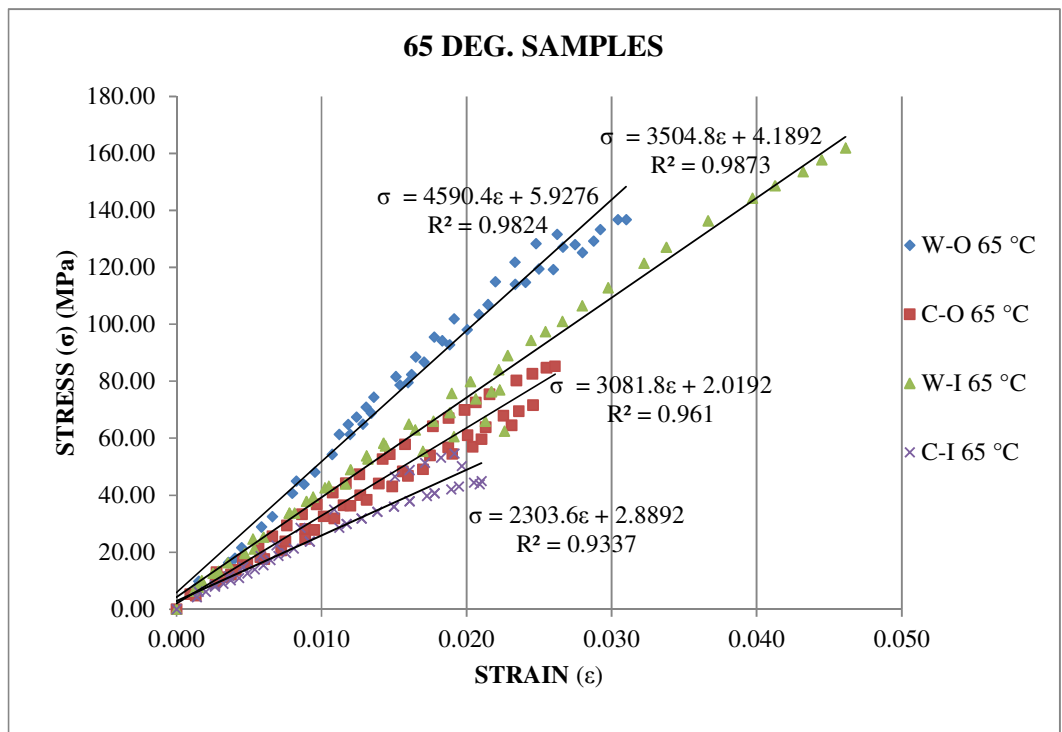
Figure 4.7: Comparison of toughness for various Woven mat - Ortho resin composite specimens under tensile test

Tables 4-5; summary of Young's Modulus for the Woven mat-ortho resin samples

| SAMPLE | R ² | Young's Modulus,(E) (MPa) | Young's Modulus, (E) Control sample W-O DRY |
|-----------------------------|----------------|---------------------------|---|
| W-O 65 ⁰ C | 0.982 | 4590 | 4775.4 |
| W-O 95 ⁰ C | 0.941 | 4653 | 4775.4 |
| W-O 65 ⁰ C SALTY | 0.902 | 4270 | 4775.4 |
| W-O 95 ⁰ C SALTY | 0.996 | 5135 | 4775.4 |

Isolating and analysing the performance of woven mat-ortho resin and varying the temperatures and salt, again it is seen ultimate tensile strengths decreased from the control sample for both temperature increase and salt additions, though small significance. As the results showed, a combination of both temperature and salt had greatest effect.

Temperature Influence Analysis



Tables 4-6; summary of Young's Modulus for the 65 deg. Samples

| SAMPLE | R ² | Young's Modulus,(E) (MPa) | Young's Modulus, (E) Control sample |
|-----------------------|----------------|---------------------------|-------------------------------------|
| W-O 65 ⁰ C | 0.982 | 4590 | 4775.4 |
| C-O 65 ⁰ C | 0.961 | 3081 | 3526 |
| W-I 65 ⁰ C | 0.9803 | 3504 | 3620.8 |
| C-I 65 ⁰ C | 0.9337 | 2303 | 2181.7 |

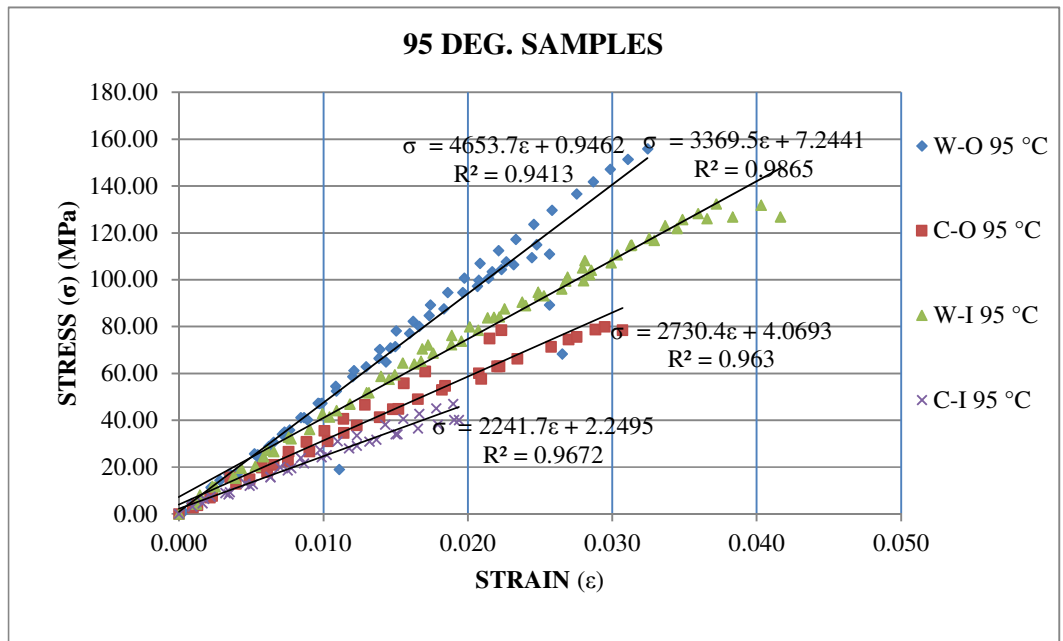


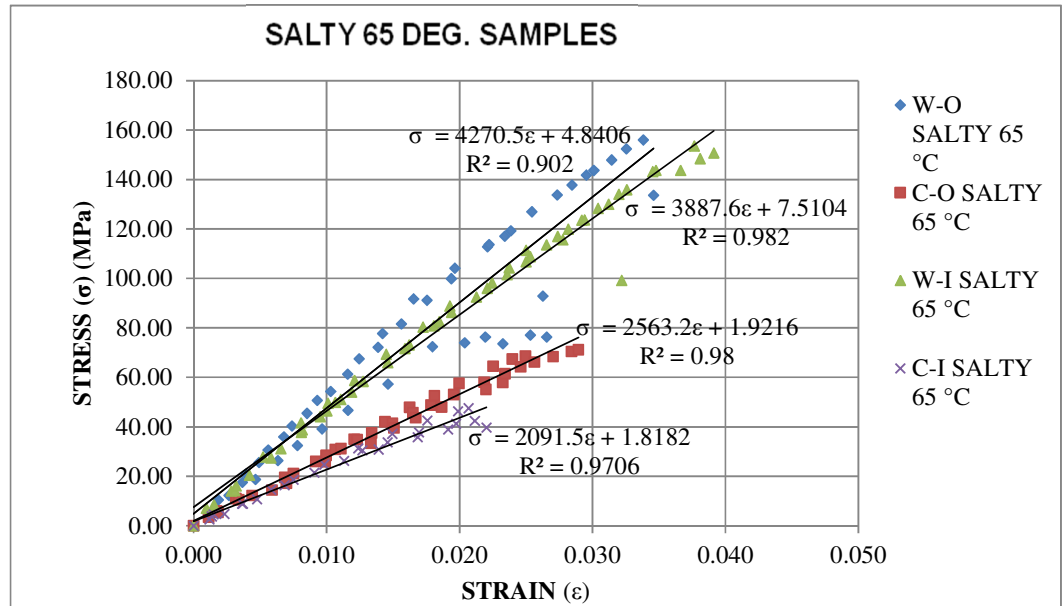
Figure 4.8: Comparison of effect of temperature on toughness for various composite specimens under tensile test at 65⁰C and 95⁰C.

Tables 4-7; summary of Young's Modulus for the 95 deg. Samples

| SAMPLE | R ² | Young's Modulus,(E) (MPa) | Young's Modulus, (E) Control sample |
|-----------------------|----------------|---------------------------|-------------------------------------|
| W-O 95 ⁰ C | 0.9413 | 4653.7 | 4775.4 |
| C-O 95 ⁰ C | 0.963 | 2730.4 | 3526 |
| W-I 95 ⁰ C | 0.9865 | 3369.5 | 3620.8 |
| C-I 95 ⁰ C | 0.9672 | 2241.7 | 2181.7 |

Looking at the effect of temperature alone from *Figure 4.8*, where temperatures were increased from 65⁰C to 95⁰C, the engineering stress were reduced in all cases hence Young's modulus reduced. This means temperature had significant effect on all the samples.

Salt Influence Analysis



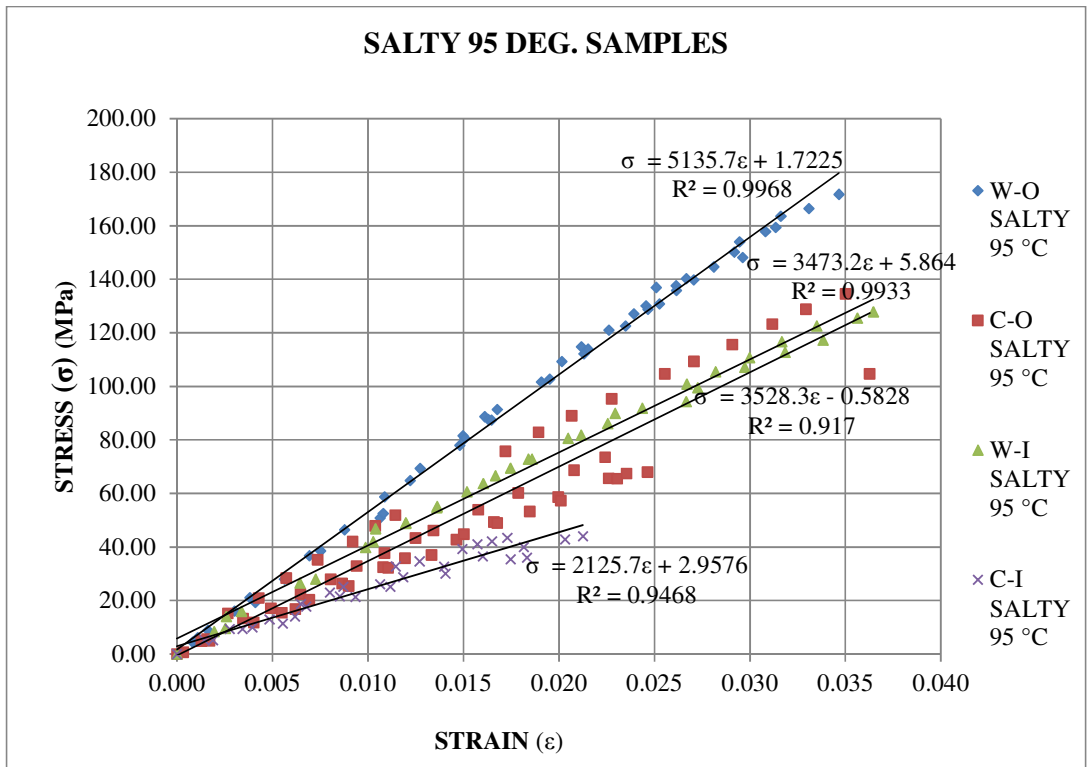


Figure 4.9: Comparison of effect of salinity on toughness for various composite specimens under tensile test at 65⁰C and 95⁰C

Tables 4-8; summary of Young's Modulus for the test at 65⁰C and 95⁰C salty samples

| SAMPLES | test at 65 ⁰ C salty | | test at 95 ⁰ C salty | | Young's Modulus, (E) Control sample |
|---------|---------------------------------|---------------------------|---------------------------------|---------------------------|-------------------------------------|
| | R ² | Young's Modulus,(E) (MPa) | R ² | Young's Modulus,(E) (MPa) | |
| W-O | 0.902 | 4270.5 | 0.9968 | 5137.5 | 4775.4 |
| C-O | 0.98 | 2563.2 | 0.917 | 3528.3 | 3526 |
| W-I | 0.982 | 3887.6 | 0.9933 | 3473.2 | 3620.8 |
| C-I | 0.9706 | 2091.5 | 0.9468 | 2125.7 | 2181.7 |

Following of exposure at ambient temperature, 65⁰C and 95⁰C, little loss in the strength was observed for samples exposed to salt water from Figure 4.8 and Figure 4.9, salt is seen to have no significant changes.

4.3 Prototype Testing

A full size prototype of a 160 liters tank was made out of both Ortho and Iso polyesters with woven mat fibre. The tank was not insulated as for the case of the real tanks.

The four tanks were fitted with all necessary fittings for solar hot water tank operations. The pressure gauge complete with a 3 bars pressure release valve and 3kw emersion heater were also attached to the tank on one side complete with both temperature adjustable thermocouple device and temperature sensing probe for the digital controller place at a distance.

The tests were taken under the following conditions:

- i. One Iso and one Ortho polyester tank were filled with clean soft water while the other two similar tanks filled with salty water.
- ii. The water was then heated to 60°C and maintained at that temperature for 8 hours. The pressure was monitored and maintained at 3 bars with excess pressure continuously released in form of steam.
- iii. This was repeated at 90°C and 120°C for each tank.

These stress limits were meant to simulate an exaggerated real working site conditions.

These gave very encouraging results where the Iso resin tanks failed at 120°C while Ortho resin tanks at 90°C. These failures were experienced after seven days continuous hygrothermo cycling. On both cases, the barrel ruptured on the upper section of the tank. These happened after the tanks have lost some water inform of steam through release valves and therefore the inside upper section of the tank was experienced hot steam heating hence penetrating to escape through fabre matrix inter facial cracks and hence resulted to wall ruptures.



Figure 4.10: *the hot water tank made from GRP-iso-polyester resin.*

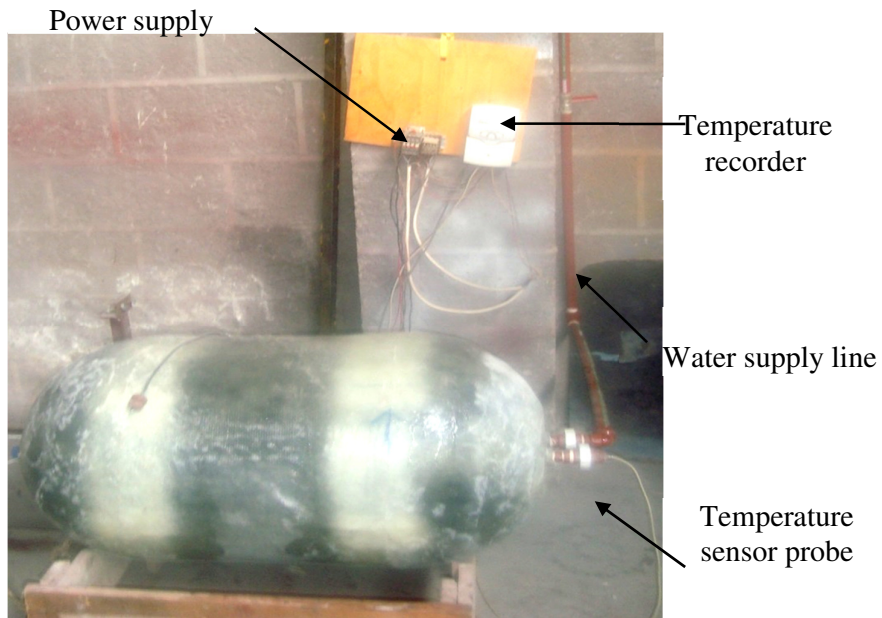


Figure 4.11: *GRP Hot Water Tank under test for water under both high*

4.4 The Hygrothermal Impact on GRP

According to Fick's Law most polymeric materials, and consequently polymer matrix composites will absorb liquid. In respect to composite materials the absorption of only small amounts of liquid may have a significant effect on

performance. Composite materials exposed to a liquid for an extended period may eventually become saturated. The absorbed moisture may plasticise and swell the matrix resulting in a reduction in mechanical properties, glass transition temperature (reduction in maximum operating temperature). After time the physico-chemical and thermo-mechanical properties of the composite will be further affected by hygrothermal ageing Rapra, (2012).

Other studies by Dutta and Hui (1996) found that low temperature thermal cycling between -60° and 50°C significantly reduced glass/polyester shear modulus, G , and Young's Modulus, E . Dutta, Kalafut, and Lord (1988) examined the effects of low temperature thermal cycling on the tensile strength of unidirectional fiberite material. They performed ten thermal cycles between -180° and 24°C . The results showed that strength in the longitudinal (0°) direction increased, while the strength in the transverse direction (90°) decreased. Kasap, Yannacopoulos, Mirchandani, and Hildebrandt (1992) studied the effects of elevated temperature thermal cycling on the bending strength of three types of E-glass fiber composites. The samples were cycled between 27° and 77°C . They concluded that the flexural strength and stiffness were decreased by thermal cycling and that this reduction was typically caused by fiber-matrix debonding.

The analysis of the results shows polyester and glassfibre composites can be used as hot water tanks with temperature limits. Because the solar hot water systems do not go beyond 100°C , within this range, the polyester GRP material can sustain these temperatures but due to strength loss as temperature increases, there should be controls incorporated in the system to limit temperature range up to 70°C . This can be achieved by the use of thermo-diverting valves and pressure release valves to maintain both pressure and temperature ranges.

CHAPTER FIVE

5.0 CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The moisture content in the GRP materials affected the glass transition temperature of the matrix while Intra laminar and inter laminar stresses are developed as a result of the thermo elastic and hydro elastic inhomogeneity and anisotropy of the materials.

Time dependent properties such as the tensile modulus and shear modulus varied with temperature and moisture concentration, failure and strength characteristics, especially interfacial and matrix dominated ones, depended on temperature and moisture.

The influence of UV radiation and salt concentration were found to be less and can take long time study to find out if there could be effect on the strength of the materials.

The woven mat and iso-polyester resins performed much better than chopped strands and ortho-polester resin respectively. However, since woven and iso resin are expensive, the use of chopped strands and ortho-polester was recommended in terms of affordability while woven mat and iso-polyester resins in terms of durability and higher operating temperatures and pressures.

The performance of the GRP under this investigation showed that GRP will perform very well and was recommended to be a better material for hot water tanks in a saline coastal environment. Therefore the material should be used to make these tanks for commercial use.

5.2 Future Work

The hot water tanks have several fittings that have to be incorporated for the tank to work. These fittings are metallic or PVC, therefore, further studies should be done to determine the sustainability of the inter bonding between the composite phase and the metallic or PVC phases. This is because the two materials have different hygrothermal characteristics hence study is require.

REFERENCE

- Altizer, S. D., Vijay, P. V., GangaRao, H. V., Douglass, N., & Paucr, R. (1996). Thermoset Polymer Performance under Harsh Environments to Evaluate Glass Composite Rebars for Infrastructure Applications. In C. Institute (Ed.), Annual, Composite Institute's 51st (pp. 3-C/I). Composite Institute.
- Ashby, M., Hugh, S., & David. (2007). Materials Engineering, Science, Processing and Design (First ed.). London, UK: Cebon University of Cambridge.
- Aiello M. A. and L. Ombre (2000), Environmental effects on the mechanical. Michael Ashby, H. S. (2007). Materials Engineering (First ed.). UK: University of Cambridge.
- Askland, Donald R. & P. Phule, Pradeep. (fourth edition). (2003). Composites, In: The Science and Engineering of Materials, (721-765), Thomson Learning, ISBN 0-534-95373-5, USA.
- A S Maxwell, W R Broughton, G Dean and G D Sims "Review of accelerated ageing methods and lifetime prediction techniques for polymeric materials" Engineering and Process Control Division (2005), HMSO and Queen's Printer, NPL Report DEPC MPR 016 ISSN 1744-0270, Scotland.
- ASM International. (1987). High Strength Medium Temperature Thermoset Matrix Composites. Engineered Materials Handbook, Composites, 1, 401-415. ASM International.
- Astrom, B. (1997). Manufacturing of Polymer Composites (pp. 1-175). Chapman & Hall.
- Arnold J.C., 'Environmental stress crack initiation in glassy polymers', Trends in Polymer Sci., 1996, 4, 403-408.

- Bank, L. (Fiber-Reinforced Plastic (FRP) for Concrete Structures: Properties and Applications. In L. C. Bank, Properties of FRP Reinforcements for Concrete (pp. 591993). -86). Amsterdam, , (A. Nanni, ed.), , Netherlands: Elsevier Science.
- Bank, L., Barkatt, A., Gentry, T., & Prian, L. (1997). Use of Physicochemical, Mechanical and Optical Tests in Accelerated Test Methodology for Determining the Long-Term Behavior of FRP Composites. Federal Highway Administration.
- Brown R.P., D. Kockott, P. Trubiroha, W. Ketola and J. Shorthouse, 'A Review of Accelerated Durability Tests', VAMAS Report No.18, Edited by R.P. Brown, Versailles Project on Advanced Materials and Standards, 1995.
- Burnay S.G., OPERA 89 Conference, Lyon, France, 2, (1999) 561.
- Buxton, A., & Baillie, C. (1994). A Study of the Influence of the Environment on the Measurement of Interfacial Properties of Carbon Fiber/Epoxy Resin Composites. Composites, 25 (7), pp. 604-608.
- Carfago and Gibson, 'A review of equipment ageing theory and technology', EPRI NP-1558, Electric Power Research Institute, Palo Alto, CA, USA, September 1980.
- Civil Engineering Research Foundation. (1993). High Performance Construction Materials and Systems: An Essential Program for America and Its Infrastructure. Civil Engineering Research Foundation.
- DIN 4753.1. Water heating installations for drinking water and service water; design, equipment and testing. German standard.
- DIN 4753.9. Water heating installations for drinking water and service water Protection against corrosion on the water side by thermoplastic coating materials. German standard.
- Dutta, PK, and Hui, D (1996). "Low-temperature and freeze-thaw durability of thick composites," Composites: Part B, Engineering, Vol. 27B, no. 3-4, pp. 371-379.
- Dutta, PK, Kalafut, J, and Lord, HW (1988). "Influence of Low Temperature

- Thermal Cycling on Tensile Strength of Fiber Composites,” In Advances in Micro-mechanics of Composite Materail Vessels and Components, PVP-Vol. 146/PD-Vol. 18, The American Society of Mechanical Engineers, New York, pp. 141-147.
- Ehrenstein G.W., A Schmiemann, A. Bledzki and R. Spaude, ‘Corrosion Phenomena in Glass-Fiber-Reinforced Thermosetting Resins’, Volume1, Handbook of Ceramics and Composites, N.P. Cheremisinoff, ed., Marcel Dekker, Inc., 1990.
- EN 12976-2. (n.d.). Thermal solar systems and components Factory made systems – Part 2: Test methods.
- Energy Regulatory Commission. (2010). Solar Water Heating Regulation. Nairobi.
- Energy(Solar Water Heating Regulations) 2010. (2010). Nairobi: Energy Regulatory Commission.
- Gentry, T., Bank, L., Thompson, B., & Russel, J. (2002). An Accelerated-Test-Based Specification for Fiber Reinforced Plastics for Structural Systems. In M. Q.-2. Construction (CDCC 02) (Ed.), Second International Conference on Durability of Fiber Reinforced Polymer (FRP) Composites for Construction (CDCC 02), (pp. 13-24). Montreal.
- Ghorbel and P. Spiteri, ‘Durability of Closed-End Pressurized GRP Pipes under Hygrothermal Conditions. Part I: Monotonic Tests’, Journal of Composite Materials", 30(14), 1996, pp 1562-1580.
- Gibson A G, Composites in Offshore Structures, Chapter 3 of Composite Materials in Maritime Structures, Volume 2, R A Sheno and J F Wellicome, Cambridge Ocean Technology Series, 1993Gillen K.T. and R.L. Clough, Polym. Degrad. Stab., 24, (1989) 137.
- Gillen K.T. and R.L. Clough, Polym.Mater. Sci. Eng. 52, (1985) 586.
- Greewood J.H., ‘Life prediction in polymers’, ERA Technology Report No. 97-0782R, 1997.
- Gueguen V., L. Audouin, B. Pinel and J. Verdu, ‘Polymer Degradation and Stability’, 1994, 46(1), 113

- Hoskin, B. C. (1986). *Composite Materials for Aircraft Structures*. New York: American Institute of Aeronautics and Astronautics, Inc.
- IEC 61244-2, determination of long-term radiation ageing in polymers-Part 2: Procedures for predicting ageing at low dose rates, 1996.
- Iowa State University. (2012). http://www.ndt-ed.org/index_flash.htm. (I. S. University, Editor, N. E. Center, Producer, & NDT Resource Center) Retrieved October 27, 2012, from www.ndt-ed.org.
- ISO 9459-2. (n.d.). *Solar heating – Domestic water heating, systems Part 2: Outdoor test methods for system performance characterization and yearly performance prediction of solar-only systems*. ISO.
- Jamond, R. M., Hoffard, T. A., & Malvar, J. L. (2012). *Naval Facilities Engineering Service Center*. University of Puerto Rico, Arsenio Caceres. Hueneme: Port Hueneme.
- Kasap, SO, Yannacopoulos, S, Mirchandani, V, and Hildebrandt, JR (1992). “Ultrasonic Evaluation of Thermal Fatigue of Composites,” *Journal of Kumar*.
- Kausch H.H. and C. Oudet, ‘Progress and challenge in polymer crazing and fatigue’, *Makrol. Chem, Macromol. Symp.*, 1988, 22, 207-224.
- Levi D.W., R.F. Wegman, M.C., Ross and E.A. Garnis, ‘Use of Hot Water Aging for Estimating Lifetimes of Adhesive Bonds to Aluminium’, *SAMPE Quarterly*, 7(3), 1976, pp 1-4.
- Mathews, F. & Rawlings, R. (1994). *Polymer Matrix Composite*, In: *Composite Materials: Engineering and sciences*, (168-200), The Alden Press, Oxford, ISBN 0-412-55960-9, UK.
- M, G., & D, E. (1982). *Encyclopedia of Chemical Technology* (3rd Edition ed., Vol. 18). New York: John Wiley & Sons.M10.1. *Mechanical Testing of Composites*.
- Min, M. C. (2008). *Descriptive approach- Corrosion Basic*. Retrieved from <http://users6.nofeehost.com/mestijaya/cmm/>.
- Nakamura, T. S. (2006). *Effects of Environmental Degradation on Flexural*

- Failure Strength of Fiber Reinforced Composites. In T. S. Nakamura, Experimental Mechanics (pp. 1-12).
- Niu, M. (1992). Composite Airframe Structures: Practical Design Information and Data (First ed.). Hong Kong.
- Norske, V. (1967). Report on Plastics in Ship building. Third International Ship Structures Congress, II.
- Parvatareddy, H., Pasricha, A., Dillard, D. A., Holmes, B., & Dillard, J. (1997). High Temperature and Environmental Effects on Polymeric Composites. 2nd, 149-173.
- Pritchard G., ed., 'Reinforced Plastics Durability', Woodhead Publishing Ltd, 1995. Engineering Materials and Technology, Vol. 114, no. 2, pp. 132-136.
- Properties of glass-FRP and aramid-FRP rebars, Mechanics of Composite Materials, Vol. 36.
- Rapra. (2012). <http://www.rapra.net/composites/material-selection/some-design-considerations.asp>. Retrieved from <http://www.net>.
- Robert, J. S., & John, H. S. (1971). Feasibility Study Of Glass Reinforced Plastic Cargo Ship. Naval Ship Engineering Center, Department of the Navy. Washington D.C.: Gibbs & Cox.
- Schwartz, M. (1996). The influence of Environmental Effects. Composite Materials, Properties, Nondestructive, Testing and Repair , pp.117-119.
- Singh B. G., , R. P., & Nakamura, T. (2002). Degradation of Carbon Fiber-reinforced Epoxy Composites by Ultraviolet Radiation and Condensation. Composite Materials (36(24)), 2713-33.
- Smith C.S., 'Design of Marine Structures in Composite Materials', Elsevier Applied Science, 1990.
- Strong, A. B. (2008). Composites Manufacturing Materials, Methods, and Applications. (S. o. Engineers, Ed.) Michigan: Dearborn.
- Wellinghoff S and E Baer, 'The mechanism of crazing in polystyrene', J. Macromol. Sci. B, 1975, 11(3), 367-387.
- Wright D.C., 'Failure of Plastics and Rubber Products – Causes, Effects and

- Case Studies involving Degradation', Rapra Technology Report, 2001, ISBN: 1-85857-261-8.
- W.R. Broughton, M.J. Lodeiro and S. Maudgal, 'Accelerated Test Methods for Assessing Environmental Degradation of Composite Laminates', NPL Report MATC(A)251, 2000.
- Wright D.C., Environmental Stress Cracking of Plastics, Rapra Technology Ltd., 1996.
- Wright D.C. and K.V. Gotham, 'Solvent crazing criteria', Polymer Eng. Sci., 1983, 23 (3) 135-139. D.C. Wright, 'An inelastic deformation criterion for delayed failure,' Brit. Polymer J., 1978, 10, 60-64.
- www.ndt-ed.org. (2012). <http://www.ndt-ed.org>. Retrieved from <http://www.ndted.org/EducationResources/CommunityCollege/Materials/Introduction/introduction.htm>.
- Wypych G., "Handbook of Materials Weathering", ChemTec publishing, 2003 White J.R. and A Turnbull, "Review: Weathering of polymers: mechanisms of degradation and stabilization, testing strategies and modelling", J. Mat. Sci., 29, 584-613, 1994.

APPENDIX 1.0

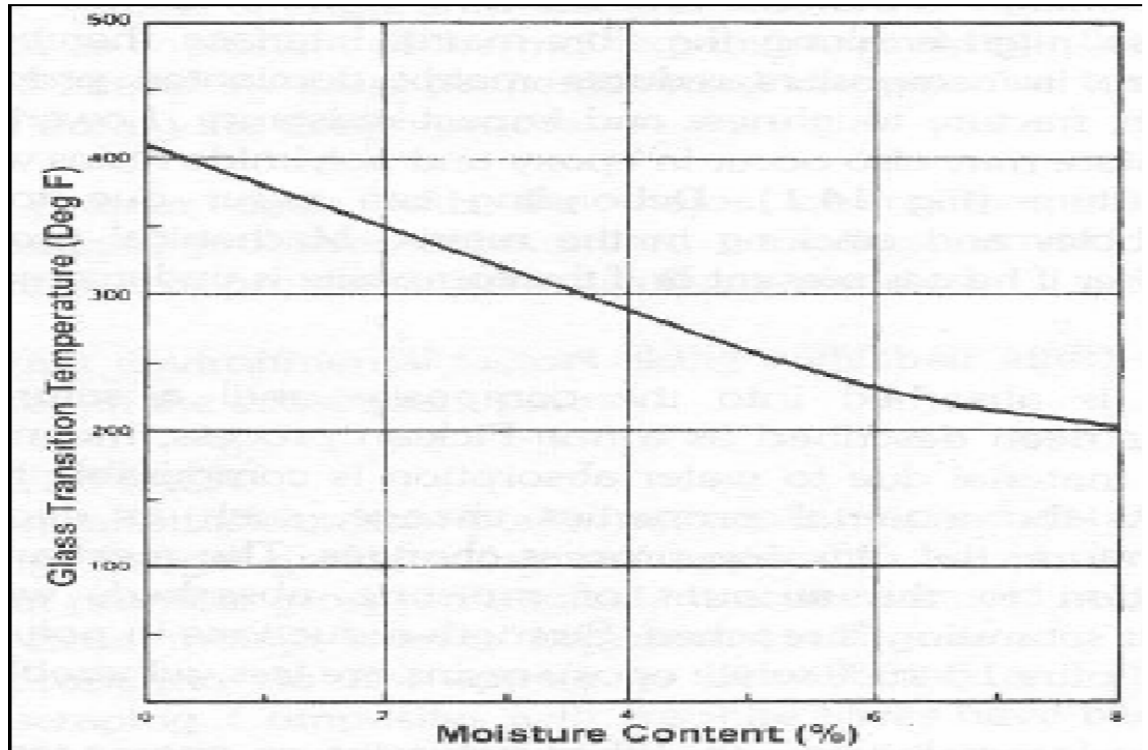


Figure M10.3.1: The relation between Moisture content and Glass transition temperature