FATIGUE CHARACTERIZATION OF GLASS FIBER REINFORCED VINYL ESTER AND POLYESTER COMPOSITES CONTAINING CORE SHELL RUBBER PARTICLES

by

Swayam Shree, B.Tech

A thesis submitted to the Graduate Council of Texas State University in partial fulfillment of the requirements for the degree of Master of Science with a Major in Engineering
August 2019

Committee Members:

Jitendra S. Tate, Chair
Bahram Asiabanpour
Abhay Deshpande
COPYRIGHT

by

Swayam Shree

2019
FAIR USE AND AUTHOR’S PERMISSION STATEMENT

Fair Use

This work is protected by the Copyright Laws of the United States (Public Law 94-553, section 107). Consistent with fair use as defined in the Copyright Laws, brief quotations from this material are allowed with proper acknowledgement. Use of this material for financial gain without the author’s express written permission is not allowed.

Duplication Permission

As the copyright holder of this work I, Swayam Shree, authorize duplication of this work, in whole or in part, for educational or scholarly purposes only.
ACKNOWLEDGEMENTS

I would like to acknowledge my thesis advisor Dr. Jitendra Tate for his guidance throughout my thesis research. His knowledge and problem-solving skill helped me a lot. I would also like to thank Mr. Jim Kaufmann of Saertex LLC for providing us the glass fiber reinforcement for this research, Mr. Jeff Peterson of Interplastic Corporation for providing us the unsaturated polyester needed for this research, Mr. Jim Payton of Ashland Specialty Chemical Company for providing us the vinyl ester needed for the research and Dr. Abhay Deshpande from Evonik Corporation for providing us the core shell rubber additives.

I would also like to acknowledge the help of Dr. Ray Cook, Mr. Jason Wagner and Mr. Ruben Villarreal for their help with fixing our test system when it broke down, water jet machining and metal machining.

Lastly, I would like to thank all the student researchers working in the Advanced Composites Laboratory for their help and input at different stages of my research.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>x</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>I.I Background Study</td>
<td>1</td>
</tr>
<tr>
<td>I.II Fatigue failure in composites</td>
<td>2</td>
</tr>
<tr>
<td>I.III Fatigue Damage Mechanism</td>
<td>3</td>
</tr>
<tr>
<td>I.IV Core Shell Rubber Particles (CSRP)</td>
<td>5</td>
</tr>
<tr>
<td>I.V Research objectives</td>
<td>6</td>
</tr>
<tr>
<td>I.V Hypothesis</td>
<td>7</td>
</tr>
<tr>
<td>II. EXPERIMENTATION</td>
<td>9</td>
</tr>
<tr>
<td>II.I Material System</td>
<td>9</td>
</tr>
<tr>
<td>II.II Manufacturing</td>
<td>9</td>
</tr>
<tr>
<td>II.III Testing</td>
<td>12</td>
</tr>
<tr>
<td>III. RESULTS AND DISCUSSION</td>
<td>20</td>
</tr>
<tr>
<td>III.I Dispersion</td>
<td>20</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>III.II Static Mechanical Results</td>
<td>21</td>
</tr>
<tr>
<td>III.III Toughening mechanism of Core Shell Rubber Particles</td>
<td>33</td>
</tr>
<tr>
<td>III.IV Fatigue Test Results</td>
<td>34</td>
</tr>
<tr>
<td>III.V Differential Scanning Calorimetry results</td>
<td>41</td>
</tr>
<tr>
<td>III.VI Thermogravimetric Analysis results</td>
<td>43</td>
</tr>
<tr>
<td>IV. CONCLUSION</td>
<td>45</td>
</tr>
<tr>
<td>V. FUTURE SCOPE OF WORK</td>
<td>47</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>48</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. List of all tests conducted on manufactured composites</td>
<td>19</td>
</tr>
<tr>
<td>2. Consolidated results of static mechanical properties of vinyl ester</td>
<td>32</td>
</tr>
<tr>
<td>composites</td>
<td></td>
</tr>
<tr>
<td>3. Consolidated results of static mechanical properties of polyester</td>
<td>33</td>
</tr>
<tr>
<td>composites</td>
<td></td>
</tr>
<tr>
<td>4. Fatigue life control and 5wt% Core Shell Rubber Particle modified</td>
<td>35</td>
</tr>
<tr>
<td>vinyl ester composites</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Fatigue life control and 5wt% Core Shell Rubber Particle modified</td>
<td>35</td>
</tr>
<tr>
<td>polyester composites</td>
<td></td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. S-N Curves for different fiber reinforced components</td>
<td>3</td>
</tr>
<tr>
<td>2. Fatigue damage mechanisms in fiber reinforced composites</td>
<td>4</td>
</tr>
<tr>
<td>3. Schematic Layout of VARTM</td>
<td>10</td>
</tr>
<tr>
<td>4. VARTM setup for control composites</td>
<td>11</td>
</tr>
<tr>
<td>5. VARTM setup for CSRP modified composites</td>
<td>11</td>
</tr>
<tr>
<td>6. Flexural strength in different manufacturing processes</td>
<td>12</td>
</tr>
<tr>
<td>7. Energy Consumption of different manufacturing processes</td>
<td>12</td>
</tr>
<tr>
<td>8. Exploded view of anti buckling fixture</td>
<td>16</td>
</tr>
<tr>
<td>9. Anti buckling fixture claspling a sample in test machine</td>
<td>17</td>
</tr>
<tr>
<td>10. SEM image of vinyl ester composite containing CSR</td>
<td>20</td>
</tr>
<tr>
<td>11. SEM image of polyester composite containing CSRP</td>
<td>21</td>
</tr>
<tr>
<td>12. Tensile and flexural strength of vinyl ester composites</td>
<td>22</td>
</tr>
<tr>
<td>13. Tensile and flexural modulus of vinyl ester composites</td>
<td>22</td>
</tr>
<tr>
<td>14. Tensile and flexural strength of polyester composites</td>
<td>23</td>
</tr>
<tr>
<td>15. Tensile and flexural modulus of polyester composites</td>
<td>24</td>
</tr>
<tr>
<td>16. Equilibrium toughness of vinyl ester composites</td>
<td>25</td>
</tr>
<tr>
<td>17. Equilibrium toughness of polyester composites</td>
<td>25</td>
</tr>
<tr>
<td>18. Percentage elongation of vinyl ester composites</td>
<td>26</td>
</tr>
<tr>
<td>19. Percentage elongation of polyester composites</td>
<td>26</td>
</tr>
</tbody>
</table>
20. Stress-Strain curve for vinyl ester composites............................................... 27
21. Percentage elongation of polyester composites............................................. 27
22. Shear strength of vinyl ester composites ...................................................... 29
23. Shear strength of polyester composites.................................................... 29
24. Short beam strength of vinyl ester composites ............................................ 30
25. Short beam strength of polyester composites ............................................. 30
26. Compressive strength of vinyl ester composites........................................ 31
27. Compressive strength of polyester composites........................................... 32
28. S-N Curves for vinyl ester composites ....................................................... 36
29. S-N Curves for polyester composites ......................................................... 36
30. Stiffness degradation curve for vinyl ester composites .............................. 38
31. Stiffness degradation curve for polyester composites ............................... 39
32. Optical microscope images of fatigue tested vinyl ester composites ............ 41
33. DSC Curves for vinyl ester composites ....................................................... 42
34. DSC Curves for polyester composites ......................................................... 43
35. TGA Curves for vinyl ester composites ....................................................... 44
36. TGA Curves for polyester composites ......................................................... 44
Glass fiber reinforced polymer matrix composites have experienced tremendous growth in wind energy, construction, marine and automotive industries. This is because of the superior mechanical strength, chemical and fire-resistant properties of fiber reinforced composites. However, polymer resins are very brittle in nature because of the large amount of cross linking that occurs during composite curing. This results in composites with low toughness. This limits the use of glass fiber reinforced composites in applications where components are subjected to cyclic loading conditions such as wind turbine rotor blades and propeller shaft of automobiles.

This research focusses on characterization of core shell rubber particles (CSRP) modified glass fiber reinforced vinyl ester and polyester composites. Composites containing 2 wt%, 5 wt% and 10 wt% core shell rubber particles were manufactured using Vacuum Assisted Resin Transfer Molding (VARTM). Composite samples were tested for tensile, compressive, shear, flexural and short beam properties according to appropriate ASTM standards.

5 wt% core shell rubber particle modified composites performed the best with higher toughness. Control composite containing no core shell rubber particles were compared with 5 wt% core shell modified composites in tension compression fatigue testing at 5Hz to compare their load bearing capacity under cyclic loading condition. The 5 wt% core shell rubber particle modified vinyl ester composite retained 92.5% of its modulus compared to the control composite which retained only 75% of its modulus at
the end of the test. The 5 wt% core shell rubber particle modified polyester composite retained 80% of its modulus compared to the control composite which retained only 45% of its modulus at the end of the test. Optical microscopy revealed that composite damage occurred during fatigue due to matrix cracking followed by localized delamination and final failure. Differential scanning calorimetry and thermogravimetric analysis revealed that addition of core shell rubber particles had no effect on the glass transition temperature and mass loss rate of the manufactured composites respectively.
I. INTRODUCTION

I.I Background Study

Fiber reinforced composites have experienced increased adoption in aerospace, automotive, marine, solar power and construction industries in recent years. This can be attributed to the superior strength, chemical resistance and lightweight nature of fiber reinforced composites when compared to traditional engineering materials like metal alloys and various solid solutions. Predominantly use of carbon fiber-epoxy composites in aerospace and automotive sectors has led to the design and manufacturing of lighter and better performing aircrafts and locomotion devices that are outperforming their metal alloy counterparts while being significantly lighter at the same time. Some notable examples include the Boeing 787 and Airbus A350-XWB that are made up of 50% and 39% composites respectively [1] and high-performance cars like Ferrari la Ferrari that has four [2] different type of carbon fiber composites in its chassis.

Carbon fiber composites, though have superior mechanical properties, are not as readily adopted by wind power and construction industries. This is because of the higher cost of carbon fiber as a reinforcement. In such cases glass fiber is a viable, cost effect alternative to carbon fibers as a reinforcement particularly in marine, construction and wind generation applications. Under similar ambient conditions glass fiber composites have higher compressive strength that carbon fiber composites and are durable in varying environmental conditions [3].

In recent years there has been a global push for rapid adoption of renewable forms of energy. Wind energy in particular has seen rapid adoption. Most of the rotor blades of these wind turbines are made out of glass fiber composites. Typically, a wind turbine blade has a service lifetime of 20 years. However, as the number of wind turbines
increases in the future, this reliable lifetime of rotor blades needs to be increased to avoid the frequency of repairs and replacements.

I.II Fatigue failure in composites

Unlike most composite structures, wind turbine rotor blades suffer cyclic flexural forces during operation. This is because of the interference in the wind flow patterns as the rotor blades cross the turbine tower during each revolution resulting in unpredictable loads. As a result, most wind turbine blades fail because of this cyclic loading rather than projectile impacts. As the turbine blades bend from side to side in their operation each side of a blade suffers tensile and compressive loading alternatively. Typically wind turbine blades rotate two to three times every second which means these blades experience cyclic loading $10^6$ times in their 20-year life cycle.

Fiber reinforced composites are different that metal alloys and solid solutions because of their anisotropic nature. This is because unlike traditional engineering materials that are homogenous, the matrix and the reinforcement maintain their distinct and different physical structure in a cured composite. This leads to different mechanical properties of composites based on the fiber orientation inside the composite.

Materials fail due to repeated cyclic loading at stresses much lower than their ultimate stresses. This kind of failure is known as fatigue failure and the number of cycles of cyclic loading that results in failure in known as fatigue life. Figure 1 shows the typical expected fatigue life of components made out of fiber reinforced composites. In composites, fatigue failure occurs suddenly and without any apparent damage noticeable to the naked eye. As composites have complex mechanical microstructures, the synergistic effect of a variety of damage mechanisms is responsible for their fatigue failure. This is why fatigue failure is a result of cumulative and progressive damage over
the total fatigue life of a composite and is defined as the cycle dependent degradation of internal integrity [4]. Research has been done in the recent decades to study and characterize these different damage mechanisms and the order in which these damages occur during fatigue loading of composites.

![S-N Curves for different fiber reinforced components](image)

**Figure 1: S-N Curves for different fiber reinforced components [5]**

I.III Fatigue Damage Mechanism

One popular theory was proposed by Reifsnider [4] that proposes a fiber reinforced composite goes through four stages of damage before failure occurs. According to this theory in the initial stages of fatigue loading cracks start to form in the matrix of the composite. As the cyclic loading continues the density of these cracks increases and they start to get coupled. According to this theory each material has a specific crack density at a particular loading level. Only when this threshold crack density is reached, the next stage of damage can occur and when a material system reaches this threshold it is said to have achieved characteristic damage state. The next stage happens when enough matric cracks get coupled and reach a fiber matrix interface. Once the cracks encounter the fabric, interfacial debonding happens which separates the fiber from the matrix. This is followed by fiber cracking. As the amount of interfacial debonding
and fiber cracking increases this leads to the localized delamination of individual fabric layers. In the final stage localized delamination grows and fabric layers are completely separated leading to fracture and at that point the material fails. Figure 2 provides a visual representation of all these damage mechanisms as the composite progresses through its fatigue life. Previous works have confirmed that matrix cracking is the first dominant damage mechanism in composite fatigue failure and these microcracks occur at loading levels as low as 10% to 20% of the ultimate strength of the material [6][7].

Figure 2: Fatigue damage mechanisms in fiber reinforced composites [4]

As wind turbine blades experience both tensile and compressive stresses during cyclic loading this kind of fatigue is called tension-compression fatigue. Research has shown that tension-compression fatigue has the most adverse effect on the integrity of composites [8-10]. Research has shown that the tensile stresses in tension-compression fatigue lead to formation of matrix cracks while compressive stresses lead to increased interfacial debonding growth [11]. This is because of the difference in the elastic properties of the fiber reinforcement and the matrix. Research has shown that fabric failure in tension-compression fatigue occurs due to fabric buckling and fiber crushing.
However, no experimental analysis was done to study the progression of this damage. As it is evident, many theories have been proposed to explain the damage mechanisms involved in composite fatigue failure however there is no experimental validation to support one unified theory that characterizes the damage in composites at micro and macro scale.

Most wind turbine blades are manufactured using glass fiber reinforcements with vinyl ester and polyester resins. Although these kind of material systems have good mechanical strength, but they are highly brittle. This is because vinyl ester and polyester resins systems have significant amount of cross linking when cured in the presence of organic peroxides. This leads to components that have lower fatigue life as the component failure will start even with the least amount of deformation.

I.IV Core Shell Rubber Particles (CSRP)

One method of improving the fatigue life of fiber reinforced composites is addition of rubber content into the matrix of these composites. Specifically, research has shown that addition of rubber content leads to an improvement in the fracture toughness and equilibrium toughness of polymer matrix composites [13-16].

However, addition of rubber content leads to a decrease in mechanical strength [17-20]. Therefore, an equilibrium must be reached to achieve a good proportion of rubber and neat resin in the matrix system to manufacture polymer composites that have higher toughness but at the same time do not lose most of their mechanical properties such as tensile, compressive and flexural strength.

The problem with traditional rubber content like Carboxyl Terminated Acrylonitrile Butadiene (CTBN) is that it goes through phase separation and rubber particle formation occurs during composite curing. This is why it is known as a soft
toughener and higher amount of CTBN is needed to achieve required toughness [21].

The disadvantages of CTBN are not found in preformed rubber. One such example is Core Shell Rubber Particles (CSRP). Core Shell Rubber Particles are spherical micron sized particles in which one copolymer surrounds another copolymer. The inner copolymer is mainly-butadiene/styrene, polybutadiene, siloxane, acrylic, etc. Outer shell is made up of polymers that are compatible with resin system these are added to and the typical size of is Core Shell Rubber Particles is little larger than 100 nanometres. Therefore, Core Shell Rubber Particles are known as micron sized additives. As Core Shell Rubber Particles are preformed, lower amount of CSRP can be added to a resin system to achieve similar toughness improvement when compared to CTBN.

Improving the toughness of composites theoretically leads to improved fatigue life because higher toughness means the material can deform more and thereby absorb more energy before fracture. Thus, a toughened composite can endure higher number of cycles before achieving characteristic damage state in fatigue loading when compared to a composite with no toughening agent. This has been proven by different research groups. One study found that 9 wt% addition of rubber in epoxy matrix leads to a threefold increase in fatigue life [22] while another study found that rubber modified carbon fiber-epoxy composites experienced a decrease in delamination growth during fatigue testing [23]

I.V Research objectives

Most of the matrix toughening research has been focussed on epoxy-based composites. As most wind turbine rotor blades are glass fiber reinforced polyester and vinyl ester composites the broader goal of this research is to study and characterise the effect of Core Shell Rubber Particles on the static mechanical properties and fatigue life
of vinyl ester and polyester composites. The specific objectives of this research are listed below:

- Manufacturing glass fiber reinforced vinyl ester and glass fiber reinforced polyester composites containing varying loading levels of Core Shell Rubber Particles.
- Qualitative analysis of dispersion of Core Shell Rubber Particles in manufactured composites using scanning electron microscopy.
- Static mechanical evaluation of composites to determine what loading level of Core Shell Rubber Particles is optimal.
- Differential scanning calorimetry and Thermogravimetric analysis of control composites and best performing Core Shell Rubber Particle modified composites.
- Fatigue characterisation of control and best performing Core Shell Rubber Particle modified composites and damage analysis.

I.V Hypotheses

Null Hypothesis:

- $H_{01}$: Addition of Core Shell Rubber Particles in glass fiber reinforced vinyl ester composites will result in higher toughness.
- $H_{02}$: Addition of Core Shell Rubber Particles in glass fiber reinforced polyester composites will result in higher toughness.
- $H_{03}$: Addition of Core Shell Rubber Particles in glass fiber reinforced vinyl ester composites will result in higher fatigue life.
- $H_{04}$: Addition of Core Shell Rubber Particles in glass fiber reinforced
polyester composites will result in higher fatigue life.

Alternate Hypothesis:

- $H_{a1}$: Addition of Core Shell Rubber Particles in glass fiber reinforced vinyl ester composites will not result in higher toughness.
- $H_{a2}$: Addition of Core Shell Rubber Particles in glass fiber reinforced polyester composites will not result in higher toughness.
- $H_{a3}$: Addition of Core Shell Rubber Particles in glass fiber reinforced vinyl ester composites will not result in higher fatigue life.
- $H_{a4}$: Addition of Core Shell Rubber Particles in glass fiber reinforced polyester composites will not result in higher fatigue life.
II. EXPERIMENTATION

II.I Material System

The vinyl ester used in this research was Derakane 510A-40 from Ashland. It was cured using 1.25 phr Methyl Ethyl Ketone Peroxide in conjunction with 0.3 phr 6% Cobalt Naphthenate to provide a geltime of 30 minutes. The unsaturated polyester used in this research was SILMAR SIL47DA-2949. 1 phr Benzoyl Peroxide was mixed with the polyester resin for thermal curing at 130° C in 10 minutes. The reinforcement used for manufacturing composites was 0°/90° stitch bonded non-crimp glass fiber from SAERTEX. The sizing on the fabrics was compatible with the vinyl ester and polyester resins chosen for experimentation. A vinyl ester-based Core Shell Rubber, Albidur VE 3940 from Evonik was used as the additive in this research.

II.II Manufacturing

To achieve desired effect of the CSRP on the mechanical properties of the composites the additive had to be properly dispersed in the resin media. To achieve proper dispersion the required amount of Albidur VE 3940 was added to the base resin systems and then mixed using a Thinky ARV-130 planetary mixer for 5 minutes at 2000 RPM under 96% percent vacuum. After this MEKP and Cobalt Naphthenate were added to the Vinyl ester resin system and mixed in the Thinky ARV-130 using the same parameters. The Benzoyl Peroxide used in this experiment was in solid form. It was mixed in the polyester resin system using a magnetic stirrer for 15 minutes.

Vacuum Assisted Resin Transfer Molding (VARTM) was used to impregnate 4 layers of 15”x15” sheets of the stitch bonded glass fiber reinforcement to make composites. After complete fabric impregnation the vinyl ester composites were left under vacuum for 24 hours for green cure and then post cured in a programmable oven at
$80^0\text{C}$ for six hours. In case of polyester composites after full fabric impregnation the system was heated for 10 minutes at $130^0\text{C}$ for 10 minutes for green cure and then the composites were post cured in a programmable oven at $110^0\text{C}$ for three hours. This process was used to manufacture eight composted laminate panels. Four Vinyl ester panels with 0 wt%, 2wt%, 5 wt% and 10 wt% CSRP respectively and 4 polyester panels with 0 wt%, 2wt%, 5 wt% and 10 wt% CSRP respectively. Figure 3 shows a schematic diagram of the VARTM setup.

![Figure 3: Schematic Layout of VARTM [24]](image)

Figure 4 and 5 show the setup used during the manufacturing phase to produce control (0 wt% CSRP) and CSRP modified panels respectively. In case of modified panels, the resin line was placed in the middle to achieve uniform distribution on the CSRP containing resin system across the whole composites.
VARTM is a low-cost composite laminate manufacturing process that is scalable and used for producing high quality parts like wind turbine blades. Figure 6 shows that VARTM produces composites with higher flexural strength when compared to other manufacturing processes. This is because in VARTM fabric impregnation is done under vacuum that prevents void formation in the final products. Figure 7 shows that VARTM uses lower energy, second only to pultrusion in the manufacturing process as the only
parts requiring power in the whole manufacturing process are the vacuum pumps.

![Figure 6: Flexural strength in different manufacturing processes [25]](image1)

![Figure 7: Energy consumption of different manufacturing processes [26]](image2)

Abrasive water jet machining was used to cut samples out of the cured composites for various mechanical testing. Abrasive water jet machining was used for sample preparation as this prevents edge delamination in fiber reinforced composites during cutting.

**II.III Testing**

The strength of fiber reinforced composites is directly related to the volume occupied by fibers inside the cured composite. Therefore, the fiber volume fractions of the cured composites were calculated using the density method according to the formula
below by taking the average fiber volume density of samples cut from all the composite panels:

\[ V_f = \frac{\rho_c \rho_m}{\rho_f \rho_m} \]

Where,

\( V_f \) = fiber volume fraction of composite  
\( \rho_m \) = density of matrix  
\( \rho_c \) = density of composite  
\( \rho_f \) = density of fibers

The dispersion of CSR particles in the manufactured composites was qualitatively evaluated using a FEI Helios NanoLab 400 DualBeam digital Field Emission Scanning Electron Microscope (SEM). Glass fiber reinforced composites are nonconductive in nature. Therefore, composite samples were coated with 10 nanometers of carbon using a Quorum Technologies EMS150T ES imaging sputter coater. The specimens were then adhered to the stub of the SEM using conductive copper tape to avoid charge buildup on the specimen surfaces.

Samples from all different manufactured composites were tested for tensile, flexural, shear, compressive and short beam strength. Tensile tests were conducted according to ASTM D3039 – “Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials” [27]. The samples were then tabbed to ensure failure occurred in the gage area. These tabs were made from a fiberglass composite material and bonded to the end of the samples using Scotch-Weld Epoxy Adhesive DP 460 Off-White. An axial extensometer was used to measure axial strain. The ultimate tensile strength (UTS), modulus and percentage elongation for each sample was calculated from
the collected data. The area under the stress-strain curve of the tensile tests was calculated to determine the equilibrium toughness of the composites. Flexural tests were conducted according to ASTM D7264 – “Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials” [28]. The flexural strength and modulus of the samples was calculated from the collected data. The short beam test was done according to ASTM D2344 – “Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates” [29]. Inter-laminar shear strength was evaluated for the samples using the collected data. The shear test was conducted according to ASTM D7078 – “Standard Test Method for Shear Properties of Composite Materials by V-Notched Rail Shear Method” [30]. The in-plane shear strength was calculated from the collected data. The compression test was done according to ASTM D6641 – “Standard Test Method for Compressive Properties of Polymer Matrix Composite Materials Using a Combined Loading Compression (CLC) Test Fixture” [31]. The compressive strength was calculated from the collected data. All static mechanical tests were done on an MTS 810 Material Testing System. The samples varied in thickness from 2.3 mm to 2.5 mm.

Based on the results of the static mechanical tests the best performing CSRP modified vinyl ester and polyester composites were chosen to be compared against the control vinyl ester and polyester composites for thermal and tension-compression fatigue testing.

Simultaneous Differential Scanning Calorimetry and Thermogravimetric analysis was done on the composite specimens using a TA Instruments SDT 650. About 10 milligrams of sample specimen were heated up from room temperature up to 600° C at a ramp rate of 10° C/minute. The percentage mass loss and normalized heat flow were
recorded in the temperature range to determine the glass transition temperature and peak temperature of the manufactured composites.

The best performing CSRP modified composites were tested against the control vinyl ester and polyester composites in tension-compression fatigue testing. As there is no standard for tension compression fatigue testing for fiber reinforced composites a custom testing methodology was developed. It was decided that samples will be cut from composites panels according to ASTM D638 [32] type III geometry. Taking the dimension from this geometry Euler’s equation shown below was used to determine critical load for buckling was determined. Solving the equation provides the values, 2395.8 Newtons and 2035.9 Newtons for vinyl ester and polyester composites respectively. As these values are too low this meant that the samples will buckle during the compressive cycle of the fatigue testing. 

\[ P_{cr} = \frac{\pi^2EI}{(KL)^2} \]

Where,

\( P_{cr} = \) Critical load for buckling

\( E = \) Modulus of composite

\( I = \) Area moment of inertia of sample cross section

\( K = \) Effective length factor

\( L = \) Unsupported length

Therefore, an anti-buckling fixture had to be used to prevent bucking of the samples during testing so that samples failed only because of repeated tension and compression and not because of bending. As glass fiber reinforced composites are not good conductors of heat the fixture also had to be such that it did not cause a lot of
friction during fatigue testing otherwise the samples will fail due to heat buildup because of hysteresis. A modified version of the fixture designed by researchers at Penn State University [33] was used to solve these problems. Figure 8 below shows a diagram of the fixture in exploded view and figure 9 shows when it is attached to a test sample. The fixture prevents the test sample from buckling by sandwiching it between two metal plates and the presence of ball bearings in the groves of the fixture allow the sample to roll over the metal plates thus preventing hysteresis heat buildup by eliminating friction between the sample surface and the fixture.

![Figure 8: Exploded view of anti buckling fixture](image)

Figure 8: Exploded view of anti buckling fixture
After fabrication of test fixture, fatigue testing was done on an MTS 810 Material Testing System. In fatigue testing fluctuating load was applied to the test sample between two constant amplitude load levels. The load was varied between the two load levels according to a sine wave pattern. Testing was conducted at 5 Hz frequency which means the load was varied between the two fixed levels 5 times per second. The endurance limit for this research was set to 1 million cycles. This means the samples were tested under cyclic loading until failure or 1 million cycles, whichever happened first. As the samples were tested under tension-compression fatigue a R value of -1 was used. The R value is the ratio between the maximum and minimum load applied during once cycle of fatigue testing.

\[ R = \frac{P_{\text{max}}}{P_{\text{min}}} = \frac{F_{\text{max}}}{F_{\text{min}}} \]

Where,

\[ P_{\text{max}} = \text{Maximum stress applied} \]
\( P_{\text{min}} \) = Minimum stress applied

\( F_{\text{max}} \) = Maximum load applied

\( F_{\text{min}} \) = Maximum load applied

In this research the same amount of load was applied in both the tensile and compressive half cycle of during fatigue testing. Therefore \( P_{\text{max}} = -P_{\text{min}} \). Therefore, this is known as fully reversed fatigue testing.

The stresses and loads applied on the test specimen were based on the compressive strength of the unmodified vinyl ester and polyester composites containing no core shell rubber particles. The percentage of compressive strength applied in this research are 90\%, 80\%, 70\%, 60\%, 50\% and 40\%. The table below lists all the tests carried out in this research and the number of samples tested in each test.
Table 1: List of all tests conducted on manufactured composites

<table>
<thead>
<tr>
<th>Test</th>
<th>ASTM Standard</th>
<th>Properties</th>
<th>Number of samples tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td>D3039</td>
<td>Strength, Modulus, Percentage elongation, Equilibrium Toughness</td>
<td>5</td>
</tr>
<tr>
<td>Flexure</td>
<td>D7264</td>
<td>Strength, Modulus</td>
<td>5</td>
</tr>
<tr>
<td>Compression</td>
<td>D6641</td>
<td>Strength</td>
<td>5</td>
</tr>
<tr>
<td>V Notch Shear</td>
<td>D7078</td>
<td>Strength</td>
<td>5</td>
</tr>
<tr>
<td>Short Beam</td>
<td>D2344</td>
<td>Inter laminar Shear Strength</td>
<td>5</td>
</tr>
<tr>
<td>Differential Scanning Calorimetry</td>
<td>D3418</td>
<td>Glass Transition Temperature, Peak Temperature</td>
<td>1</td>
</tr>
<tr>
<td>Thermogravimetric Analysis</td>
<td>E2550</td>
<td>Percentage Mass Loss</td>
<td>1</td>
</tr>
<tr>
<td>Tension-Compression Fatigue</td>
<td>Non-Standardized Test</td>
<td>Fatigue Life</td>
<td>2</td>
</tr>
</tbody>
</table>
III. RESULTS AND DISCUSSION

III.I Dispersion

10 mmx10 mm samples of 5 wt% core shell rubber particle modified vinyl ester and polyester composites were scanned under SEM. The images of vinyl ester composite and polyester composite containing Core Shell Rubber Particles are displayed in figures 10 and 11 respectively. The results show uniform distribution of the rubber additives in the manufactured composites and no agglomeration was observed. Certain core shell rubber particles selected at random have been encircled in red. This result validates the method of using planetary centrifugal mixer for properly dispersing micron sized additives in the vinyl ester and polyester media.

Figure 10: SEM image of vinyl ester composite containing CSRP
III.II Static Mechanical Results

III.II.I Tensile Test Results

As expected, addition of Core Shell Rubber Particles led to a decrease in the tensile strength and tensile modulus of both vinyl ester and polyester composites. This is because rubber is a toughening agent, and this plasticizes the composite leading to lower strength. However, the strength was observed to be dependent upon the Core Shell Rubber Particle concentration in the composite.

In vinyl ester composites the control had the highest tensile strength and modulus. The 2 wt% Core Shell Rubber Particle loaded composite performed the worst with a drastic decrease of 30% and 35% in tensile strength and modulus respectively. The 5 wt% Core Shell Rubber Particle loaded composite had the least degradation with only 7% and 7.8% loss in strength and modulus. The 10 wt% Core Shell Rubber Particle composite lost 10.9% and 10.4% of its strength and modulus respectively when compared to the control composite. The tensile strength and modulus of vinyl ester composites are
shown in figure 12 and 13 respectively.

**Figure 12: Tensile and flexural strength of vinyl ester composites**

**Figure 13: Tensile and flexural modulus of vinyl ester composites**

In polyester composites a similar trend was observed too. The control had the highest strength and modulus of all the manufactured polyester composites. The 2 wt% Core Shell Rubber Particle loaded composite performed the worst with 32% and 36.6%
loss in tensile strength and modulus respectively. The 5 wt% Core Shell Rubber Particle loaded composite suffered least degradation with 2.7% and 3.5% loss in strength and modulus respectively and the 10 wt Core Shell Rubber Particle composite lost 16% and 15.67% of its strength and modulus respectively. The tensile strength and modulus of polyester composites are shown in figure 14 and 15 respectively.

Figure 14: Tensile and flexural strength of polyester composites
As hypothesized addition of Core Shell Rubber Particles led to an increase in the equilibrium toughness of both polyester and vinyl ester composites. Equilibrium toughness was determined by calculating the area under the curve of stress strain curves from results of tensile tests. The stress-strain curves of vinyl ester and polyester composites are shown in figure 20 and 21 respectively. Both vinyl ester and polyester composites containing 5 wt% Core Shell Rubber Particles had an 2.4% and 2.6% improvement in toughness when compared to their respective control composites. However, the 2 wt% and 10 wt% Core Shell Rubber Particle loaded vinyl ester and polyester composites had lower equilibrium toughness when compared to their respective control composites. Equilibrium toughness for vinyl ester and polyester composites are shown in figures 16 and 17 respectively. Percentage elongation to failure for vinyl ester and polyester composites are shown in figures 18 and 19 respectively.
Figure 16: Equilibrium toughness of vinyl ester composites

Figure 17: Equilibrium toughness of polyester composites
Figure 18: Percentage elongation of vinyl ester composites

Figure 19: Percentage elongation of polyester composites
Tensile properties are fiber dominant. Addition of Core Shell Rubber Particles increases the elastic properties of the vinyl ester and polyester resins but the glass fibers used as reinforcement are very brittle. Therefore during testing this leads to easier debonding between the fiber and matrix in Core Shell Modified Composites leading to
lower strength and modulus.

III.II.II Flexure Test Results

Flexure test results follow the same trend as tensile tests with the notable exception of 10 wt% Core Shell Rubber Particle loaded composite which had strength equal to that of control composite in vinyl ester composites and only lost 5.43% strength in case of polyester composites.

In vinyl ester composites the 2 wt% Core Shell Rubber Particle loaded composite performed the worst with a drastic decrease of 84% and 74.9% in flexure strength and modulus respectively. The 5 wt% Core Shell Rubber Particle loaded composite had a degradation of 32% and 23.4% loss in strength and modulus. The flexure strength and modulus of vinyl ester composites are shown in figure 12 and 13 respectively.

In polyester composites a similar trend was observed too. The control had the highest strength and modulus of all the manufactured polyester composites. The 2 wt% Core Shell Rubber Particle modified composite lost 85% and 75.4% loss in flexure strength and modulus respectively. The 5 wt% Core Shell Rubber Particle loaded composite a degradation of 29.4% and 19.7% loss in strength and modulus respectively. The flexure strength and modulus of polyester composites are shown in figure 14 and 15 respectively.

III.II.III Shear Test Results

Shear test results followed a pattern similar to the tensile test results. In both vinyl ester and polyester composites, the control performed the best with having highest shear strength. The 2 wt% Core Shell Rubber Particle modified composite lost 54.8% of its strength in case of vinyl ester composites and 55% of its strength in case of polyester composites. The 5 wt% Core Shell Rubber Particle modified composite had the least
degradation with a loss of 6% strength in vinyl ester composites and 1.6% strength in polyester composite during shear test. The shear test results of vinyl ester and polyester composites are shown in figure 22 and figure 23 respectively.

III.II.IV Short Beam Test Results

Short beam test results also followed a pattern similar to tensile test results. In both vinyl ester and polyester composites, the control composite had the highest short
beam strength (Inter laminar shear strength). In vinyl ester composites the 2 wt%, 5 wt% and 10 wt% Core Shell Rubber Particle modified composite lost 30.6%, 6.9% and 10.9% strength in short beam tests while in polyester composites the 2 wt%, 5 wt% and 10 wt% Core Shell Rubber Particle modified composite lost 32.3%, 2.6% and 16.2% strength in short beam tests. The short beam test results of vinyl ester and polyester composites are shown in figure 24 and 25 respectively.

**Figure 24: Short beam strength of vinyl ester composites**

**Figure 25: Short beam strength of polyester composites**
III.IV Compression Test Results

Compression test results also followed a pattern similar to tensile test results. In both vinyl ester and polyester composites, the control composite had the highest compressive strength. In vinyl ester composites the 2 wt%, 5 wt% and 10 wt% Core Shell Rubber Particle modified composite lost 55.8%, 7.2% and 11.3% strength in compression tests while in polyester composites the 2 wt%, 5 wt% and 10 wt% Core Shell Rubber Particle modified composite lost 57%, 3% and 16.8% strength in compression tests. The compression test results of vinyl ester and polyester composites are shown in figure 26 and 27 respectively. Table 2 and table 3 show the consolidated results of all the static mechanical tests of vinyl ester and polyester composites respectively.

![Figure 26: Compressive strength of vinyl ester composites](image)
Figure 27: Compressive strength of polyester composites

Table 2: Consolidated results of static mechanical properties of vinyl ester composites (Values in parenthesis are standard deviations)

<table>
<thead>
<tr>
<th>Tests</th>
<th>Control</th>
<th>2 wt% CSRP</th>
<th>5 wt% CSRP</th>
<th>10 wt% CSRP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>473.1 (8.8)</td>
<td>328.23 (6.1)</td>
<td>440.13 (8.2)</td>
<td>421.98 (9.6)</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>23.43 (0.43)</td>
<td>15.20 (0.39)</td>
<td>21.59 (0.41)</td>
<td>20.99 (0.45)</td>
</tr>
<tr>
<td>% Elongation</td>
<td>2.61 (0.048)</td>
<td>2.34 (0.046)</td>
<td>2.90 (0.05)</td>
<td>2.37 (0.051)</td>
</tr>
<tr>
<td>Equilibrium Strength (MJ/m³)</td>
<td>7.36</td>
<td>5.32</td>
<td>7.54</td>
<td>7.21</td>
</tr>
<tr>
<td>Flexure Strength (MPa)</td>
<td>743.24 (13.5)</td>
<td>113.69 (9.2)</td>
<td>500.49 (14.1)</td>
<td>746.79 (15.3)</td>
</tr>
<tr>
<td>Flexure Modulus (GPa)</td>
<td>22.59 (0.42)</td>
<td>5.67 (0.39)</td>
<td>17.30 (0.41)</td>
<td>16.15 (0.40)</td>
</tr>
<tr>
<td>Shear Strength (MPa)</td>
<td>58.22 (1.1)</td>
<td>26.58 (0.76)</td>
<td>54.7 (1.2)</td>
<td>55.16 (0.9)</td>
</tr>
<tr>
<td>Short Beam Strength (MPa)</td>
<td>51.75 (0.95)</td>
<td>35.88 (0.62)</td>
<td>48.13 (1.1)</td>
<td>46.06 (1.02)</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>247.67 (4.2)</td>
<td>109.04 (2.9)</td>
<td>229.76 (4.5)</td>
<td>219.84 (4.3)</td>
</tr>
</tbody>
</table>
Table 3: Consolidated results of static mechanical properties of polyester composites
(Values in parenthesis are standard deviations)

<table>
<thead>
<tr>
<th>Tests</th>
<th>Control</th>
<th>2 wt% CSRP</th>
<th>5 wt% CSRP</th>
<th>10 wt% CSRP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>402.13 (6.3)</td>
<td>272.43 (8.5)</td>
<td>391.72 (6.12)</td>
<td>337.59 (7.3)</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>19.91 (0.45)</td>
<td>12.61 (0.39)</td>
<td>19.21 (0.58)</td>
<td>16.79 (0.43)</td>
</tr>
<tr>
<td>% Elongation</td>
<td>2.21 (0.0003)</td>
<td>1.94 (0.0029)</td>
<td>2.45 (0.0021)</td>
<td>2.35 (0.0035)</td>
</tr>
<tr>
<td>Equilibrium Strength (MJ/m3)</td>
<td>4.95</td>
<td>3.50</td>
<td>5.08</td>
<td>4.89</td>
</tr>
<tr>
<td>Flexure Strength (MPa)</td>
<td>631.75 (15.57)</td>
<td>94.36 (13.26)</td>
<td>445.44 (13.85)</td>
<td>597.43 (9.52)</td>
</tr>
<tr>
<td>Flexure Modulus (GPa)</td>
<td>19.20 (0.75)</td>
<td>4.71 (0.21)</td>
<td>15.40 (0.58)</td>
<td>12.92 (0.36)</td>
</tr>
<tr>
<td>Shear Strength (MPa)</td>
<td>49.48 (2.1)</td>
<td>22.06 (0.96)</td>
<td>48.68 (1.02)</td>
<td>44.12 (3.24)</td>
</tr>
<tr>
<td>Short Beam Strength (MPa)</td>
<td>43.99 (0.86)</td>
<td>29.78 (0.49)</td>
<td>42.83 (1.25)</td>
<td>36.85 (1.62)</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>210.52 (5.3)</td>
<td>90.50 (4.85)</td>
<td>204.48 (6.54)</td>
<td>175.87 (5.48)</td>
</tr>
</tbody>
</table>

III.III Toughening mechanism of Core Shell Rubber Particles

As explained earlier, Core Shell Rubber Particles are preformed rubber that are added to a matrix. These particles affect the composites in two different ways. First the rubber particles sit at reaction zones during curing of the composite and thus restrict the amount of cross linking that the matrix experiences [34]. This reduces the brittle nature of the composites and thus improving the elastic properties of the composites. This improvement in elastic properties leads to improved toughness. Another way in which these rubber particles affect the composites can be explained by their small size. In a cured composite containing these rubber particles crack propagation is arrested through
cavitation of rubber particles in which the outer copolymer is separated from the inner copolymer, followed by particle deformation and ultimately shear yielding before the particle ruptures [35]. As all these three steps absorb energy, therefore, higher stress needs to be applied to fracture a core shell rubber particle modified composite when compared to an unmodified composite. The concentration of these rubber particles also plays a vital role in composite toughening. At 2wt% loading most of the rubber particles can be assumed to be engaged in stopping cross linking at reaction zones and not enough rubber particles were left for toughening after composite curing. While at 10 wt% loading the density of rubber particles might have been so high that interaction between particles started and effective toughening couldn’t be achieved because of this. Based on these results the control and 5 wt% Core Shell Rubber Particle modified composites were chosen for thermal and fatigue testing.

III.IV Fatigue Test Results

III.IV.1 Fatigue life

Results of fatigue test for vinyl ester and polyester composite are shown in table 4 and table 5 respectively. It was observed that control and Core Shell Rubber Particle modified composites failed in the first cycle at a stress level of 90% of the compressive strength of the control in both polyester and vinyl ester composites. However, at each subsequent stress level the 5wt% Core Shell Rubber Particle modified composite outperformed the control composite by a wide margin in terms of number of cycles to failure.

In vinyl ester composites at stress levels of 80%, 70%, 60% and 50% of the compressive strength of the control composite, the 5 wt% modified composite experienced 269%, 440%, 87% and 32% improvement in fatigue life. At the 40% stress
level both the unmodified and modified composites survived 1 million cycles. In polyester composites at stress levels of 80%, 70%, 60% and 50% of the compressive strength of the control composite, the 5 wt% modified composite experienced 77%, 125%, 43% and 81% improvement in fatigue life. At the 40% stress level both the unmodified and modified composites survived 1 million cycles.

Table 4: Fatigue life control and 5wt% Core Shell Rubber Particle modified vinyl ester composites

*Runout: Sample did not break

<table>
<thead>
<tr>
<th>Stress Level (% of Control UCS)</th>
<th>Stress Applied (in MPa)</th>
<th>Cycles Survived</th>
<th>Percentage Improvement in fatigue life</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Control 5wt% CSRP panel</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>222</td>
<td>1 1</td>
<td>0%</td>
</tr>
<tr>
<td>80</td>
<td>197</td>
<td>103 407</td>
<td>269%</td>
</tr>
<tr>
<td>70</td>
<td>173</td>
<td>16483 89041</td>
<td>440%</td>
</tr>
<tr>
<td>60</td>
<td>148</td>
<td>186001 348625</td>
<td>87%</td>
</tr>
<tr>
<td>50</td>
<td>123</td>
<td>562144 740592</td>
<td>32%</td>
</tr>
<tr>
<td>40</td>
<td>99</td>
<td>1000000* 1000000*</td>
<td>Undetermined</td>
</tr>
</tbody>
</table>

Table 5: Fatigue life control and 5wt% Core Shell Rubber Particle polyester composites

*Runout: Sample did not break

<table>
<thead>
<tr>
<th>Stress Level (% of Control UCS)</th>
<th>Stress Applied (in MPa)</th>
<th>Cycles Survived</th>
<th>Percentage Improvement in fatigue life</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Control 5wt% CSRP panel</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>189</td>
<td>1 1</td>
<td>0%</td>
</tr>
<tr>
<td>80</td>
<td>174</td>
<td>87 154</td>
<td>77%</td>
</tr>
<tr>
<td>70</td>
<td>147</td>
<td>16403 36982</td>
<td>125%</td>
</tr>
<tr>
<td>60</td>
<td>126</td>
<td>84521 121056</td>
<td>43%</td>
</tr>
<tr>
<td>50</td>
<td>105</td>
<td>196524 356014</td>
<td>81%</td>
</tr>
<tr>
<td>40</td>
<td>84</td>
<td>1000000* 1000000*</td>
<td>Undetermined</td>
</tr>
</tbody>
</table>
Stress-Number of Cycles (S-N) curves were plotted for graphical representation of the fatigue life of the tested composites. The S-N curves for vinyl ester and polyester composites are shown in figure 28 and 29 respectively. It was observed that in both vinyl ester and polyester composites the Core Shell Rubber Particle modified composites

Figure 28: S-N Curves for vinyl ester composites

Figure 29: S-N Curves for polyester composites
outperformed the control at each stress level. It was also observed from S-N curves that the data points roughly follow a polynomial curve which can be used for a rough estimate of the fatigue life of composites at different stress levels.

III.IV.II Stiffness Degradation Models

Fatigue test data only shows the fatigue life of a composite. It cannot be used for determination of cycles to failure in composites. Fatigue life prediction from S-N curve is only a rough estimate as the fitting curve only follows a rough trend among the data points. A much more reliable method of predicting fatigue life is through the measurement of modulus loss throughout the fatigue life of a composite [36]. These degradation models show how a composite loses modulus in different stages of the fatigue life. The equations below explain how the modelling was done. For each composite tested in tension compression fatigue at 40% stress of the compressive strength of the control composite, load applied, and displacement was collected from the test system for each cycle. Using this information and the sample specimen dimensions the stress, strain and modulus at each cycle were calculated. The modulus was normalized with respect to modulus at 1st cycle and cycle number was normalized with respect to the 1000000th cycle. These values were then plotted on a graph to show the percentage modulus loss at different cycles during fatigue testing. The stiffness degradation curves for vinyl ester and polyester composites for 1000000 cycles at 40% stress level of compressive strength of the control composites are shown in figure 30 and 31 respectively.

\[
\text{Stress} = \frac{\text{Load}}{\text{Area}}
\]

\[
\text{Strain} = \frac{\text{Displacement}}{\text{Gauge Length}}
\]
\[ E_i = \frac{\text{Stress}_i}{\text{Strain}_i} \]

Modulus Ratio = \[ \frac{E_i}{E_1} \]

Cycle Ratio = \[ \frac{N_i}{N_f} \]

\text{Stress}_i = \text{Stress at cycle number i}

\text{Strain}_i = \text{Strain during cycle number i}

\text{E}_i = \text{Modulus at cycle number i}

\text{E}_1 = \text{Modulus at cycle number 1}

\text{N}_f = \text{Cycle number f}

\text{N}_i = \text{Cycle number 1}

Figure 30: Stiffness degradation curve for vinyl ester composites
From the stiffness degradation curves it was observed that there are three different stages of failure. In stage 1 the composites experienced a sudden loss of modulus in the first few thousand cycles. This can be attributed to initiation of matrix cracking in the composites. In case of vinyl ester composites the control lost 8% of its modulus while the 5 wt% Core Shell Modified Composite lost only 3% of its modulus at the end of this stage. In case of polyester composites the control lost 19% of its modulus while the 5 wt% Core Shell Modified Composite lost only 7% of its modulus at the end of this stage. This is because of Core Shell Rubber Particles have improved the toughness of the composite therefore more mechanical stress has to be applied to achieve the same number of cracks in the matrix material.

In stage two there is a gradual loss of modulus but not as suddenly as in stage 1. In this stage it can be theorised that density of matrix cracks increases and at the end of this stage the material achieves characteristic damage state. In case of vinyl ester composites the control lost 15% of its modulus while the 5 wt% Core Shell Modified
Composite lost only 6% of its modulus at the end of this stage. In case of polyester composites the control lost 25% of its modulus while the 5 wt% Core Shell Modified Composite lost only 16% of its modulus. This is because the Core Shell Rubber Particles are arresting crack propagation by cavitation and plastic deformation thus limiting the amount of interfacial debonding.

In stage 3 both the control vinyl ester and polyester composites suffer drastic decrease in modulus. This can be presumed to be happening because the test specimen might have started to delaminate after reaching characteristic damage state. The vinyl ester control composite lost 25% of its modulus while the polyester control composite lost 55% of its modulus at the end of this stage. This drastic decrease in modulus due to delamination is a sign that material is very close to its actual fatigue life and will fail soon. However, because of the crack arresting mechanisms of the Core Shell Rubber Particles in the modified vinyl ester and polyester composites no such drastic drop in modulus is observed indicating delamination has not started yet. The 5 wt% Core Shell Rubber Particle modified vinyl ester composite only lost 7.5% modulus by the end of this stage while the 5 wt% Core Shell Rubber Particle modified polyester composite only lost 20% modulus by the end of this stage.

Even though both the vinyl ester and polyester composites had the same concentration on Core Shell Rubber Particles the polyester composite lost more modulus because the core shell rubber used in this research are vinyl ester based therefore it can be assumed that these rubber particels were more compatible with the vinyl ester resin as compared to the polyester resin.

The tested samples were observed under an optical microscope to determine the failure mechanisms at the beginning and end of the fatigue test. It was observed that
structured matrix cracking started to appear in composites at the first fatigue cycle. Samples that survived 1 million cycles had suffered matrix cracking that had led to localised delamination and fiber crushing. These results are shown in figure 3.2. The red circles show areas where matrix cracking has occurred in the sample tested for 1 cycle. The green arrows shows localised delamination and the red arrow shows fiber crushing in the sample.

Figure 3.2: Optical microscope images of fatigue tested vinyl ester composites

III.V Differential Scanning Calorimetry results

The results of differential scanning calorimetry (DSC) for control and 5 wt% loaded vinyl ester and polyester composites are shown in figure 3.3 and 3.4 respectively. DSC results showed that addition of Core Shell Rubber Particles did not cause any significant change in the first phase transition temperature for both vinyl ester and polyester composites. This shows that glass transition temperature $T_g$ was unaffected by the presence of rubber particles in the composites. The Glass transition temperature for
The Glass transition temperature for polyester control composite was 146.53°C and for the 5wt% Core Shell Rubber Particle modified composite it was 146.44°C. The peak temperature increased from 419.30°C of the control composite to 425.06°C in the 5wt% Core Shell Rubber Particle modified composite.

![Figure 33: DSC Curves for vinyl ester composites](image-url)
III.VI Thermogravimetric Analysis results

The thermogravimetric analysis results (TGA) for control and 5 wt% loaded vinyl ester and polyester composites are shown in figure 35 and 36 respectively. The TGA tests reveal the same trend as the DSC results. The addition of Core Shell Rubber Particles has no effect on the percentage mass of the composites at elevated temperatures. In case of vinyl ester composites the control lost 89.4% of its mass while the 5wt% Core Shell Rubber Particle modified composite lost 85.2% of its mass. In case of polyester composites, the control lost 94.83% of its mass while the 5wt% Core Shell Rubber Particle modified composite lost 93.64% of its mass.
Figure 35: TGA Curves for vinyl ester composites

Figure 36: TGA Curves for polyester composites
IV. CONCLUSIONS

Eight different composites were manufactured using vacuum assisted resin transfer molding. Four vinyl ester composites containing 0 wt%, 2 wt%, 5 wt% and 10 wt% Core Shell Rubber Particles and four polyester composites containing 0 wt%, 2 wt%, 5 wt% and 10 wt% core shell rubber particles. Scanning electron microscopy revealed that there was no agglomeration of Core Shell Rubber Particles in both vinyl ester and polyester composites and uniform distribution was achieved. Manufactured composites were tested for tensile, compressive, shear, short beam and flexural properties. Addition of Core Shell Rubber Particles led to a decrease in mechanical strength, but the 5 wt% core shell rubber particle modified vinyl ester and polyester composites had the least amount of degradation in mechanical properties and improved equilibrium toughness. These results support the hypotheses that addition of core shell rubber particles will lead to an improvement in equilibrium toughness of vinyl ester and polyester composites. 5 wt% Core Shell Modified composites were compared in tension-compression fatigue against control composites. Stiffness degradation modelling showed that the Core Shell Rubber Particle modified vinyl ester composite retained 92.5% of its modulus after testing while the control composite only retained 75% of its modulus. In case of polyester composites, the Core Shell Rubber Particle modified vinyl ester composite retained 80% of its modulus after testing while the control composite only retained 45% of its modulus. These results support the hypotheses that addition of core shell rubber particles will lead to an improvement in fatigue life of vinyl ester and polyester composites. It can be theorized from optical microscopy that composites suffered matrix cracking followed by localized delamination and fiber crushing in fatigue testing. Results of differential scanning calorimetry and thermogravimetric analysis
showed that addition of core shell rubber particles had no significant effect on the glass transition temperature, peak temperature and mass loss of the composites respectively.
V. FUTURE SCOPE OF WORK

In future SEM imaging can be done on samples tested in static mechanical conditions to determine what is the dominant core shell rubber toughening mechanism in different types of loading conditions. Progressive failure analysis can be done at different stages of fatigue test to determine the dominant failure mechanism at different stages of fatigue testing and how interdiction of core shell rubber particles inhibited the damage onset in samples under cyclic loading conditions. Also, hybridization can be done by adding stiffening agents like nano silica along with core shell rubber to compensate the loss of mechanical strength in modified composites.
REFERENCES


