Elevated temperature performance of hybrid polymer composites

A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Technology

In

Metallurgical and Materials Engineering

By

MEET JAYESH SHUKLA

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Department of Metallurgical and Materials Engineering
National Institute of Technology Rourkela
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Under the guidance of

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2015

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CERTIFICATE

This is to certify that the thesis entitled**, "Elevated temperature performance of hybrid polymer composites"** submitted by Mr. **Meet Jayesh Shukla** in partial fulfilment of the requirements for the award of Master of Technology in Metallurgical and Materials Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under our supervision and guidance. To the best of our knowledge, the matter embodied in the thesis has not been submitted to any other university/institute for the award of any Degree or Diploma.

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ABSTRACT

FRP composites are the most promising and reliable materials in today's world. Their outstanding properties make them unique and distinct. Apart from many advantages, during application, they start degrading when exposed to harsh environmental condition like elevated temperature. Hybridising a composite using two different reinforcements has proved to be a method for improving their performance in such conditions. Present study aims at evaluating the mechanical performance of GFRP and Glass/Carbon/epoxy (G/C hybrid) composites at ambient and in-situ elevated conditions. When tested for in-situ at +70 ^{o}C and +100 ^{o}C, significant reduction in inter-laminar shear strength (ILSS) was observed for both the composites as compared to that at room temperature. The ILSS of G/C hybrid was found out to be 28.2 % more than that of GFRP at room temperature, which became nearly equal for both the composite systems when tested at +100 ^{o}C and thus the fiber hybridisation effect was completely diminished. On the other hand, incorporation of carbon nanotubes (CNTs) in epoxy resin has also caused drastic improvement in strength over conventional GFRP. In the present study, epoxy of GFRP composite was modified with 0.1wt. %, 0.3 wt. % and 0.5 wt. % of CNT and laminates were fabricated. Testing was done for these composites at room temperature, 70 ^{o}C, 90 ^{o}C and 110 ^{o}C. Composite with 0.1 wt. % CNT showed the maximum increment in strength by 32.74 % over GFRP at room temperature. Decrease in flexural properties was noted at elevated temperatures for all the composites. Composite with 0.3 wt. % CNT showed the maximum strength at 70 ^{o}C and 90 ^{o}C among all the fabricated composites. It was found that testing near glass transition temperature caused high reduction in properties and also confirms the ineffectiveness of hybridisation at such temperature.

Keywords: FRP composite; Elevated temperature; Carbon nanotube; Flexural performance; hybrid composite; Fractography.

Chapter 1

Introduction

1.1 Introduction to Composites

Composite is a judicious combination of two or more distinct materials, whose combination produces a synergistic effect. The constituents do not lose their individual identities and are separated by an interface. Composites have presently become one of the essential materials in present industrial world. They provide promising mechanical properties like low density, high strength to weight ratio, greater wear and corrosion resistance than conventional materials and many more. The major two phases include (a) Matrix phase and (b) Dispersed phase i.e. reinforcement. Matrix phase is the primary phase which is soft and ductile while the dispersed phase is the secondary phase (stronger than matrix) embedded in matrix. Composites can be divided on basis of matrix phase as Metal Matrix Composites (MMCs), Polymer Matrix Composites (PMCs) and Ceramic Matrix Composites (CMCs) as shown in figure 1.1. Composites are also classified on the basis of Reinforcement as (1) Particulate composite, (2) Fibrous composites and (3) Laminated composites.

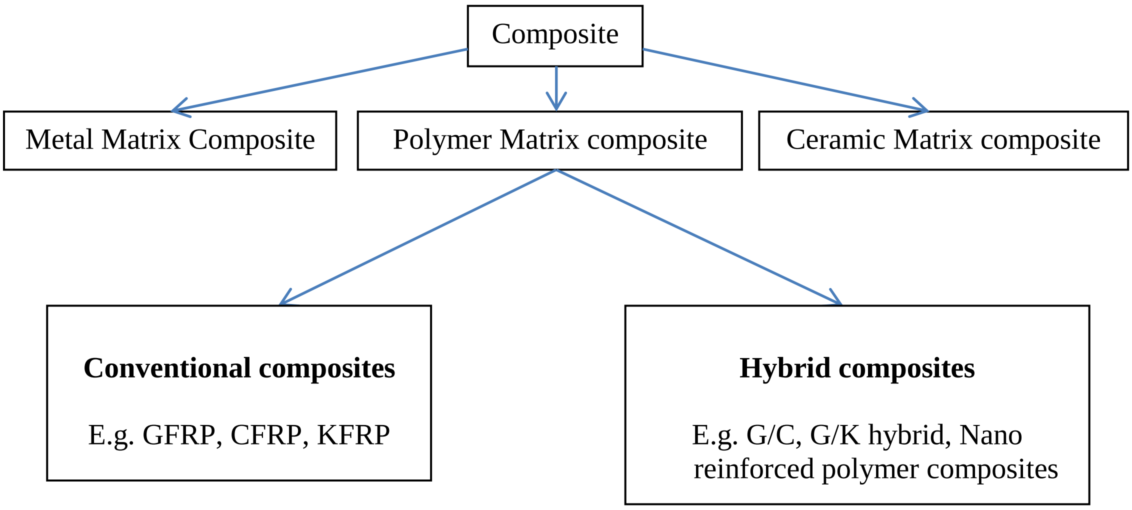

Figure 1.1: Types of Composites.

1.2 Fiber reinforced Polymer (FRP) composite

Fiber reinforced polymer composites are composites which consists of fibrous reinforcement along with a soft and ductile matrix resin. These composites find application in Aerospace structures, Marine equipment, parts of Automobile bodies, biomedical applications, Sporting goods, structural applications, etc. The commonly used matrix and fibers for PMCs include Epoxy and Glass/Carbon/Kevlar respectively. The methods for fabricating the composites are Hand Lay-Up method, Bag Moulding Process, Pultrusion, Filament Winding, Preformed

Moulding Compounds, Resin Transfer Moulding, Injection Moulding etc. Among these the most common method for fabricating the PMC is the Hand Lay-Up Process.

Another class of composite used presently is Hybrid composite. In hybrid composites there is either incorporation of two or more types of fibers or using nano fillers with matrix i.e. either fiber hybridisation or matrix hybridisation respectively. The behaviour of a hybrid composite will be the weighted average of the individual components. Using hybrid composites with two or more types of fibers, the lack of properties in one fiber can be complemented with the other fibers. For example using Glass fiber reinforced Polymer (GFRP) composite can result in a soft laminate as compared to the Carbon fiber reinforced Polymer (CFRP) composite due to the high strength of carbon fibers. Hence in hybrid composite we use glass and carbon fibers both for appropriate properties. Likewise CFRP composite has a less impact resistance as compared to GFRP composite. Here as the carbon fiber is costlier than glass fiber, a balance among performance and economy of the obtained composite should be maintained. Proper material design can lead to an improved composite. The types of hybrid composites include (1) Interply or tow by tow hybrid, (2) Sandwich hybrids, (3) Laminated hybrids, (4) Intimately mixed hybrids and (5) Intraply laminated. The judicious designing of hybrid composites result in a good balance of properties along with incurred cost.

1.3 Reinforcements

In fibrous form, many materials are recorded to be stiffer and stronger than their bulk form. This fibrous shape leads to easy and effective transfer of load through matrix while providing more contact area. Reinforcements are generally the stiff and hard phase of an FRP composite. On application of load, reinforcements serve as major load carriers in bulk composite. The fibers used in fabrication of conventional composites and hybrid composites are listed below:

a) Glass fibers
b) Carbon fibers

1.3.1 Glass fibers

Glass fibers are based on silica (SiO_2) with additives like boron oxide, sodium, aluminium, calcium, and iron. In spite of being amorphous, minor amount of crystallisation can occur after heating it at high temperature for long time. This results in reduction in strength. The appearance of E-glass fibers is as shown in figure 1.2 (a). Below mentioned 3 types of glass fibers which are popularly used:

1. E (Electrical)-glass fibers: It is used in electrical applications due to its insulating nature. It has good strength, stiffness, electrical and weathering properties. It also possesses good resistance to heat and electricity.
2. C (Corrosion)-glass fibers: It is calcium borosilicate glass, which has very high resistance to corrosion and is used mostly in acid and corrosive environments.
3. S (Strength)-glass fibers: It is magnesium alumina silicate glass, which has high strength, high young's modulus and high temperature resistance.

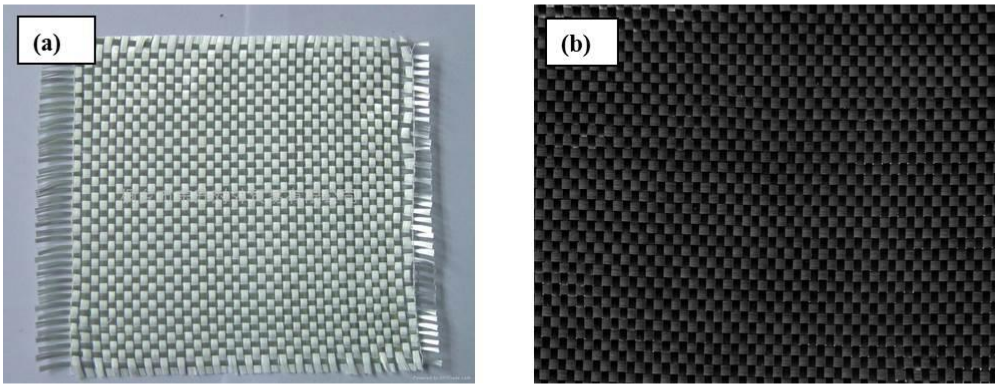

Figure1.2: (a) E-glass fiber and (b) Carbon fiber.

1.3.2 Carbon fibers

Carbon fibres are the most expensive of the widely used reinforcements. Its excellent performance in space application along with its low density makes the cost a secondary factor. Carbon fibres consist of small amount of crystallinity along with graphite. In a graphite crystal, the carbon atoms are arranged in a hexagonal arrangement and strong covalent bonds are responsible for this binding. Weak Vander-waal forces are acting among the atoms in the basal plane. Therefore they are highly anisotropic. The modulus in the basal plane axis is 100 GPa as compared to the modulus in perpendicular plane i.e. 75 GPa. Thus it is beneficial if the basal planes are oriented parallel to the fiber axis. The coefficient of thermal expansion is very less as compared to glass and aramid fibers. They show very less strain to failure due to their high modulus. The appearance of carbon fibers is as shown in figure 1.2 (b).

1.4 Nano-reinforcement

Carbon nanotube (CNT) is one among the most widely used nano-fillers in current time. Its unparalleled characteristics like high specific strength, high stiffness, high resilience etc.

make it the most widely used nano-reinforcement. The tensile strength of CNT is between 200 and 500 GPa and the Young's modulus is more than 1.0 TPa. As a result, CNTs are utilized for the development of new material systems, particularly, structural nano composites. On adding carbon nanotubes in composites, the mechanism of bridging restricts the growth and propagation of crack and improves the toughness of the material. Moreover, during fiber pull-out high increase in fracture energy can be due to the enhanced interface area. Moreover, the weaker strength van der Waals forces at the interfaces could result in slippage at interface which can thereby result in inefficient transfer of load to fibres via the matrix and prevent attainment of high strength in composites. Incorporating very low amount of fillers of the size of nanometres significantly increases matrix properties by effectively transferring load at the interface. CNT also has a plasticization effect on polymers by increasing its free volume and hence lowering the glass transition temperature.

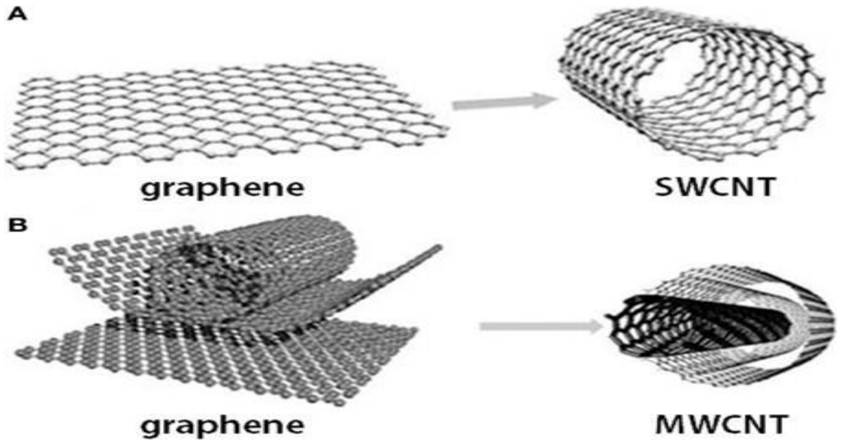

Figure 1.3: Types of Carbon nanotubes (CNT) (A) Single walled CNT and (B) Multiwalled CNT.

1.5 Matrix

The matrix is the continuous phase of a composite. The chief purpose of matrix is to hold the reinforcement together and also provide the path for transfer of load to the reinforcing phase. The matrix also acts as a protection to save the reinforcement from abrasive wear, environmental contamination and other damages. The most commonly used matrix materials are polymer matrix, metal matrix and ceramic matrix.

1.5.1 Polymer matrix

Polymer is an organic material which is composed of repetition of monomeric chains. The repeating chains mainly consist of carbon, hydrogen and oxygen. Their properties include low modulus, low strength, high moisture susceptibility and a low temperature tolerance.

There are two types of polymer matrices used

- Thermoset polymer
- Thermoplastic polymer

1.5.1.1 Thermoset polymer

They are made from semisolid or liquid precursors, which undergo polymerisation or even curing when it is heated to high temperature. The final polymer obtained is a very hard solid. This hardening obtained is due to the formation of crosslinks in the polymer. These polymeric chains further form 3D network and hardens it. Common use polymers are epoxies, polyesters, phenolic resins, vinyl ester, etc.

1.5.1.2 Thermoplastic polymer

These polymers get soft on heating and harden on cooling. They possess amorphous structure where there is disorder/random arrangement of polymeric chains. They are mostly preferred in the application where forming is to be done by the liquid flow of it at high temperature. Commonly used thermoplastic polymers include polystyrene, polyethylene, PMMA, etc.

1.5.2 Epoxy

It is the most commonly used matrix material (polymer) that. It is available ranging from low viscous liquids to solids of high melting point and can be modified to a wide range for use. It offers high strength, easy and rapid curing by different of curing agents, low shrinkage, better electric insulation, etc. These are the properties which make them suitable for use in composites. The widely used epoxy is termed as diglycidyl ether of bisphenol A (DGEBA). The chemical structure is as shown in figure 1.4.

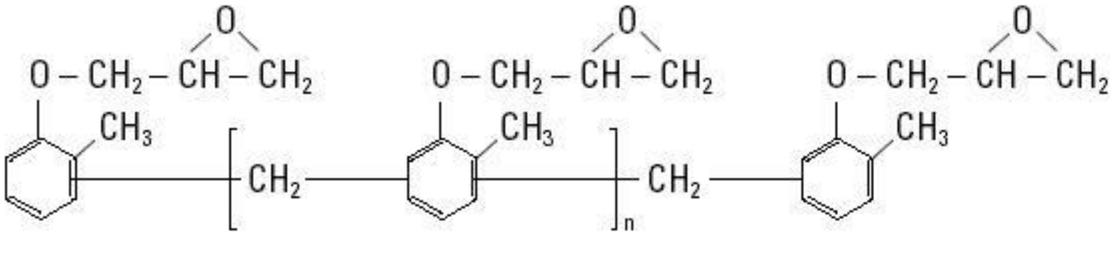

Figure 1.4: Chemical structure of Epoxy.

1.6 Applications of FRP composites

FRP composites are most widely used materials in today’s industries due to its many desired properties like low weight to strength ratio, high corrosion resistance, high wear resistance, high strength and stiffness, high impact resistance, high fatigue resistance, etc. They are generally used in structural, aerospace and various engineering applications. Low density property of these composites is well utilised in applications like automobiles, space crafts, boat hulls, sporting goods, etc. Their non-corrosiveness property is beneficial in applications like marine, sea water exposure, high humid environment, chemical storage tanks, pressure vessels, etc. Few applications are shown below in figure 1.5.

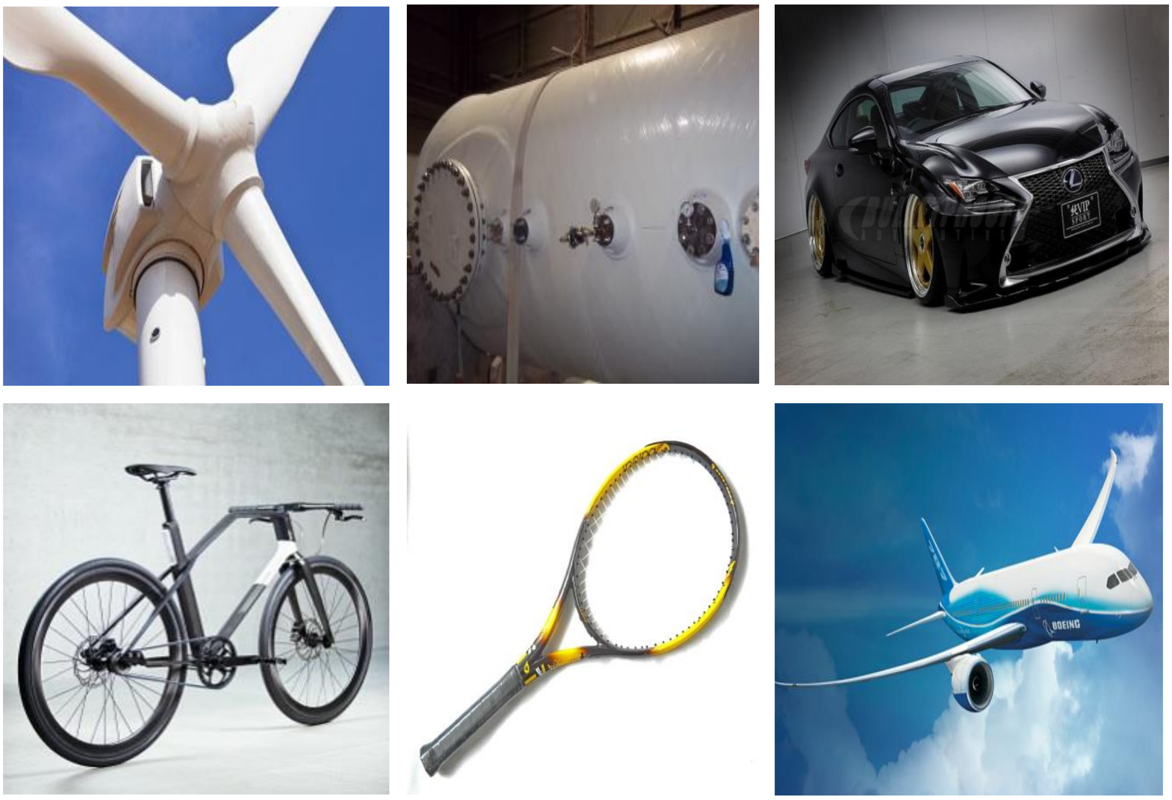

Figure 1.5: Applications of FRP composites.

1.7 Limitations of FRP composites

FRP made components and structures are normally exposed to various environmental conditions like high temperature, low temperature, humid climate, alkaline environment, etc.[1–5] and can be more perilous if continuous cyclic variation of temperature occurs like thermal spike, low earth orbit space environment and hygrothermal exposure [6]. These composites are more subtle to environmental damage. The interface is the most important and critical part of composites and it administers the behaviour of these composites The most common mode of failure found at interface includes fiber/matrix debonding. A high differential thermal expansion coefficient between matrix and fibers can lead to different expansion at elevated and thus leading to interfacial debonding. Thus debonding is the common culprit in reducing the ILSS of the composite [7,8]. While at low temperature, polymer matrix exhibits brittle manner and avoids the internal residual stress removal or stress concentration. Large debonding at the interface can be because of these residual stresses induced in the matrix at low temperature. Interface is also badly affected by presence of moisture. This moisture at interface can alter the chemical reactions occurring at it and thus affects the mechanical performance of the composite in bulk level.

1.8 Objectives of the present research work

- Present work focuses on understanding the behaviour and evaluating the mechanical performance of Glass/epoxy (GE) composite and Glass/Carbon/epoxy (G/C) hybrid composite at elevated temperatures **[Chapter 2].**
- Fabrication of GE composite and GCE composite was done by hand layup process. Interlaminar shear strength (ILSS) of samples was assessed at elevated temperatures.
- Finally determination of failure modes was undertaken using Scanning Electron Microscope (SEM).
- Further, hybridization was done using carbon nanotubes (CNTs) in epoxy resin and fabrication of nanophased glass/epoxy composite (CNT-GE composite) was done. Flexural performance was evaluated for both GE and CNT-GE composites at various elevated temperatures **[Chapter 3].**
- Failure mechanisms of the fractured samples were identified using SEM.

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Chapter 2

Elevated temperature performance of GFRP and G/C hybrid composite

Hybrids composite are those which include two or more types of reinforcements or hybridization matrix with some nano reinforcement. The concept in fabricating them is to take positive effects from both the reinforcements [1–4]. Glass fibers possess low strength, low modulus and a high strain to failure as compared to carbon fibers. They are less costly than carbon fibers. Carbon fibers possess high strength, high modulus but a lower strain to failure as compared to glass fibers. Hence for obtaining optimum strength, modulus and strain to failure, hybridization of carbon fibers in GE composite should be done to improve the mechanical performance and also economic consideration. It is thus economical to keep balance between the performance and the cost of the overall composite because of high cost and low failure strain of carbon fiber.

2.1 Literature Survey

Wang et al. [5] tested the CFRP plates at steady and transient states. The range of temperature was 20 to 700 °C. It was obtained that in the range of 20–150 °C and 450–706 °C, decrease in tensile strength of the CFRP plate was noted. Little drop in tensile strength was observed in these range. But at 300 °C, the ultimate strength was noted to be half of its strength at room temperature. Also at 700 °C, the tensile strength was 7% of the tensile strength at ambient.

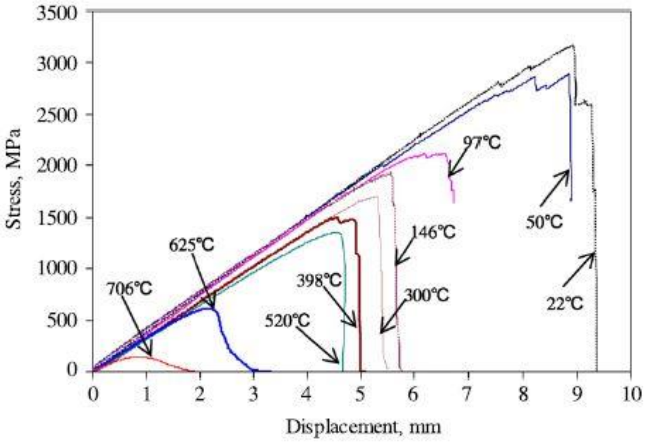

Figure 2.1: Stress-displacement relationship for CFRP.

Hanson [6] experimentally determined the strength and creep characteristics of PRD49 fiber in epoxy. Tensile strength properties were generally retained to 450 K (350 F); however, at 477 K (400° F), the tensile strength was about 73 percent of that at 297 K (75° F). The tensile modulus showed no significant change at elevated temperatures; however, at 20 K (-423° F), the modulus increased by about 40 percent as compared to the modulus at 297 K (75° F). In creep testing, the PRD49 fiber experienced an accelerated primary creep followed by a much lower secondary creep rate. At room temperature, the fiber exhibited a low secondary creep rate and sustained a tensile stress of about 80 percent of the ultimate tensile strength for 1000 hours without failure. Humidity caused a minor effect on creep behaviour of the fiber.

Birger et al. [7] analysed the failure mechanism of thermally aged samples and concluded that aging of composites at high temperature is affecting both the mechanical as well as physical properties. FRPs are very sensitive to change in temperature due to the different expansion of matrix and fiber. Hence this leads to development of thermal stresses in the composite. These thermal stresses can be released on the cost of crack formation in the matrix and sometimes it may result in fiber failure. It was observed that there was reduction in shear strength and flexural strength due to thermal aging. Weakening of the interface takes place. As the time of aging increased, the failure transitioned from ductile appearance to more brittle appearance.

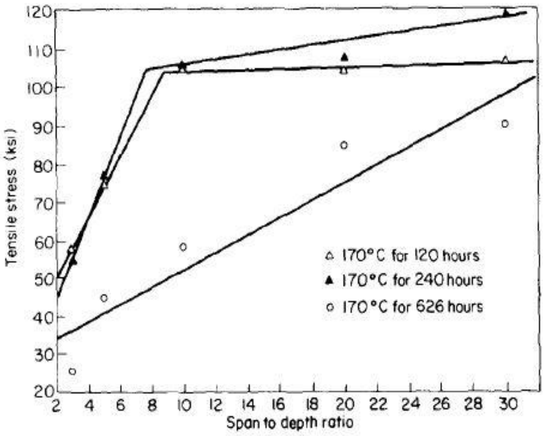

Figure 2.2: Variation in tensile strength with span to depth ratio for various dry thermal aging conditions.

Cao et al. [8] evaluated the tensile performance of CFRP, hybrid C/GFRP and hybrid C/BFRP composites in the range of 16 ^{o}C to 200 ^{o}C. Reduction in tensile strength was observed as the temperature was elevated to glass transition temperature. Wang et al. [9] demonstrated the mechanical performance of steel reinforcing bars at elevated temperatures and inferred that 350 ^{o}C temperature was found to be perilous temperature for FRP bars. At such temperature, reduction in strength for GFRP and CFRP composite bars by 45 % and 35

% respectively was noted as compared to their ambient strength. Also the resin of GFRP bar got ignited at temperature of 500 °C.

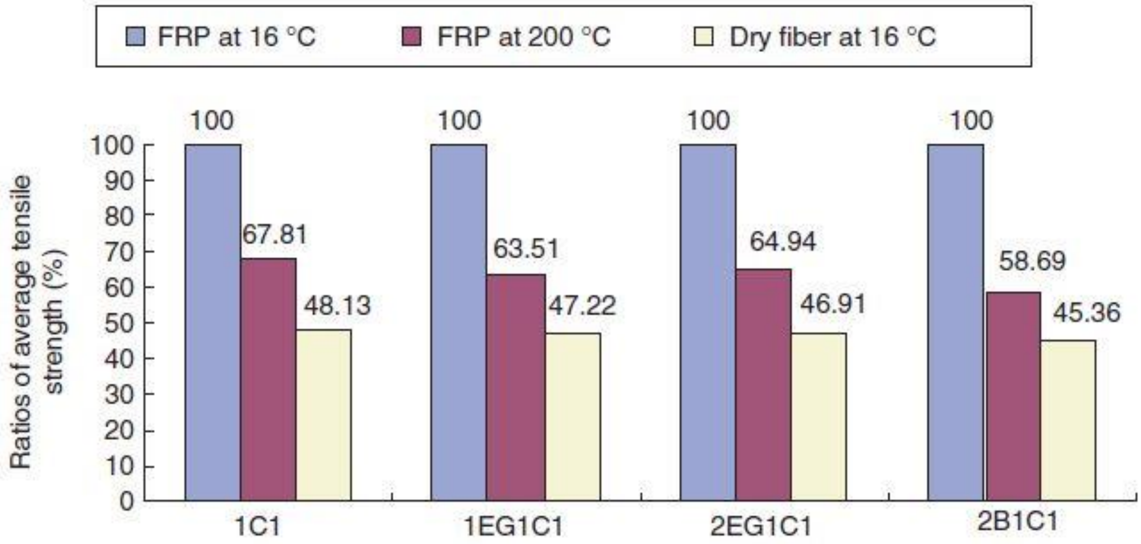

Figure 2.3: Evaluation of average tensile strength ratios with changing fiber system.

Sayer et al. [10] experimentally investigated impact performance of hybrid composite laminates and found the following: Delamination and minor matrix cracking were observed on glass fiber and while there was matrix breaking and indentation on carbon fiber surface. On increase of impact energy, the major mode of failure observed was fiber fracture. The impact sustainability of CG hybrid composite was found to be less than that of GC hybrid composite. Hence the excessive energy is more for CG than GC. The perforation threshold also increased by few values on increasing thickness of carbon fiber [10].

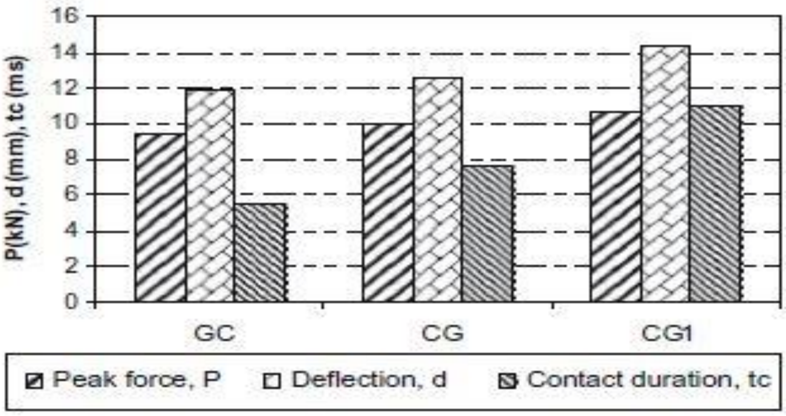

Figure 2.4: Impact properties of hybrid composites.

Ghasemnejad et al. [11] improved impact property of single and multi-delaminated FRP composites by using natural Flax yarn as the reinforcement.

From the above literatures, it can be noted that hybridisation of FRP composites has a beneficial effect on performance at room temperature and elevated temperature. Hence the objective of this study is to evaluate the mechanical performance of G/C composite (glass and carbon fibers are alternately stacked in the laminate) in room and elevated temperature environments.

2.2 Materials

Below mentioned materials were required for fabricating conventional GE composite as well as GCE composite.

1. Plain weave woven fabric E-glass fibers (FGP, RO-10) as reinforcement
2. Plain weave woven fabric carbon fibers (TC-33) as reinforcement.
3. Epoxy resin (Lapox, L-12) based on Bisphenol A as matrix.
4. Triethylene tetra amine (TETA) (K6-primary amine) as hardener.

Table 2.1: Properties of constituents

Material	Tensile strength (MPa)	Young's Modulus (GPa)	Density (g/cc)
E-glass fibers	2000	80	2.58
Carbon fiber	2900	525	1.85
Epoxy	85	3.5	1.2

2.3 Experimental procedure

E-Glass fibers sheets/layers were cut from the fiber roll in the size of 25 cm x 25 cm. 14 layers of this size were weighed using a digital weighing machine. For fabricating glass/epoxy laminate, 60 wt. % glass fibers and 40 wt. % epoxy resin was taken. Hardener was taken about 10 wt. % of epoxy. The laminate was prepared by hand lay-up process and was followed by curing in a compression press at $60^{o}C$ for 20 minutes with the applied pressure of 10 kg/cm^2. The cured laminate was cut for Short beam shear test as per the ASTM D2344-84 standard with the help of Diamond cutter. The samples were dried in an oven for 3 hr maintaining 50^{o}C to remove moisture and other volatile entities. Specimens were then post cured at 140^{o}C for 6 hr [12].

Other batch of samples was obtained by fabricating hybrid glass/carbon epoxy composite. 5 sheets of woven E-glass fibers (0.3 weight fraction) and 4 sheets of woven carbon fibers (0.3 weight fraction) were cut in 25cm x 25cm size. They were weighed using a digital weighing machine. Glass/carbon/epoxy (G/C hybrid) composite was fabricated using alternate stalking sequence of glass and carbon fiber (keeping glass fiber at both ends). Diamine hardener was taken about 10 % weight of epoxy. The hybrid laminate was prepared by hand lay-up method. The laminate was then cured in compression moulding hydraulic press at 60^{o}C for 20 minutes with pressure of 10 kg/cm^{2}. The cured laminate was cut for Short beam shear test as per the ASTM D2344-84 standard with the help of Diamond cutter. The samples (as shown in figure 2.5 (a, b)) were dried in an oven for 3 hr maintaining 50^{o}C to remove moisture and other volatile entities. Specimens were then post cured at 140^{o}C for 6 hr [12].

2.4 Material characterization

2.4.1 Short Beam Shear (SBS) test.

The SBS test was carried out in environmental chamber of UTM (Instron 5967) using 3 point bend fixture as shown in figure 2.5 (c)) to find apparent ILSS of the standard samples. In-situ testing of samples was done at 70^{o}C and 100^{o}C with the holding time of 10 minutes. Also, ex-situ conditioning of samples was done at 70^{o}C and 100^{o}C for 60 hrs. in an oven. The samples were tested after they were furnace cooled to room temperature. The loading rate was set to 1 mm/min.

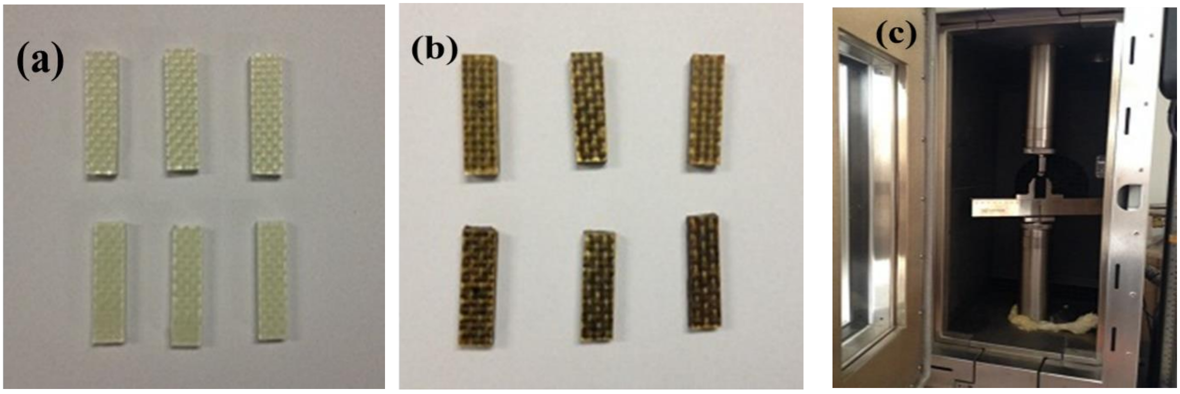

Figure 2.5: (a) GFRP samples, (b) G/C hybrid samples and (c) 3 point bend fixture.

2.4.2 Fractographic analysis

The fractured samples were further analysed to identify the failure modes and understand the mechanisms behind failure of the composite. This was done using JEOL-JSM 6480 LVSEM operated at 20KV.

2.5 Results and discussion

2.5.1 In-situ high temperature testing

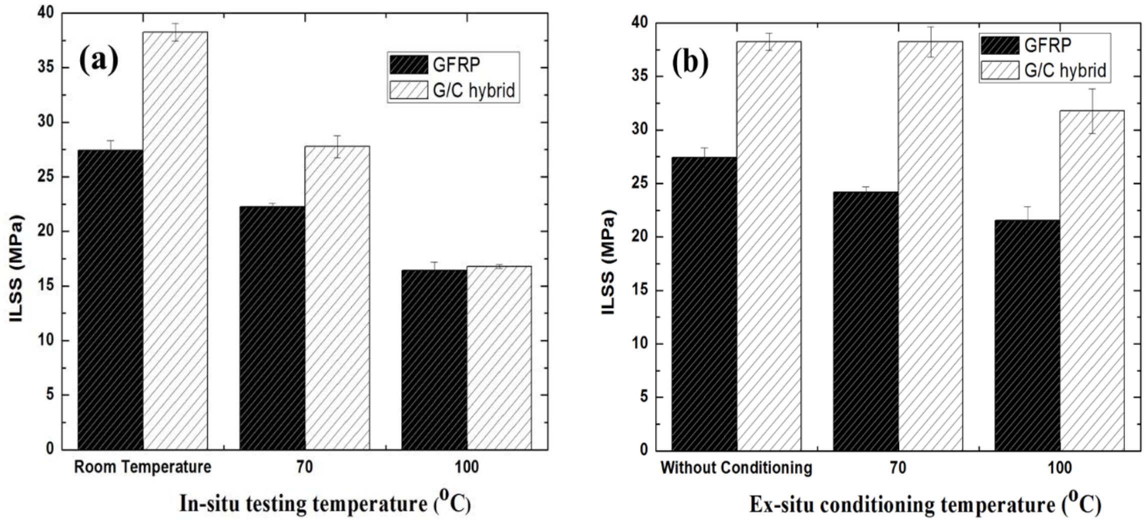

Figure 2.6: Variation in ILSS with (a) in-situ testing temperature for GFRP and G/C hybrid samples and (b) ex-situ conditioning temperature for GFRP and G/C hybrid samples.

It can be seen from figure 2.6 (a) that there is decrement in ILSS of GFRP at 70^{o}C and 100^{o}C by 18.9 % and 40 % respectively as compared to that at room temperature. This decrease was 27 % and 56 % at 70^{o}C and 100^{o}C respectively for G/C hybrid composite. Due to different degree of expansion for epoxy and reinforcement, thermal residual stresses are induced in the matrix at elevated temperatures. This difference in expansion will lead to generation of micro cracks and voids at the interface as well as in the matrix. On application of load, these micro cracks coalescence together and generate a major crack. This crack may be the cause of decreased performance of the composite. The ILSS of G/C hybrid was noted to be increased by 28.2 % over GFRP at room temperature. This increased strength is due to presence of carbon fibers (high strength and stiffness) in the composite. Also the bond between carbon fibers and epoxy is much stronger than bond between glass fibers and epoxy. The ILSS of both the composite systems were nearly equal at testing temperature of 100^{o}C. The glass transition temperature of epoxy resin is nearly 110 °C. Hence testing near this temperature will soften the matrix and thus the effectiveness of load transfer will reduce. Thus the performance of the composite will be governed totally by the matrix and hybridising effect will be found diminishing at such temperature.

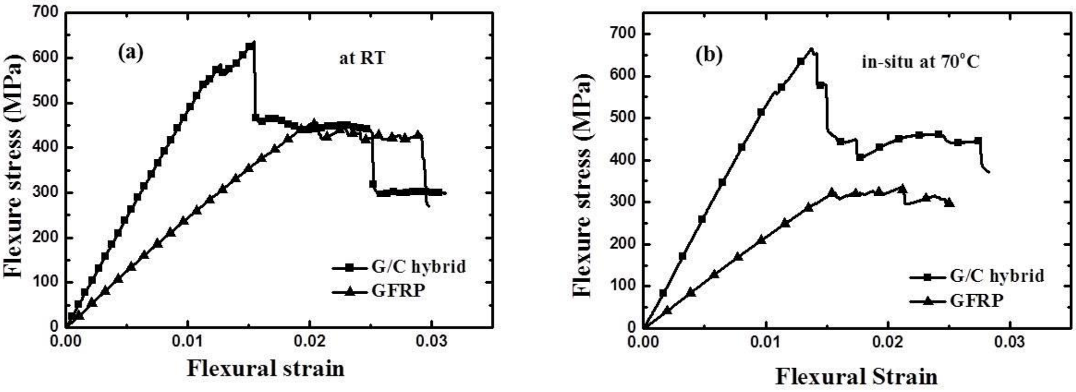

Figure 2.7: Flexural stress vs. strain curves for GFRP and G/C hybrid at (a) room temperature and (b) 70 °C.

Figure 2.7 shows the flexural stress vs. strain curves for GFRP and G/C hybrid composites tested at ambient and 70 °C. It is seen that the curves at 70 °C shows more ductile nature than that at room temperature.

2.5.2 Ex-situ high temperature conditioning

It can be seen from figure 2.6 (b) that testing of GFRP at 70°C and 100°C caused decrement in ILSS by 11.8 % and 21.5 % respectively over ILSS at room temperature. The decrement in ILSS for G/C hybrid was 0.05 % and 17 % at 70°C and 100°C respectively as compared to ambient ILSS. As the bonding between carbon fibers and epoxy is stronger than the bonding between glass fibers and epoxy, so the G/C hybrid exhibits high strength. The interface between glass fibers and epoxy degrades at a higher rate as compared to carbon fiber/epoxy. Hence this may be the cause of generation of cracks at the interface after certain time of conditioning.

2.6 Fractographic analysis

To identify and understand various mechanisms responsible for failure of the composite, it is analysed under SEM. Figure 2.8 (a) it is evident that GFRP showed large amount of fiber/matrix debonding when tested at ambient. This debonding further may have resulted in separation of fibers from matrix. Thus due to this, imprints of fibers were observed on the matrix surface. The figure 2.8 (b) is a clear indicative of high cohesive bonding between carbon fiber and epoxy. The figure indicates that the interface was too strong to initiate failure and finally the failure initiated at a distance away from interface i.e. in the matrix. Thus this can be ascribed to the high ILSS of hybrid as compared to GFRP composite.

It is seen from figure 2.9 (a) that for GFRP composite at +70^{o}C formation of voids take place as a result of coalescence of micro-voids. Little epoxy adherents are observed on fiber surfaces in case of G/C hybrid tested at 70 ^{o}C as shown in figure 2.9 (b). This separation between fiber and matrix is a clear indicative of poor performance at elevated temperature.

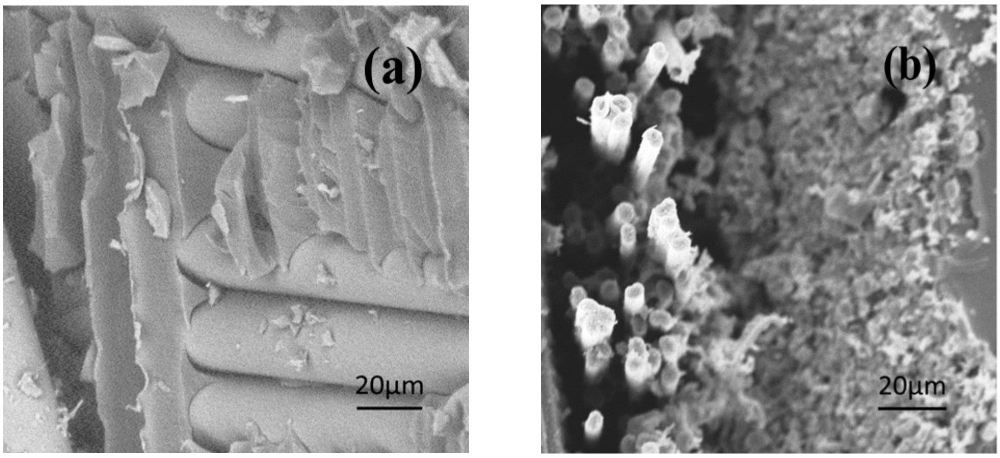

Figure 2.8: SEM images of room temperature tested (a) GFRP and (b) G/C hybrid composite.

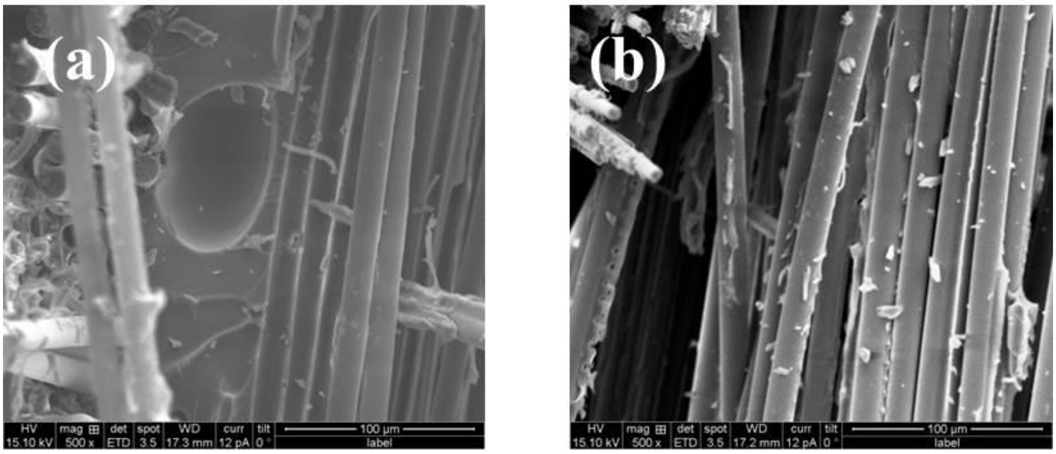

Figure 2.9: SEM images of in-situ tested (a) GFRP and (b) G/C hybrid composite at 70^{o}C.

2.7 Conclusion

. The following inferences can be made from the present investigation.

- At room temperature G/C hybrid shows better interlaminar property as compared to GFRP. But as the testing temperature increases, G/C hybrid degrades at a higher rate than GFRP. The ILSS of both the composite systems were nearly equal at testing temperature of 100^{o}C. Hence testing near this temperature i.e. the glass transition temperature of epoxy, softening of matrix will take place and would further reduce the effectiveness in transferring load to the fibers. It can be concluded that behaviour of composite will be only matrix dependent when the testing temperature is near glass transition temperature of matrix used.

- During in-situ elevated temperature testing, the matrix attains glassy characteristics and starts softening. This soft matrix will not be able to transfer load/stress efficiently and hence low ILSS will be attained. On the other hand, ex-situ conditioning is less perilous than in-situ testing. Here after getting conditioned at elevated temperature, the sample is brought to room temperature. This will help the material to recover its original properties upon cooling from elevated temperature. Generation of micro-cracks and their coalescence may be the reason for decrease in ILSS.

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Chapter 3

Elevated temperature performance of CNT-GE composite

CNTs are well acknowledged around the world due to its out throwing mechanical properties like high specific surface area, high strength, high stiffness, excellent electrical [1] and thermal properties, etc. [2–5]. The recent trend in the field of FRP composites involves incorporation of CNTs in composites to tailor the interface as per the need. As interface is the most important part in a composite, its modification is necessary to improve the final property of the composite. As the in-plane properties are fiber dominated, CNTs are incorporated in order to enhance the z-direction (or transverse) property of the composite.

3.1 Literature Survey

Jeelani et al. [6] fabricated and characterised multi-walled carbon nanotubes embedded carbon/epoxy composites. Ultrasonic cavitation was done to infuse CNTs in epoxy. They found that 0.3 % CNT addition in epoxy caused higher increment in tensile strength than neat epoxy and nano-systems. They also noticed improvement in flexural strength by 28.3 %, glass transition temperature by 2.4 ^{o}C and decomposition temperature.

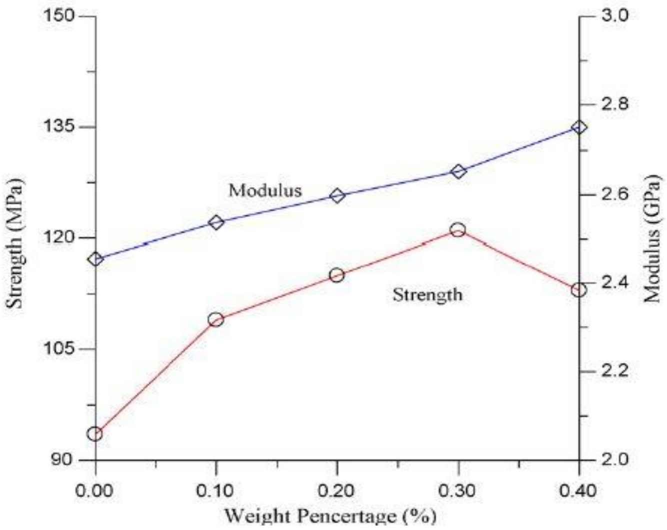

Figure 3.1: Variation in strength and modulus with weight % CNT.

Rahman et al. [7] studied the improvements in flexural and visco elastic properties of functionalised MWCNTs incorporated glass/epoxy composites. 0.3 % CNTs was found optimum in improving mechanical and thermo mechanical properties. The flexural modulus, flexural strength and strain of 0.3 % MWCNT incorporated glass/epoxy composites was found to be enhanced by 21 %, 37 % and 21 % respectively over glass/epoxy samples. Thermal analysis showed that the storage modulus of 0.3% samples was increased by 41 %, loss modulus by 52 % and increase in glass transition temperature by 10 ^{o}C. Also this study demonstrated that amino-functionalised MWCNTs can enhance the mechanical as well as thermo mechanical performance of glass/epoxy composite significantly.

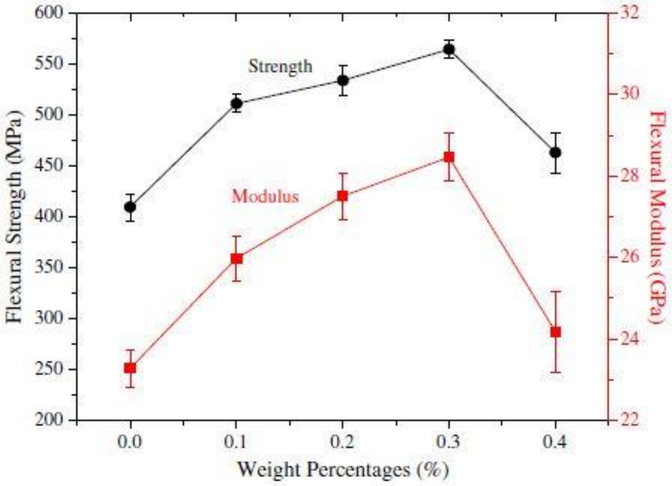

Figure 3.2: Variation in flexural strength and modulus with weight % of CNTs.

Kim et al. [8] evaluated surface modification effects on the mechanical and rheological properties of CNT/epoxy composites and demonstrated that plasma treated CNTs showed more improvement as compared to the other surface modification techniques. It was also noticed that the dispersion of surface modified CNTs in the matrix was very good and uniform as compared to the untreated CNTs and it also showed a good interfacial bonding with the resin.

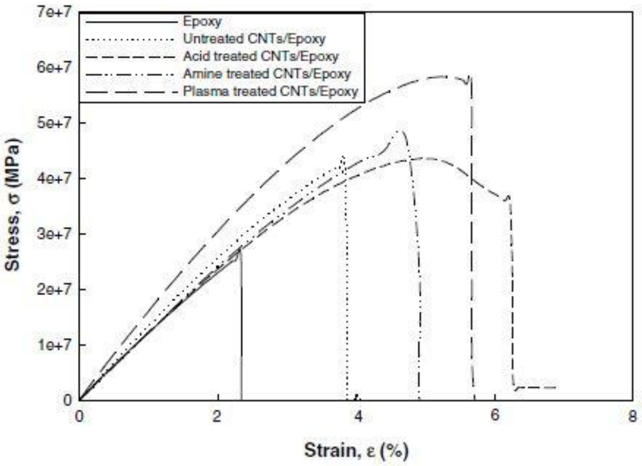

Figure 3.3: Stress vs. strain plots for epoxy and 1 wt. % CNT composites.

Allaoui et al. [9] evaluated the electrical and mechanical performance of MWCNT embedded epoxy composites. Improvement in properties was noticed when epoxy was improved with 1

% and 4 wt. % of CNT. Young's modulus and the yield strength of the 1 wt.% composite increased by 100 % and 200 % respectively over neat epoxy. Also the conductivity was increased on increasing the amount of CNT by 0–4 wt. %.due to percolation phenomenon.

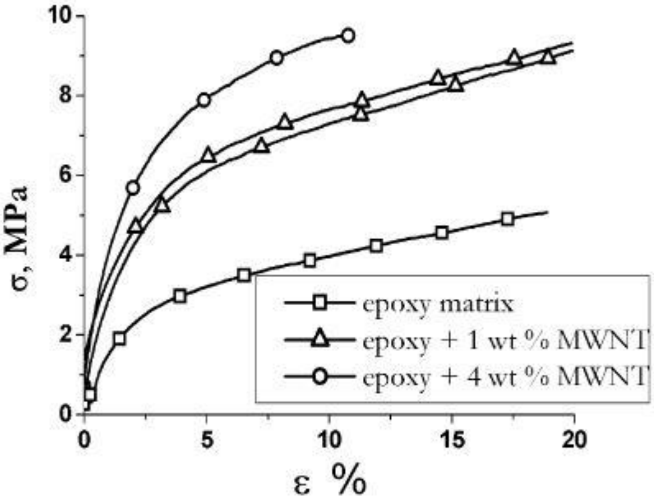

Figure 3.4: Tensile stress vs. strain curves for epoxy and nano composites.

The above stated literatures show that the improvement in mechanical performance at room temperature is possible by incorporating nano reinforcement in the epoxy composites. But very less literature has evaluated the performance of these nano particle embedded FRP composite at elevated temperature. As FRP composites are prone to degrade under elevated temperature, study of these nano particle embedded FRP composite and identification of failure modes generating at elevated temperature is also essential.

3.2 Materials

Below mentioned materials were required for fabricating conventional polymer composites as well as hybrid polymer composites.

1. Plain weave woven fabric E-glass fibers (FGP, RO-10) as reinforcement
2. Epoxy resin (Lapox, L-12) based on Bisphenol A as matrix.
3. Triethylene tetra amine (TETA) (K6-primary amine) as hardener.
4. Multi-walled carbon nanotubes (Outer diameter 6-9 nm and length 5 µm) as nano reinforcement.

3.3 Experimental procedure

3.3.1 Dispersion of MWCNT into epoxy resin

Before commencing the fabrication of MWCNT embedded glass/epoxy (CNT-GE) composite, the epoxy resin was modified by incorporating MWCNT to it using below mentioned procedure. The amount of CNT in GE composite was varied as 0.1 wt. %, 0.3 wt. % and 0.5 wt. % of epoxy. Three different laminates were fabricated using these different CNT compositions. Required amount of CNT was dispersed in 150 mL of acetone. This suspension was agitated for half hour at 1000 rpm using magnetic stirrer. Sonication of this suspension was done for 30 minutes in an ultrasonicator. The purpose of stirring and sonication is to deagglomerate the existing agglomerates of CNTs. The figure 3.5 shows the process of stirring and sonication for dispersing CNT in acetone. This CNT/acetone mixture was added to pre-weighed epoxy, which was brought to sufficient fluidity by heating. Further, stirring of epoxy/CNT/acetone mixture was done at 1000 rpm for 2 hr at 70 °C. Sonication was thereafter again carried out at 70 °C for 1 hr. At this stage, evaporation of all acetone was made certain. The left epoxy/CNT suspension was kept in vacuum for 12 hr to aid in removal of air bubbles entrapped in the suspension.

Magnetic stirring

Sonication

Figure 3.5: Dispersing CNT in acetone.

3.3.2 Fabrication of Fiber reinforced nano-composites

Sufficient amount of hardener (10 wt. % of epoxy) was blended and stirred properly in the epoxy/CNT suspension. Matrix and fibers were taken approximately in 1:1 proportion by weight. Fabrication of laminates was done by hand lay-up process using 14 layers of E-glass fibres and the modified epoxy resin. Curing was done in a hot press at 60 °C with applied pressure of 10 kg/cm^2 for 20 minutes. Similarly using the same parameters as used in CNT-GE composite, the control glass fiber/epoxy (GE) composite laminate was fabricated using neat epoxy and 14 layers of glass fiber by hand lay-up method followed by hot pressing. The laminates were allowed to keep at room temperature for 24 hrs. Flexural (as per ASTM D7264) samples were cut from the prepared laminates with a diamond cutter. The samples were kept in oven at 140 °C for 6 hr for post-curing. The methodology is shown in figure 3.6.

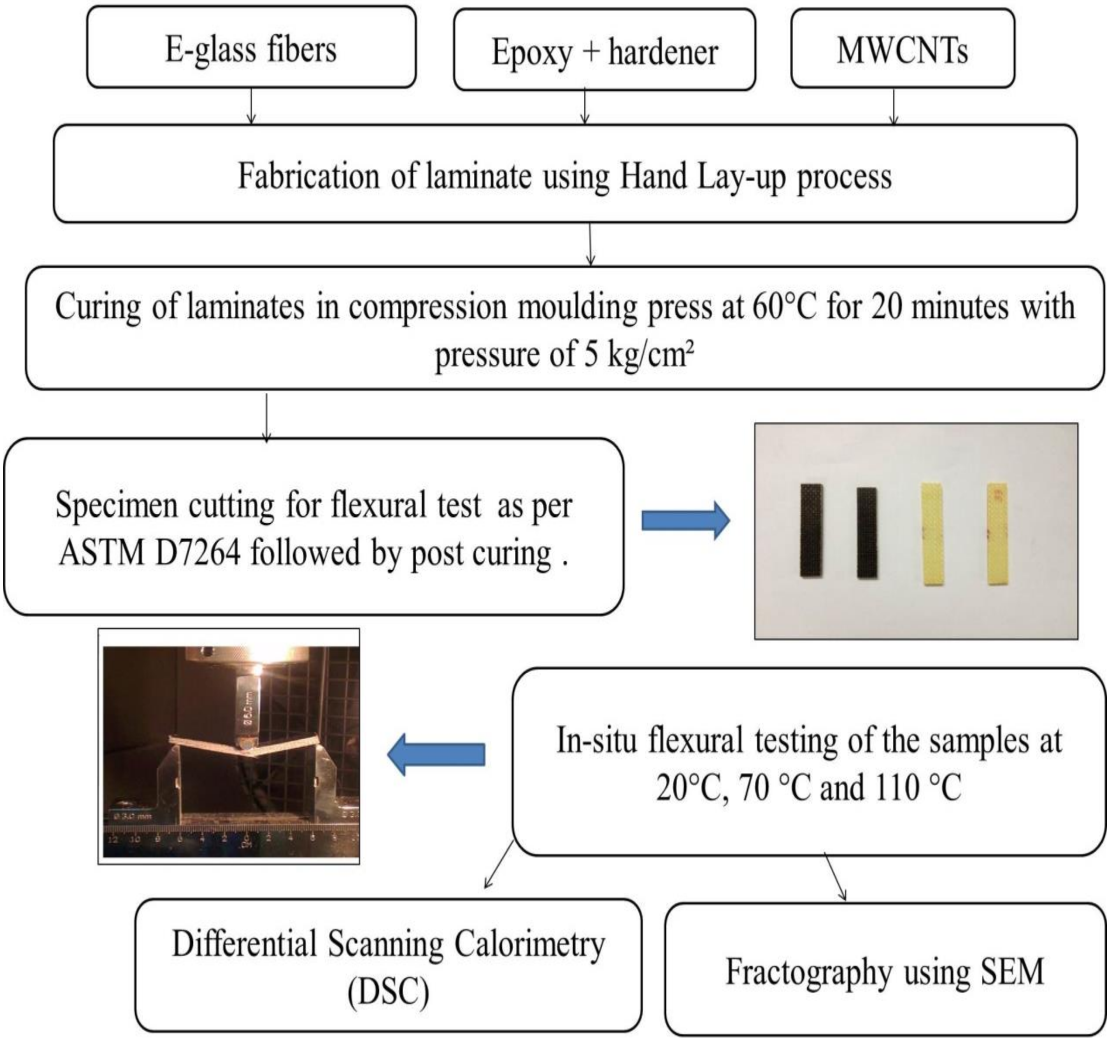

Figure 3.6: Experimental methodology of fabricating CNT incorporated GE composite.

3.4 Material characterization

3.4.1 Mechanical characterization

In-situ flexural testing of the samples was done at room temperature (20 °C), 70 °C, 90^{o}C and 110 °C (with a holding time of 10 minutes) with a 1 mm/min loading rate using the 3-point fixture of UTM (Instron 5967) (as seen in figure 3.7) following ASTM D7264 standard.

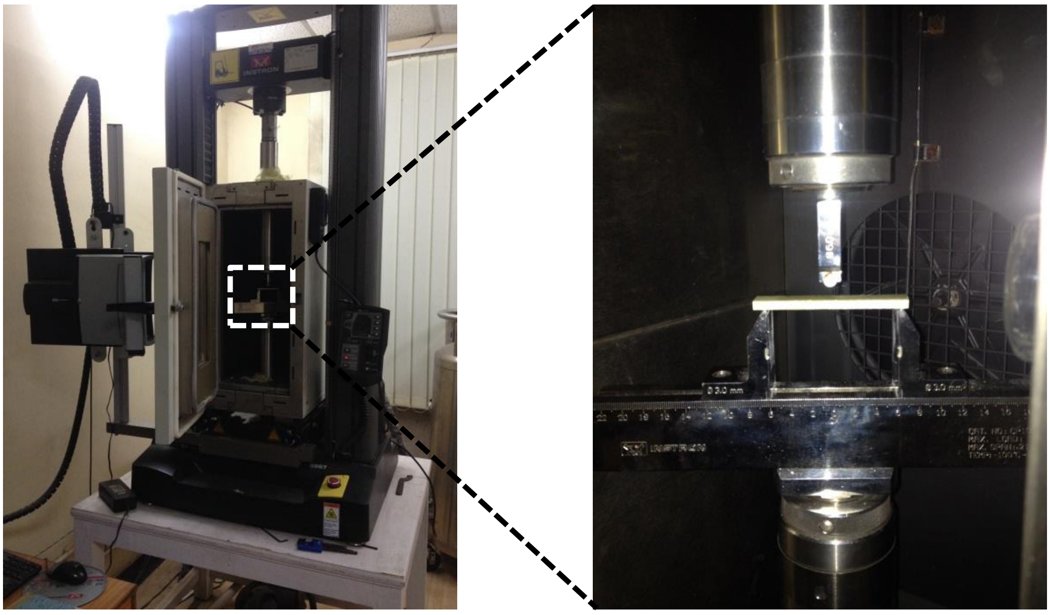

Figure 3.7: Experimental chamber of UTM (Instron 5967).

3.4.2 Fractographic analysis

The post fractured samples were analysed to identify various damage and degradation micro-mechanisms responsible for the bulk failure of the material using scanning electron microscope JEOL-JSM 6480 LVSEM operated at 20KV.

3.5 Results and discussion

3.5.1 Flexural behaviour at various testing temperatures

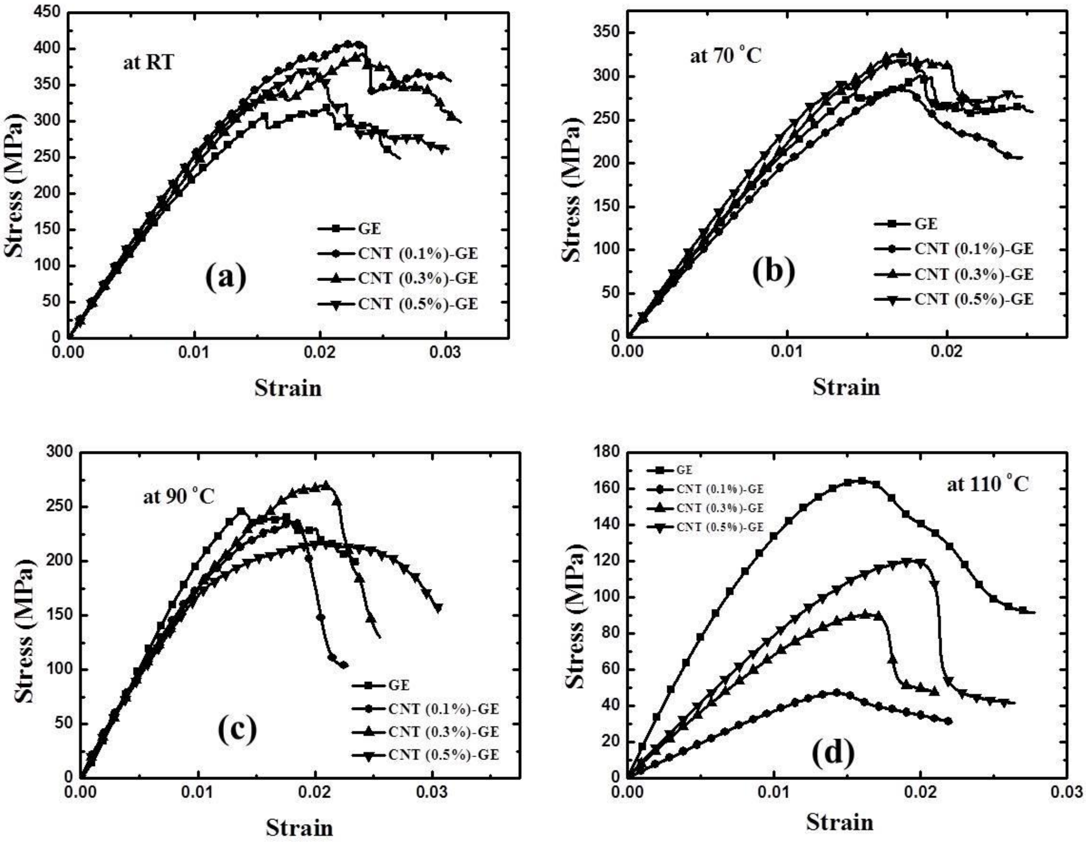

Figure 3.8: Stress vs. strain curves of GE and CNT-GE composites at (a) room temperature (20 ^{o}C), (b) 70 ^{o}C, (c) 90 ^{o}C and (d) 110 ^{o}C.

The above figure 3.8 shows the stress vs. strain plots of GE composite and CNT (0.1%, 0.3% and 0.5%)-GE composites when tested at various in-situ testing temperatures i.e. at room temperature (20 ^{o}C), 70 ^{o}C, 90 ^{o}C and 110 ^{o}C.

Figure 3.9 shows the variation in strength and modulus vs. wt. % of CNT. It can be seen that on incorporating CNTs, increment in flexural strength was noticed in its as fabricated condition. CNT (0.1%)-GE showed the maximum increment in strength of 32.74 % as compared to GE composite among all the composites fabricated. The reinforcement efficiency (i.e. the ratio of increment in strength over content of CNT) noticed in this study was 1038 MPa per % CNT which came out to be quite near to the one obtained by Rahman et al. [7] when he fabricated glass/epoxy composite by fusing amino-functionalised CNTs in it. The reinforcement efficiency obtained was 1000 MPa per % CNT. The reason for this increased strength and modulus might be ascribed to the availability of high CNT/epoxy interfacial area because of very high specific surface area of CNTs, thus leading to more load/stress transfer across interface. Thus, this results in requirement of more stress in breaking a specimen. On the contrary, CNT (0.3%)-GE composite and CNT (0.5%)-GE composite showed less strength as compared to CNT (0.1%)-GE composite. Due to high amount of CNTs, formation of CNT agglomerates takes place in the matrix. These agglomerates acts as stress enhancers and thus lower the stress required in breaking the sample. Hence results in less strength as compared to CNT (0.1%)-GE composite.

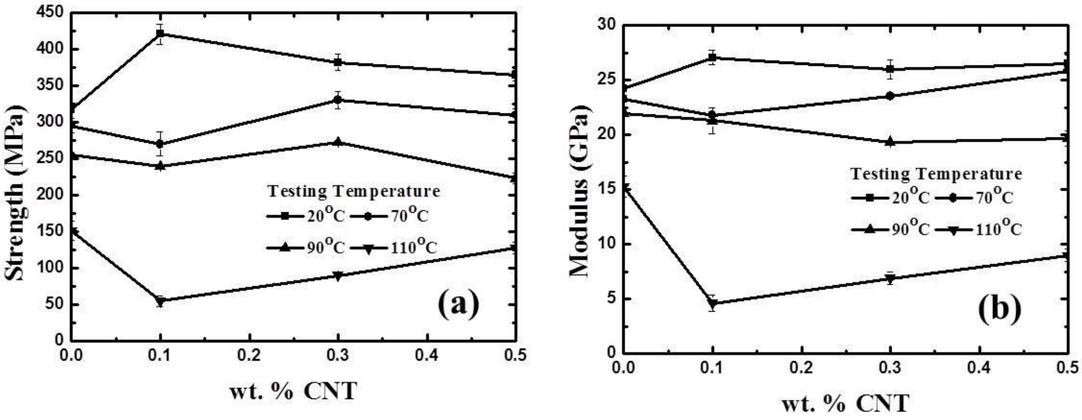

Figure 3.9: Variation in (a) strength and (b) modulus with wt. % of CNT.

In-situ testing at 70 ^{o}C and 90 ^{o}C caused decrease in strength of GE composite as well as all the CNT-GE composites. The reduction in strength for GE composite may be because of formation of micro-voids and micro cracks in matrix as well as at interface due to different co-efficient of thermal expansion of epoxy (6.2×10^{-5} K^{-1}) and E-glass fibers ($5\text{-}12 \times 10^{-6}$ K^{-1}) [10]. In addition to the glass fiber/epoxy interfacial area, CNT/epoxy interfacial area also exists in case of CNT-GE composites. Hence due to more interfacial area, more micro voids and micro-cracks are generated due to different thermal expansion co-efficients of CNT ($0.73\text{–}1.49 \times 10^{-5}$ K^{-1}) [11], epoxy and glass fibers. The reduction in strength noticed at 70 ^{o}C for GE composite, CNT (0.3%)-GE composite and CNT (0.5%)-GE composite was 6.8 %, 13.54 % and 14.91 % respectively as compared to as fabricated conditions.

The maximum reduction in flexural strength by 35.38 % was observed in case of CNT (0.1%)-GE composite as compared to the strength in as fabricated condition. The reason may be ascribed to even distribution of CNTs in epoxy leading to more interfacial area as compared to CNT (0.3%)-GE and CNT (0.5%)-GE composites, where agglomerated decrease the interfacial area. Further at elevated temperature, micro cracks and voids generation sites are more in CNT (0.1%)-GE due to more availability of interfacial area. Hence it shows the least strength among all the fabricated composites.

At 90 °C, the maximum reduction in strength was noticed for CNT (0.1%)-GE composite and the reduction was by 43.14 %. The decrement in strength noticed at 90 °C for GE composite, CNT (0.3%)-GE composite and CNT (0.5%)-GE composite was 19.45 %, 28.81 % and 38.71 % respectively as compared to as fabricated condition.

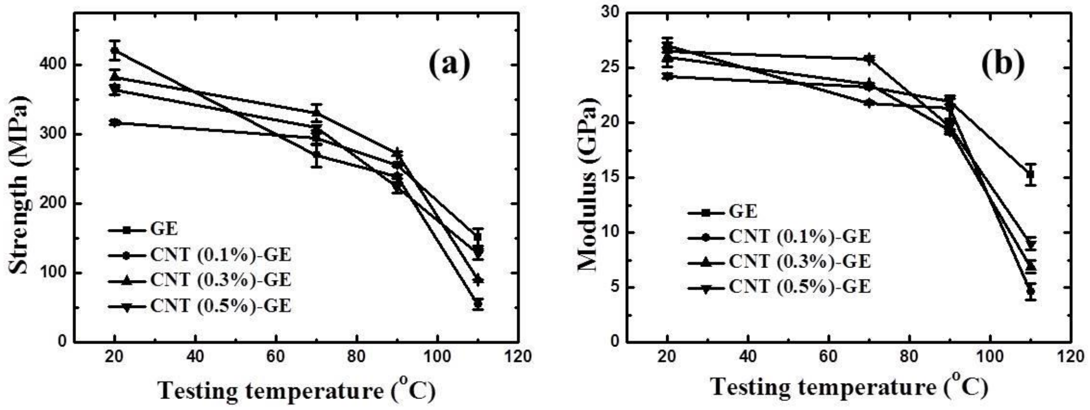

Figure 3.10: Variation in (a) strength and (b) modulus with testing temperature.

When the GE and CNT-GE samples were tested at 110 °C, very high reduction in strength was obtained. The maximum decrement in flexural strength by 87 % was noticed for CNT (0.1%)-GE composites as compared to as fabricated condition. As the samples are tested near the glass transition temperature of the matrix, very high softening of matrix occurs. This softening of matrix leads to huge decrement in strength. Also the cracks formed due to coalescence of micro-voids increase in number and result in overall decrement in strength for all the composites. The decrement in strength noticed at 110 °C for GE composite, CNT (0.3%)-GE composite and CNT (0.5%)-GE composite was 52.19 %, 87 % and 64.91 % respectively as compared to as fabricated condition.

It can be visible from the figure 3.9 (b) that the modulus also has nearly followed the same trend as strength for both GE as well as CNT-GE composites at various testing temperatures.

3.5.2 Constitutive flexural deformation model

The deformation/failure of laminated composite is the result of a number of failure mechanisms like buckling, formation of shear cusps, kink bands, etc. this finally lead to failure modes like matrix cracking, fiber/matrix interfacial debonding, fiber fragmentation, etc. The stress (σ) - strain (ε) relationship for a FRP composite can be modelled using Weibull distribution function [6,12].

$$\sigma = E\varepsilon \exp\left[-\left(\frac{E\varepsilon}{\sigma_o}\right)^{\beta}\right] \tag{1}$$

Here, E represents flexural modulus. σ_o and β represents scale and shape parameters respectively of Weibull function respectively. σ_o is measure of nominal strength of the composite and β is measure of unpredictability in strength. To evaluate σ_o and β, consider taking double log on both the side of equation 2.

$$\ln\left[\ln\left(\frac{E\varepsilon}{\sigma}\right)\right] = \beta\,\ln(E\varepsilon) - \beta\ln(\sigma_o) \tag{2}$$

Equation 2 is an indicative of straight line between $\ln(E\varepsilon)$ and $\ln\left[\ln\left(\frac{E\varepsilon}{\sigma}\right)\right]$, which can be seen from figure 3.11. The slope of this straight line gives the value of β and from the value of intercept and β, σ_o can be determined.

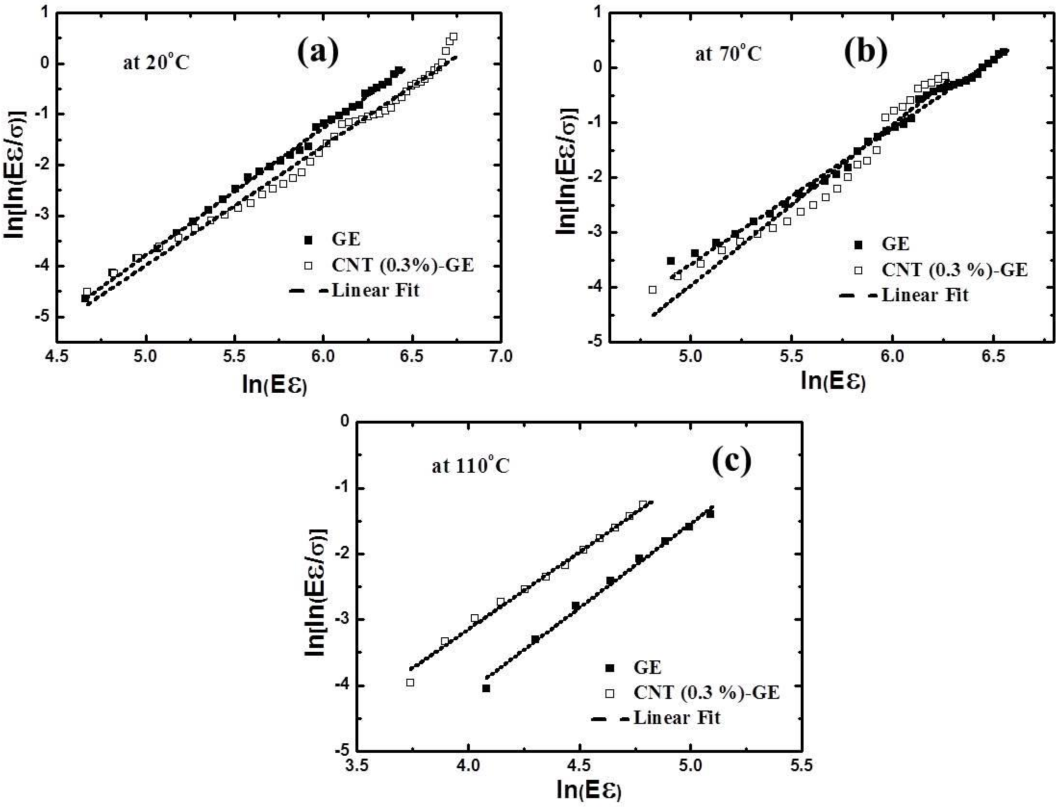

Figure 3.11: Weibull fitting of GE and CNT (0.3%)-GE composites at (a) room temperature, (b) 70 °C and (c) 110 °C.

Critical parameters of Weibull function for GE and CNT-GE composites are obtained from figure 3.11 and are reported in tables 3.1 and 3.2.

Table-3.1: Shape (β) parameters for GE and CNT-GE composites at various temperatures

Temperature (^{o}C)	GE	CNT (0.1%)-GE	CNT (0.3%)-GE	CNT (0.5%)-GE
20	2.52	2.48	2.38	2.34
70	2.48	2.55	2.93	2.60
90	2.79	2.19	1.94	2.19
110	2.23	2.08	2.35	2.44

Table-3.2: Scale parameter (σ_o) (MPa) for GE and CNT-GE composites at various temperatures

Temperature (^{o}C)	GE	CNT (0.1%)-GE	CNT (0.3%)-GE	CNT (0.5%)-GE
20	663.69	845.75	813.77	769.16
70	627.17	580.51	567.72	667.95
90	522.94	533.77	652.56	503.32
110	312.22	101.0	208.18	267.65

The experimental and simulated stresses vs. strain plots were drawn for GE and CNT (0.1% and 0.5%)-GE composite at room temperature and 90 ^{o}C using the data obtained from table 3.1 and 3.2 as seen from figure 3.12. This figure indicates that the experimental data and the simulated results are in close agreement with each other.

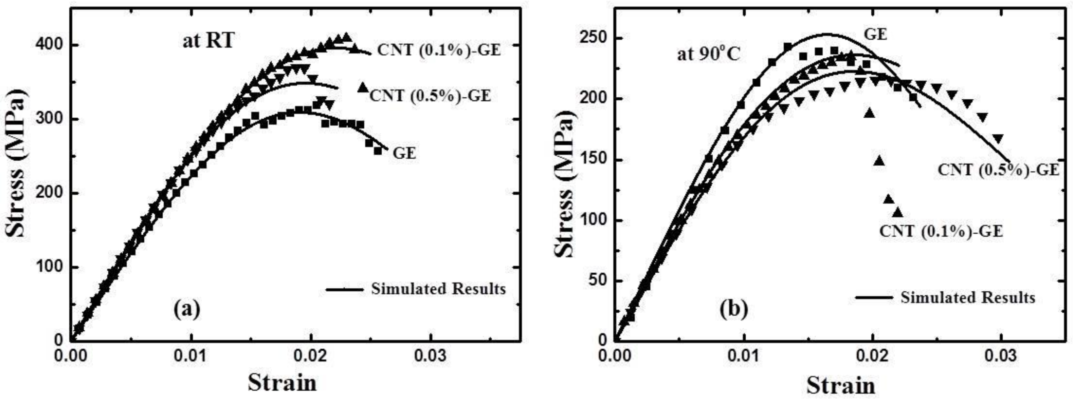

Figure 3.12: Comparison between experimental and simulates stress-strain relationship.

Figure 3.13 shows the variation in shape parameter and scale parameter with respect to testing temperature. It shows that the shape parameter has an irregular and a non-linear trend for all the composites and for all the testing temperatures.

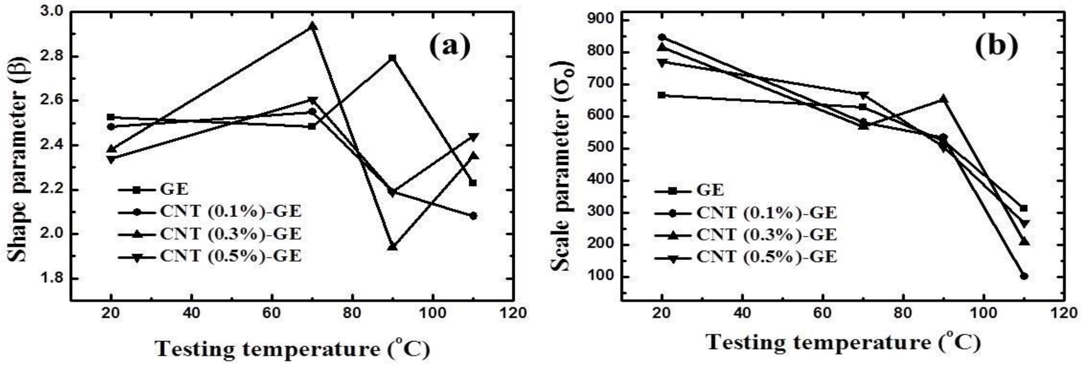

Figure 3.13: Variation in shape parameter and scale parameter with testing temperature.

3.5.3 Thermal analysis using DSC

From figure 3.14 it is observed that for as fabricated samples, on adding 0.1 % CNT in epoxy there was lowering in glass transition temperature (T_g) by 13°C as compared to control GE composite. This lowering in T_g may be due to entrapment of CNTs between polymer cross-links chains and thus will give rise to increase in free volume. The uniform dispersion of CNTs in matrix of CNT (0.1%)-GE may be the reason of this entrapment. On further increasing the amount of CNT i.e. in case of 0.3 % and 0.5 %, agglomerates of CNT may form in the resin. These agglomerates, due to their micro size, may not be able to hinder the cross-link chains and restrict the mobility of matrix around these agglomerates. Thus this results in further increase in T_g.

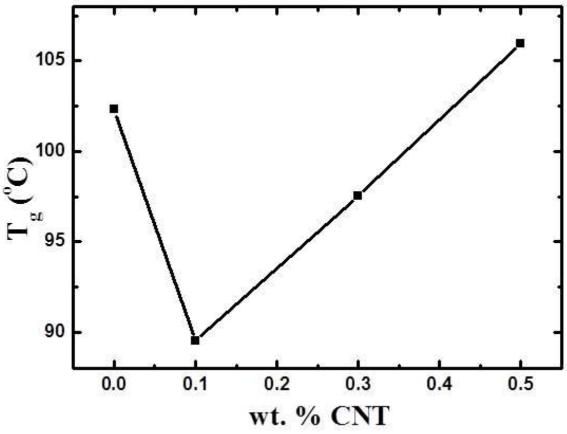

Figure 3.14: Variation in glass transition temperature with wt. % of CNT.

Also from the figure it can be seen that the T_g of CNT (0.1%)-GE composite is the lowest of all the composites fabricated. Homologous transition temperature i.e. T/T_g obtained for CNT (0.1%)-GE was the maximum among all and hence this also reflected the reason behind high strength of CNT (0.1%)-GE in as fabricated condition.

3.6 Fractography

The fractured surfaces of GE and CNT-GE composites were analysed under SEM to identify damage mechanisms responsible for the overall failure of the composites.

Figure 3.15 shows the SEM micrographs of the fractured GE surface at (a) room temperature and (b) 110 ^{o}C. At room temperature it can be noticed that Delamination is the cause of failure of the composite. Delamination is generally occurring due to fiber/matrix debonding when the composite is undergoing application of load. But as the testing temperature is increased to 110 ^{o}C, riverlines markings are observed on the surface of matrix. These riverlines are formed due to soft behaviour of matrix. At this temperature i.e. near glass transition temperature of matrix, epoxy becomes soft and starts flowing. Thus it also reflects drastic reduction in strength at 110 ^{o}C (as evident from figure 3.9).

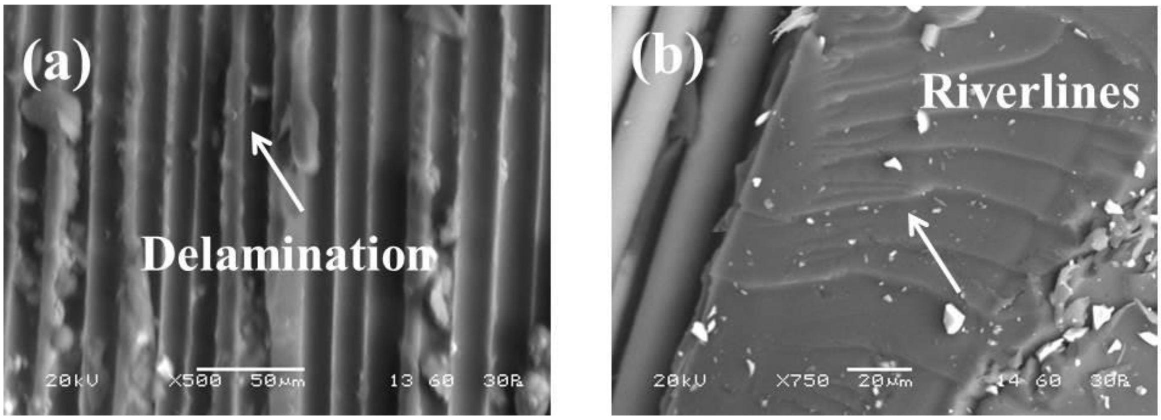

Figure 3.15: SEM images of fractured surfaces of GE composite at (a) 20 °C and (b) 110 °C.

Figure 3.16 shows SEM images of CNT-GE composite’s surface at (a) room temperature and (b) 110 ^{o}C. It is seen that at room temperature the failure mode observed in CNT (0.1)-GE composite was delamination. At 110 ^{o}C in addition to delamination, ply splitting is also observed in this composite. This delamination along with ply splitting will lower the strength and stiffness of the composite to a much high extend. This is also reflected from the figure 3.9.

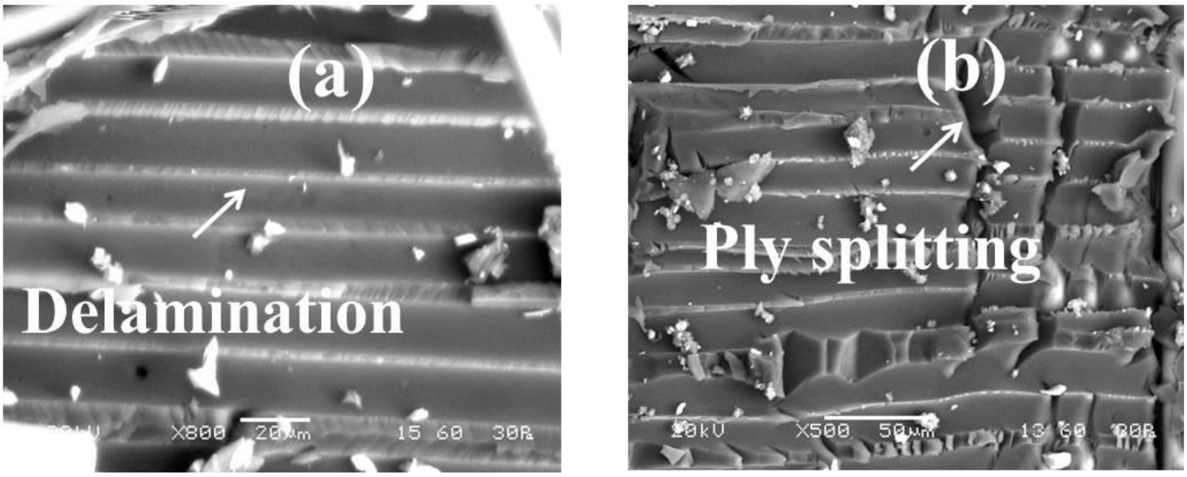

Figure 3.16: SEM images of fractured surfaces of CNT-GE at (a) 20 °C and (b) 110 °C.

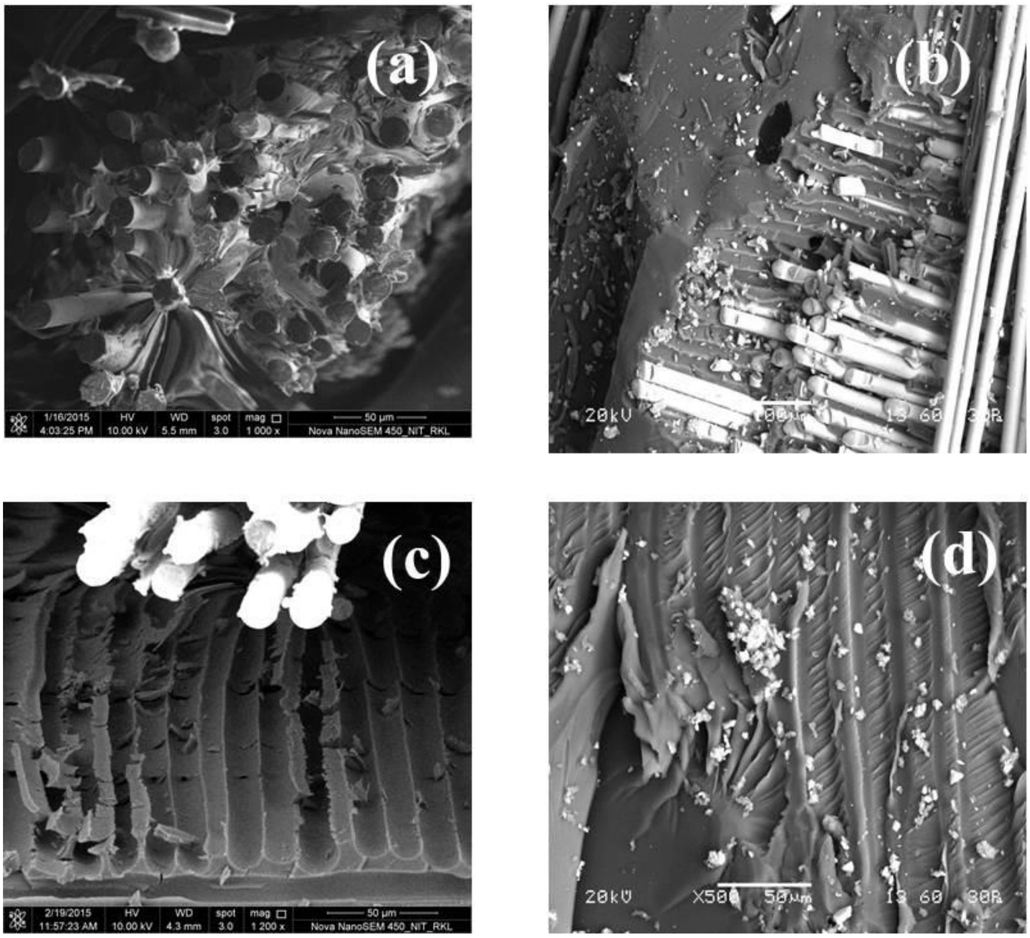

Figure 3.17: SEM images of fractured surfaces of (a) GE at 20 °C, (b) GE at 90 °C, (c) CNT (0.3%)-GE at 20 °C, and (d) CNT (0.3%)-GE at 90 °C.

Fiber/matrix debonding is the main culprit for generation of delamination. It is shown here in figure 3.17 (a) for GE composite at 20 ^{o}C and (c) for CNT-GE at 20 ^{o}C. Apart from riverlines marking, generation of micro voids are also observed in GE composite at 90 ^{o}C as shown in figure 3.17 (b). Extensive riverlines are visible on the surface of epoxy in case of CNT (0.3%)-GE at 90 ^{o}C. These lines as shown in figure 3.17 (d) will meet on load application and end in a potential crack.

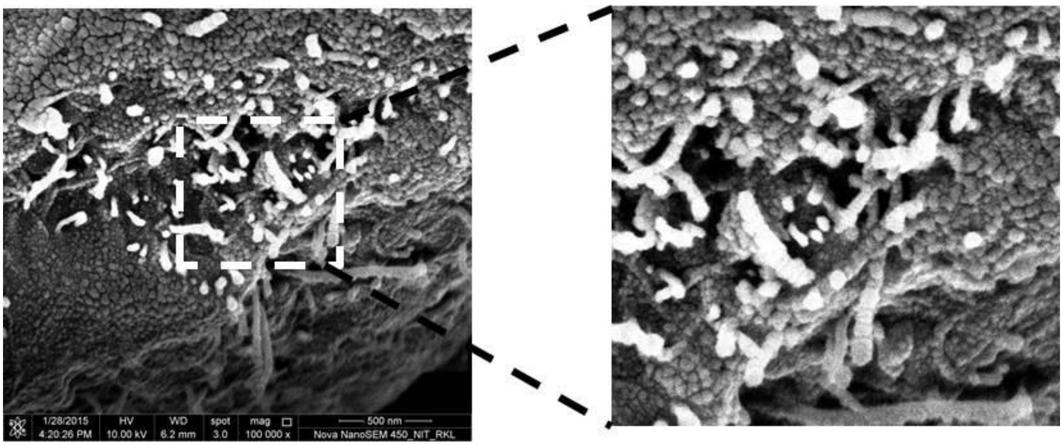

Figure 3.18: Dispersion of CNT in CNT (0.1%)-GE composite.

The uniform dispersion of CNTs in epoxy resin of CNT (0.1%)-GE composite is evident from figure 3.18. This even distribution of CNTs in matrix may hold the key for higher strength of this composite at room temperature as compared to all other composites fabricated.

3.7 Conclusion

The following conclusions can be drawn from the above investigation.

- Incorporating CNT in GE composite increased the mechanical properties of GE composite in its as fabricated condition. CNT (0.1%)-GE showed 32.74 % increment in flexural strength as compared to GE due to increased load transfer because of increased interfacial area.
- Elevated temperature testing at 70 ^{o}C and 90 ^{o}C caused reduction in strength and modulus of GE as well as CNT-GE composites. This decreased performance is attributed to the formation of micro voids and cracks at the interface due to differential expansion co-efficient of epoxy, CNT and glass fibers.
- At 70 ^{o}C the maximum reduction in flexural strength was observed in case of CNT (0.1%)-GE composite by 35.38 % as compared to the strength in as fabricated

condition due to availability of more interfacial area which provides more potential sites for generation of micro cracks and voids.

- At 110 ^{o}C, GE composite shows the maximum strength among all the composites. Hence CNT reinforcement becomes ineffective when the testing is done at a temperature which is near the glass transition temperature of matrix.

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List of Publications during M.Tech Project

[1] K. K. Mahato, **M. J. Shukla**, D. S. Kumar, and B. C. Ray, “In- service Performance of Fiber Reinforced Polymer Composite in Different Environmental Conditions: A Review,” J. Adv. Res. Manuf. Mater. Sci. Metall. Eng., vol. 1, no. 2, pp. 55–88, 2014.

[2] **M. J. Shukla**, D. S. Kumar, K. K. Mahato, D. K. Rathore, R. K. Prusty, and B. C. Ray, “A comparative study of the mechanical performance of Glass and Glass/Carbon hybrid polymer composites at different temperature environments,” IOP Conf. Ser. Mater. Sci. Eng., vol. 75, no. 1, p. 012002, Feb. 2015.

[3] D. S. Kumar, **M. J. Shukla**, K. K. Mahato, D. K. Rathore, R. K. Prusty, and B. C. Ray, “Effect of post-curing on thermal and mechanical behavior of GFRP composites,” IOP Conf. Ser. Mater. Sci. Eng., vol. 75, no. 1, p. 012012, 2015.

[4] R. K. Prusty, D. K. Rathore, **M. J. Shukla** and B. C. Ray, “Flexural behaviour of CNT-filled glass/epoxy composites in an in-situ environment emphasizing temperature variation,” Journal: Composites Part B, Elsevier (under review after minor revision).

[5] **M. J. Shukla**, D. S. Kumar, D. K. Rathore, R. K. Prusty, "An assessment of flexural performance of MWCNT embedded glass/epoxy composite after liquid nitrogen conditioning", Journal of Composite Materials, Sagepub (under review).

Symposium/Conference attended

[1] Presented a poster on “Flexural behaviour of CNT-filled glass/epoxy composites in an in-situ environment emphasizing temperature variation”, at National symposium for Materials Research MR-15, IIT Bombay during 21st -22nd May, 2015.