MECHANICAL INVESTIGATION OF CRYO-TREATED SILANIZED GRAPHENE OXIDE MODIFIED CARBON FIBER REINFORCED POLYMER COMPOSITE

A PROJECT REPORT

submitted by

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to

the APJ Abdul Kalam Technological University

in partial fulfillment of the requirements for the award of the Degree

of

Master of Technology

In

Computer Integrated Manufacturing

Department of Mechanical Engineering

TKM College Of Engineering

Kollam

SEPTEMBER, 2022

DECLARATION

I, Rajalekshmi S, hereby declare that the project report “Mechanical Investigation of Cryo-Treated Silanized Graphene Oxide Modified CFRP”, submitted for partial fulfillment of the requirements for the award of degree of Master of Technology ofthe APJ Abdul Kalam Technological University, Kerala is a bonafide work done by me under supervision of Dr. K.E. Reby Roy, Professor, Department of Mechanical Engineering, TKM College of Engineering, Kollam. This submission represents my ideas in my own words and where ideas or words of others have been included, I have adequately and accurately cited and referenced the original sources. I also declare that I have adhered to ethics of academic honesty and integrity and have not misrepresented or fabricated any data or idea or fact or source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the institute and/or the University and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been obtained. This report has not been previously formed the basis for the award of any degree, diploma or similar title of any other University.

Kollam

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CERTIFICATE

This is to certify that the report entitled **“MECHANICAL INVESTIGATION OF CRYO-TREATED SILANIZED GRAPHENE OXIDE MODIFIED CARBON FIBER REINFORCED POLYMER COMPOSITE”** submitted by **RAJALEKSHMI S, TKM20MECI11** to the APJ Abdul Kalam Technological University in partial fulfillment of the requirements for the award of the Degree of Master of Technology in Computer Integrated Manufacturing, Department of Mechanical Engineering, is a bonafide record of the project work carried out by him/her under my/our guidance and supervision. This report in any form has not been submitted to any other University or Institute for any purpose.

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ACKNOWLEDGEMENT

I take this opportunity to express my deep sense of gratitude and sincere thanks to all who helped me to complete the project successfully.

I am greatly thankful to **Dr. T.A. Shahul Hameed**, Principal, TKM College of Engineering and **Dr. Dileep P.N.**, Head of Mechanical Engineering Department for providing all required resources for successful completion of my project.

I am deeply indebted to my guide **Dr. K.E. Reby Roy**, Professor, Department of Mechanical Engineering for his excellent guidance, positive criticism, and valuable comments.

I am thankful to **Prof. Kannan S.** , P.G. Coordinator, Department of Mechanical Engineering & **Prof. Faizal N.S.**, Assistant Professor, Department of Mechanical Engineering for their great support and guidance throughout my project.

I am highly thankful to **Mr. Manu M.** Research Scholar (Ph.D.), Department of Mechanical Engineering for his great support and guidance in the successful completion of this project.

I am thankful to Sophisticated Instrumentation Facility, National Institute of Technology Tiruchirappalli, India for their timely help and support to complete my project.

I am also thankful to the teaching and non-teaching staff of T.K.M. College of Engineering who have supported us in the successful completion of our project.

Finally, I thank my parents, friends, and near and dear ones who directly and indirectly contributed to the successful completion of my project.

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ABSTRACT

The Space industry is still in search for a suitable material for cryogenic tanks. Carbon Fiber Reinforced Plastic composites is identified as a compatible material for cryogenic applications. Various researches are being conducted using many modifiers and additives to study its effect on different properties of CFRP composites. Silane Graphene Oxide is being coated on the carbon fiber using Electrophoretic Deposition method. Composite panels of epoxy and the Silane Graphene Oxide coated carbon fibers are fabricated by Vacuum Assisted Resin Transfer Molding technique (VARTM). The samples required for determining tensile strength, flexural strength and impact strength were cut out according to the ASTM standards. The 1g/L SGO-modified CFRP samples at room temperature have shown an enhancement in tensile strength, and impact energy by 13.16 % and 14.03% respectively. While the 1.5g/L SGO-modified CFRP showcased an increment in the flexural strength by 24.18% at room conditions. To study the improvement in the cryo-treated SGO modified CFRP the tests are conducted after dipping the samples in liquid nitrogen for 20 minutes. The results obtained after the tests showed an improvement in the corresponding properties. The tensile strength, impact energy and flexural strength of cryo-treated 1g/L SGO- modified CFRP portrayed an increase by 15.17%, 17.59% and 35.29% respectively. Thermogravimetric analysis and Differential Scanning Calorimetry tests were also conducted to study about the thermal stability and specific heat capacity range of modified samples. From the inference obtained from the thermal analysis and mechanical tests 1g/L SGO-modified CFRP has the better performing composition.

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ABBREVIATIONS

3-APTES	3-Aminopropyltriethoxysilane
CF	Carbon fiber
CFRP	Carbon fiber reinforced polymer
CT	Cryo-treated
CTE	Coefficient of thermal expansion
DGEBA	Diglycidyl ether of bisphenol A
DSC	Differential Scanning Calorimetry
EP	Epoxy
EPD	Electrophoretic deposition
FRP	Fiber reinforced polymer
FTIR	Fourier transform infrared
GO	Graphene oxide
PES	Polyethersulfone
PMC	Polymer matrix composite
RT	Room temperature
SGO	Silanized graphene oxide
TGA	Thermogravimetric analysis
UT	Untreated
VARTM	Vacuum-assisted resin transfer molding

CHAPTER 1

INTRODUCTION

1.1 GENERAL BACKGROUND

Even before the onset of technologies, newly advanced materials, and sophisticated manufacturing techniques, composite systems naturally existed between us. Numerous things, including plants and animals, are composed of fibers clearly visible in trees and their leaves, as well as in bird wings and fish fins. The most intricate fiber composite system is the human body. It is composed primarily of a musculoskeletal system, which includes bones, muscles, and tendons. These things are composite systems on a microscopic level perception. Similarly, on macroscopic scales, composite systems can be created by combining two or more constituents. In 400 B.C. Egyptians found the first-ever paper which was formed by stacking the leaves of Papyrus plants. Likewise in earlier days, straws were used in mud bricks as reinforcements which can be quoted as an example of fiber-reinforced ceramic matrix composites. Thus, even before coining the term “composites” there were many instances in their life where they used composites for different applications.

Meanwhile, material competition is an ever-evolving process that focuses on identifying new and better materials for various applications. The driving force for the identification of a better-performing material considers many elements such as cost, availability, ease of application, design requirements and the list go on. In earlier days metals were considered as an important category of industrial material for all applications including structural applications, automotive applications, construction applications, space applications, etc. Improved performance demands on engineering materials have paved the way to extensive research and development of new and advanced materials. This inevitably led to a revival of the old idea of fusing various materials together to create an entire composite material that meets the needs of the user. Composites are made up of two or more materials with desirable properties in a pre-defined manner to cult a new material possessing better properties than that of its homogenous constituents. Such composite material systems provide a performance that is impossible by the individual constituents and have the significant benefit of a flexible design; in other words, one can theoretically tailor-make the material in accordance with the requirements of an ideal design. Hence, they are also called as Engineerable materials.

As the composites are made up of different combinations, a myriad of new materials with different properties can be identified. Conventionally composites are made up of two main constituents i.e., matrix the constituent present in larger proportion, and reinforcements the constituent present in smaller proportion. The reinforcements come in a variety of shapes, including flakes, sheets, short fibers, whiskers, and particles. Since materials are stronger and stiffer in their fibrous form than in any other form, it turns out that the majority of reinforcements employed in composites have this form. Our study is mainly interested in the so-called advanced fibers in this category, which have extremely high strength, extremely high stiffness, and extremely low density. While considering the matrix material, is the main constituent that gives shape to the composite, keeps the reinforcements in place, and effectively transfers and shares the load on the composite part. Composites can be broadly classified according to the type of matrix material, there are different classes of composites such as Polymer Matrix Composites (PMCs), Ceramic Matrix Composites (CMCs), Metal Matrix Composites (MMCs). Among these, the PMCs have gained higher importance in applications like the automotive industries, aerospace and aircraft industry, sports and electronic gadgets, biomedical applications, etc., due to their appreciable properties such as low specific weight, high corrosion resistance, electrical and thermal insulative property, ease of processing and production, etc. This study is focused on polymer matrix composite system.

A polymer primary phase with a secondary phase embedded as fibers, particles, or flakes makes up a polymer matrix composite (PMC). Of the three synthetic composite groups, PMCs are the most significant from a commercial standpoint. They consist of the majority of plastic molding compounds, carbon-black-reinforced rubber, and fiber-reinforced polymers (FRPs). The term "composite" is most closely associated with FRPs of the three. FRP is typically the composite that comes to mind when "composite material" is mentioned to a design engineer. The matrix polymer can be thermosetting or thermoplastic polymer. Usually, thermosetting polymers like unsaturated polyester or epoxy are used. The PMCs' fibers might be continuous, woven as a fabric, or discontinuous (chopped). The main fibers used in FRPs are Kevlar 49, carbon, and glass.

The matrix acts as a crucial foundation for evenly distributing the fibers throughout the structure. The matrix, reinforcing fibers, and interphase contents of PMC affect its mechanical and physicochemical properties. The PMC's properties such as tensile strength, fracture toughness, stiffness, etc., are altered by the reinforcing fibers. Thus, it enables more scope for the alteration of properties according to the application. The laminar structure, which is the most popular type of FRP, is created by stacking and adhering small layers of fiber and polymer together until the appropriate thickness is reached. A specific degree of anisotropy in the properties of the laminate can be achieved by altering the fiber orientation among the layers. This technique is used to create thin-section pieces for things like boat hulls, car and truck body panels, and aviation wing and fuselage sections.

Fiber-reinforced plastics stand out as engineering materials due to a variety of appealing qualities. Most prominent are low specific gravity, high modulus-to-weight ratio, and high strength-to-weight ratio. Although the weight of a typical FRP is only approximately 5% of steel, its strength and modulus are comparable in the fiber direction. As the fiber content increases the properties can also be enhanced. Aside from their dimensional stability and corrosion resistance, fiber-reinforced plastics also have significant anisotropy in their properties, the low thermal expansion for many FRPs, which results in good dimensional stability, and good fatigue strength contribute to their appreciable qualities, despite the fact that polymers are soluble in a variety of chemicals.

Fiber-reinforced polymers have steadily increased in use during the past three decades, frequently replacing metals in applications that need great strength and low weight. One of the greatest markets for advanced composites is the aircraft sector. Aircraft weight reduction is a constant design goal to improve fuel economy and payload capacity. The use of sophisticated composite materials in both commercial and military aircraft has continuously expanded. FRPs make up a sizable portion of the structural weight of modern aircraft and helicopters. 50% by weight of the new Boeing 787 Dreamliner is made of composite material (carbon fiber reinforced plastic). That makes up around 80% of the aircraft's volume. The fuselage, wings, tail, doors, and interior are all made of composite materials. Comparatively, the Boeing 777 only features roughly 12% of composites. Another significant industry that uses FRPs is the automotive sector. FRP body panels for cars and truck cabs are the most obvious uses. Other applications include sports equipment, recreational products, etc.

Carbon Fiber Reinforced Polymer (CFRP) is a common PMC material that is being widely used in the aerospace and automotive industries. CFRP is considered as a material for weight-critical parts since it has high weight-specific stiffness and strength compared to conventional engineering materials like steel. The strength of the CFRP depends on the type of application, the right combination of fiber to resin, length, type, the orientation of fibers, use of anchors, and form (sheet, plate). By adjusting the fiber to matrix ratio, stacking order, number of plies, and direction of the plies, CFRPs can also be customized to their intended use. To have the best-performing material for the particular loading and geometry, all of these factors can be optimized. Moreover, the ease of machinability and its inertness towards moisture, and alkaline environments had made it eligible for constructional purposes also. Thus, the application arena of CFRP is very huge and it is important to carry out various explorative studies on CFRP’s performance so that we can utilize the material in an efficient and effective manner.

As mentioned earlier the properties of PMCs can be altered by numerous means including the fiber-matrix ratio, the orientation of fibers, the number of plies, etc. Further, with a microscopic approach, the region between the fibers and matrix i.e., the interphase, contributes unique micromechanical properties and influences the bulk composite properties. Due to the very smooth surface of CF and its chemical inertness, the interface needs to be changed and carefully managed, which can be done by boosting the carbon fiber's surface polarity, enhancing the wettability of the fiber with the resin, and encouraging chemical reactions. One such modification which can bring a significant change in the behavior of CFRP includes chemical modifications such as matrix modification, fiber modification, and fiber/matrix modification. In matrix modification, materials like fillers, modifiers, toughening agents, thermoplastic particles, carbon nanoparticles, etc. are added into a matrix which in turn can alter the curing of the matrix, and its viscous properties, while in fiber modifications the CFs are coated with different materials to improve the interfacial properties [1]. Likewise, the modifier material can alter the thermal and electrical properties also.

Since the scale of the interface region is so small, it is particularly challenging to characterize the chemical makeup, physical qualities, and mechanical traits. A number of efficient characterization techniques have recently been studied. Graphene, the allotrope of carbon turns out to be one of the important materials used to improve the mechanical, thermal, and electrical properties of PMCs as it makes them more suitable for structural applications as well as for lower temperature applications. Especially many researchers are focusing on using Graphene Oxide (GO) for enhancing the interfacial properties of CFRPs. Since GO structures have oxygen-functionalized groups such as epoxides, carboxyl, and hydroxyl groups, they form stronger bonds with the carbon fibers and thus interfacial adhesion between the CF and epoxy can be improved. Initially, GO nanoparticles were added to the epoxy matrix to improve the mechanical, and thermal properties of PMCs, but recent studies are being carried out to identify its effect on fibers as well. Some researchers are exploring further functionalization of GO by adding amine, silane, and nitride compounds and their effect on different properties. This functionalization alters the innate properties of GO in many ways, while some of its responses towards the epoxy polymer can be favorably utilized to improve the properties of PMCs.

1.2 OBJECTIVES

The objectives of this investigation include the following: -

- To investigate the change in mechanical properties of the Silanized Graphene Oxide-modified CFRP (SGO-modified CFRP) at room temperature.
- To analyze the enhancement in mechanical properties after cryo-treating the modified samples.
- To study the thermal stability of SGO-modified CFRP.
- To determine the specific heat capacity of SGO-modified CFRP samples.

1.3 SCOPE

Material selection for cryogenic applications must be careful because exposure to cryogenic temperatures can produce significant changes in the material. While some materials will become more ductile at cryogenic temperatures, others that are ductile at ordinary temperatures may become brittle when subjected to extremely low temperatures. Based on the distinctive nature of the substance, all of these behaviors exist. Before selecting any material for cryogenic applications, it must first undergo an experimental examination. In earlier days metal alloys were used for cryogenic storage purposes. The first materials employed for low temperature applications include copper, brass, and carbon. Tobern Bergmann's discovery of carbon steel in 1774 led to its use in lower-temperature applications. Harry Brearley discovered stainless steel in 1913, and he discovered that it has good resistance to acid corrosion and temperature when the chromium content is increased above 12%.[2]

The corrosion-resistant steel known as stainless steel, which has a minimum chromium content of 10.5%, forms a self-regenerating chromium oxide protective barrier over the steel atoms to prevent iron from rusting and can be utilized in cryogenic applications. Cryogenic applications utilize a variety of materials, including stainless steel (300 series and austenitic series), copper, brass, aluminum-monel alloys, Teflon, quartz, Kapton, invar (Ni/Fe alloy), mylar, ceramics and composites. Since it has a low thermal expansion coefficient, invar can be used to create washers. In the realm of cryogenics, steel is the most frequently utilized material. Compared to other structural materials, metal has good strength and plasticity.

Most of the metals exhibit the decline in the trend of ductility when exposed to extremely low temperatures. While keeping strength as an important deciding factor along with weight reduction has led to the use of composites for lower temperature applications. Cryo-tanks made of carbon fiber have been the subject of extensive research over the past 30 years. CFRP is employed in the production of load-bearing components for the Boeing 787, Airbus 350, and F-35 as well as in low temperature applications. Epoxy resins serve as the reinforcement matrix in CFRP composites, which utilize carbon fiber as the reinforcing material. Compared to E-glass fibers, carbon fibers have a greater Young's modulus. The carbon fiber's ultimate strength and tensile modulus are comparable to those of steel and aluminium, and appropriate surface modifications or surface treatments can improve the fibers' attributes.[3]

Contrastingly, when the epoxy matrix composites are exposed to cryogenic temperatures, they lose their strength and stiffness. In the heating process the energy required to warm up the object acquired either by increasing the temperature or changing its volume. The relationship between change in energy to change in temperature is known as the specific heat, and the relationship between change in volume to change in temperature is known as thermal expansion. Thermal contraction, which occurs when a material is exposed to an extremely low temperature, is a very significant phenomenon in the cryogenics domain.

When engineering materials for cryogenic applications, thermal contraction is a crucial factor since excessive contraction causes material to fail quickly and develop cracks. The main issue with cured epoxy is that it becomes brittle when exposed to extremely low temperatures. The thermal pressures brought on by the differing rates of thermal expansion of the fiber and matrix cause the composite material to collapse suddenly [4]. The toughening of epoxy resins is more important since it makes them useful in several low temperature applications.

Hence in this study an attempt to alter the brittle nature of cured epoxy is made by coating Silanized Graphene Oxide on the woven carbon fabric by Electrophoretic deposition method (EPD), is used for the fabrication of SGO- modified Carbon Fiber Reinforced Polymer (SGO-modified CFRP) composite panels. The concentration of the SGO plays an important role in determining their properties, so 3 compositions were also chosen. The range of concentrations is kept low, i.e., 0.5g/L, 1g/L, 1.5g/L because as concentration increases it may increase the viscosity of the epoxy resin matrix as well, which may lead to unnecessary errors in the composite panels during fabrication process. Hence the study concentrates on the abovementioned lower concentrations and its effect on different properties. In order to learn about its performance in cryogenic conditions the samples were cryo-dipped and tested for tensile strength, impact energy and flexural strength. For characterizing the SGO-modified CFRP, FTIR, DSC and TGA analysis were also done.

CHAPTER 2

LITERATURE REVIEW

Composite materials have played an important role throughout humanity's history, from historical development to empowering future advancements. In comparison to heavy materials such as metals (e.g., steel, aluminium, and so on), composites provide numerous advantages such as low weight, greater strength and rigidity, enhance vibration damping property, ease of design, chemical resistance and resistance to wear, and so on. Because of their tailorable and improved properties, composite materials have been extensively used for a broad array of applications encompassing everything from small white goods to the most technologically advanced aircrafts and aerospace vehicles. Great efforts are being made to increase fuel gain through the use of lighter materials in automobiles, railroad tracks, ships, and aerospace vehicles, among other things. According to predictions, a 10% decrease in vehicle weight might lead to up to 7% less fuel consumption. [5]

The application of polymeric matrix composites, particularly in cryogenic fields, has become a hotspot for researchers due to their lightweight materials, high specific strength, enhanced corrosion resistance, good anti-fatigue performance, and designability. [6]. Weight reductions of 25% to 35% and cost savings of nearly 50% are possible with polymer-based composite materials in space applications. [7]. The rise of space tourism has increased the demand for lightweight structural components in space vehicles in order to maximise economic gains. Fiber Reinforced Polymer composites are being used for cryogenic storage tank applications as a potential replacement for metallic alloys such as stainless steel, aluminium alloys, titanium alloys, and so on. [1-2].

Carbon Reinforced Fiber Polymer (CFRP) composites have got a keen attention as a cryogenic storage tank material. Numerous researchers are investigating the adequacy of the CFRP composites at cryogenic conditions. Because epoxy resin is the most commonly used continuous phase for cryogenic applications, it must have specific properties at low temperatures. Lockheed Martin Space Systems Company used Carbon/epoxy prepreg to manufacture a Honey-Comb (HC) sandwich structured composite tank for storing LH_2. Numerous investigations on the structure and research of composite cryogenic tanks have accelerated since the X-33 RLV fuel tank failure, where fuel breached onto the tank wall. The leak was caused by the polymer's fractures and the high thermal stress caused by the mismatch between the polymer's and carbon fiber's coefficient of thermal expansion (CTE). [8]

Shindo's extensive and detailed studies on the design and use of PMC in extremely cold environments can be viewed as a first step toward more exploratory research on CFRP's suitability for cryogenic composite tanks. When a fiber-reinforced polymer-based composite structure is subjected to combined thermal and mechanical pressures at cryogenic temperatures, microcracks may occur at stresses substantially below the ultimate strength of the composite materials. [9]. The longitudinal tensile stress of the matrix, which is the carbon/epoxy composite's maximum residual thermal stress, threatens the structural integrity of composites employed in cryogenic applications. [10]. At cryogenic temperatures, the residual thermal stress significantly affects the distribution of stress near to the crack boundaries in the composites. It is consequently preferred to increase the mechanical properties of polymer composites, such as strength, ductility, impact resistance, and CTE, in order to deliver highly advanced composites for cryogenic engineering applications.[11]

Thermosets and thermoplastics, as well as their mixtures, are the matrix materials in most of the FRPs. The matrix is a low molecular weight material in thermoset composites. The resin develops into a stiff, high molecular weight structure after the curing process. The stiffness is caused by the crosslinks (typically covalent connections) formed among the polymer chains, which offer strength to the the resin and make them thermally stable. When crosslinking density (the number of crosslinks per unit volume) enhances and chain length diminishes, polymer chain mobility becomes progressively inhibited, and the resin stiffens.The mobility of polymer chains is increasingly limited and the resin stiffens when crosslinking density (crosslinks per unit volume) rises and chain length falls. When the resin is exposed to cryogenic temperatures, this action is amplified hence its brittle nature is enhanced which is unfavorable for cryogenic applications. [12, 13]

EP-based thermosets stand out among the many thermoset polymers because of their strong adhesion, superior mechanical capabilities, and easy processing. [14,15]. The thermosets' fracture toughness and resistance to crack initiation, however, are decreased by the high cross-link density. This significantly limits their use in a cryogenic environment.[12].

To establish the viability of PMCs for real-world applications, thermoset polymers must now be toughened. Interfacial properties have a significant impact on the effectiveness of carbon fiber/epoxy composites. Effective transfer of load from the matrix to the fillers require strong interfacial qualities, which curtail the stress concentrations and enhance comprehensive mechanical properties. [16,17] By reducing the cross-link concentration of thermoset resin or adding additives like stiff inorganic nanomaterial, soft polymers such as hyperbranched polymer, block copolymers, elastomers and high-performance plastic polymer to heterogeneous phases, these shortcomings can be solved [18,19]. Modified polymers' enhanced or diminished tensile strengths at ambient temperature may not necessarily translate into the same fluctuation trend when the materials are exposed to cryogenic conditions. The tensile strength and modulus of polymers at normal or cryogenic temperatures can be increased by adding fillers like Carbon Nano-Tubes, Graphene, and Polyether sulfone (PES). However, it is impossible to forecast how a modification procedure will transform the behavior of PMCs.

Due to its great mechanical stiffness (130 GPa), electrical conductivity, and thermal conductivity, graphene, a novel two-dimensional carbon nanomaterial, has added a new level to the field of nanotechnology [20,21]. Graphene, a good choice for improving the cryogenic performance of thermoset polymer because, in comparison to other nanofillers, its presence effectively stopped fracture development by causing a significant degree of plastic deformation [22,23]. Additionally, it is widely acknowledged that graphene functionalization may enhance the distribution of graphene in the polymer matrix.

The subzero (77 K) tensile strength, modulus of elasticity, and impact strength could all be improved simultaneously by adding graphene oxide sheets to the epoxy matrix, as proposed by Shen et al. [24]. The graphene/EP composite reached its maximum tensile and impact strengths with improvements of 10.5% and 23.7%, respectively, at 77 K. Effectively dispersed graphene can halt the spread of cracks in the polymer at a comparatively low percentage. Therefore, compared to pure epoxy, the fractured surfaces of the epoxy modified by graphene are more rougher.

Due to its excellent qualities, including its high affinity towards water nature from a variety of oxygen-containing functional groups [25,26] and huge surface area, negative surface charges, and attractiveness to researchers, graphene oxide (GO) has recently become one among the most sought-after nanofillers. GO outperforms other types of nanofillers like CNT [27] and carbon black in terms of strength and weight. The mechanical characteristics of composites can be typically improved with just a tiny volume of GO, often less than 1 wt.% [28,29]. GO/CFRP composites are a potential material for structural applications because of the impressive mechanical, electrical, and thermal properties of GO [30,31]. Few explorative studies have focused on the behaviour of GO/CFRP composites at LT, despite the fact that their mechanical properties are popular study subjects. Glass fiber/epoxy composites were tested for their flexural properties at 30^{O}C, 70^{O}C, 90^{O}C, and 110^{O}C by Prusty et al. [32]. The findings demonstrated that the addition of GO to composites caused striking differences in flexural characteristics in response to changes in the ambient temperature. At 30^{O}C, 0.1 wt% of GO increased strength and modulus by 18.5% and 15.6%, respectively; however, when temperature was raised to 110^{O}C, flexural characteristics decreased. Huang et al. recently investigated two distinct methods for incorporating GO into Carbon Fiber/epoxy composites. One involves mixing Graphene Oxide into an epoxy matrix, while the other involves coating CF with it [33]. The outcome showed that two methods could boost CFRP's mechanical qualities at cryogenic temperatures. Due to the robust chemical reactions and mechanical locking between carbon fiber and polymer, the latter is an effective employment strategy for the manufacture of GO-modified PMCs. When compared to the controlled sample, the modulus and bending strength of CF reinforced composites with GO coating increased at 77 K by 47.62% and 23.28%, respectively. Due to the increased interface strength brought about by the aforementioned studies, it has been established that crack deflection and plastic void formation are the means by which graphene helps to strengthen the CFRP composite.

The GO employment strategy affects how well mechanical characteristics of composites are improved by GO. The most efficient and quickest way to coat a specific amount of graphene oxide onto the skin of automotive fabrics is electrophoretic deposition (EPD) [34]. The thickness of the deposited layers can be altered by balancing the deposition period, power supply, and GO concentration in the EPD solution. Prior research [35,36] emphasized how crucial it is to maintain

When a high voltage is used, there is a high tendency for gases to evolve in the vicinity of the electrodes [37], whereas when a low voltage is used, particles in an EPD suspension have a tendency to aggregate and the GO particles may not settle over the surface of fabrics. As a result, an optimal voltage supply should be considered while using EPD to deposit GO onto the surface of carbon fibres to form GO/CFRP composites.

CHAPTER 3

METHODOLOGY

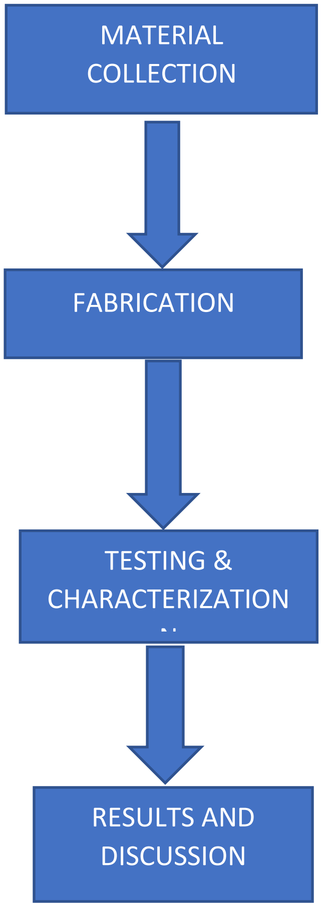


Fig.3.1. Flowchart of methodology

3.1 MATERIAL COLLECTION

The journey begins by accumulating the needed materials for the fabrication of Silanized Graphene Oxide modified Carbon Fiber Reinforced Polymer Composite (SGO-modified CFRP). After conducting a detailed literature survey, we found that DGEBA epoxy resin was the most commonly used thermoset polymer for CFRPs due to its superior mechanical and adhesive properties. To identify whether the SGO modification has improved the mechanical properties of CFRP, the DGEBA resin was chosen as the matrix material for our study. The essential materials required for fabricate SGO-modified CFRP are as follows

- DGEBA (Bisphenol A diglycidyl ether) YD 128
- Hardener TH 7301
- Carbon plain weave fabric cloth
- Silane coupling agent, 3-Aminopropyltriethoxysilane (3-APTES)
- Graphene oxide

3.1.1. Epoxy Resin

Epoxy resins and polyester are two popular polymer matrices that are employed with continuous fibers. Epoxy is a polymer that has an epoxide group as part of its chemical composition. DGEBA is an organic liquid with a low molecular weight that consists of two epoxide groups shown in fig. 3.1. To alter the properties of epoxies, several additives are frequently used. Diluents, for instance, are used to lower viscosity. The flexibility of the epoxy is increased using flexibilizing chemicals. Cross-linking is achieved by adding chemicals that interact with the epoxy and hydroxy groups between neighboring chains which acts as a curing agent. Generally, curing agents are organic amino or acid molecules. Diethylene triamine is a typical curing agent for DGEBA epoxy (DETA). The amount of curing agent used determines how much cross-linking occurs. Amines or acid anhydrides are often added at a weight percentage of 10 to 15 percent, where they become a component of the epoxy structure. The curing process can be accelerated by the addition of an accelerator. In general, as cross-linking is increased, toughness falls but properties like stiffness, strength, and glass transition temperature improve.

Epoxy resins cost more than polyesters, but they are better at resisting moisture, shrinking less during the curing process (by about 3%), having a higher maximum working temperature, and adhering well to glass fibers. Epoxies come in a wide variety of proprietary formulations, and thermosetting epoxies make up a significant portion of the matrices in high-performance polymer matrix composites.

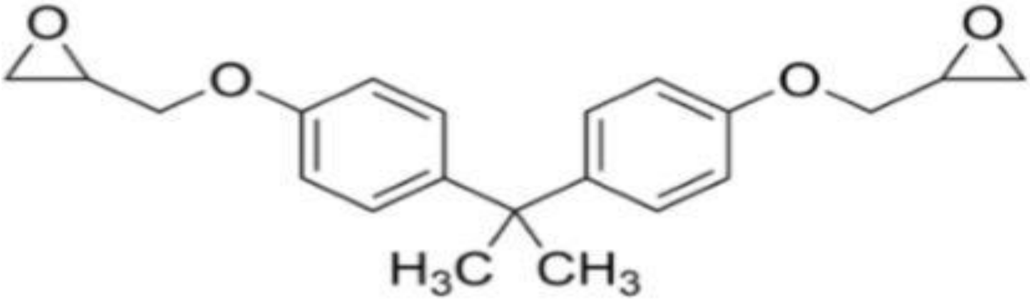


Fig.3.2. Chemical structure of DGEBA epoxy resin

Bisphenol A diglycidyl ether, often known as BADGE or DGEBA, is an organic substance that is a component of epoxy resins. The substance is a colourless solid that melts only a little bit above room temperature (commercial samples can appear yellow). It is made by O-alkylating epichlorohydrin with bisphenol A. The major product of this process is bisphenol A diglycidyl ether, along with certain oligomers. The polymerization degree could be as low as 0.1. [2] Such epoxy resins are interesting because of their epoxide concentration. This quantity is frequently stated as either the equivalent weight (Eq./mol) or the epoxide number (Eq./kg), which is the number of epoxide equivalents per kilogram of resin (Eq./kg). The bis epoxide has three stereoisomers, however they are not separated because unsymmetrical epoxides are chiral.

The properties of the purchased Epoxy resin purchased from Aditya Birla Chemicals Ltd. Thailand are collected in the table 3.1.

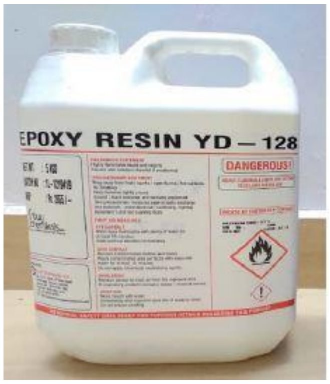


Fig.3.3. DGEBA epoxy resin YD-128

Table 3.1. Details of the Epoxy resin

Sl. No.	Property	Standard	Typical value
1	Appearance	Visual	Clear, colorless to light yellow liquid
2	Epoxy equivalent weight	ASTM D 1652-04	185-194 g/eq
3	Epoxide value	ASTM D 1652-04	5.15 – 5.40
4	Viscosity @ 25℃	ASTM D 2196-05	11,000-14,000 cPs
5	Flash point	ASTM D 93	252 ºC
6	Density @25ºC	ASTM D 1475-98	1.16 g/ml

3.1.2. Carbon Fibers

By carbonizing organic precursor fibers and then graphitizing them at high temperatures, carbon fibers with an extraordinarily high modulus can be produced. A particular textile polymeric fiber that can be carbonized without melting is often the organic precursor fiber or the raw material for carbon fiber. The precursor fiber is made up of long-chain molecules that are randomly ordered and measure between 0.1 and 1 mm when fully stretched, much like any other polymeric fiber. Due to the disordered nature of the polymer chains, these polymeric fibers typically exhibit fairly substantial deformations at low loads and have poor mechanical characteristics. Precursor fibers made of polyacrylonitrile are frequently employed (PAN). Other precursor fibers come from pitches, polyvinyl alcohol, polyimides, and phenolics. They also contain rayon.

Carbon fibers are frequently woven into fabrics after being produced and size-sorted. Tows are bundles of carbon fibers that manufacturers make to start making fabrics. Tows are classified as 3k, 6k, 12k, or 15k based on the amount of fiber, or filament, in each one. Considering that the k stands for "thousand," a 3k tow is made up of 3,000 carbon filaments. Carbon fiber composites are incredibly strong because there are so many strong carbon fibers packed into a small area. A weaving loom is used to create fabrics from carbon fiber spools. The most popular weaves are harness satin, twill, and plain weave which are explained below.

(i) Unidirectional Fabric

All of the fibers are aligned in the same direction, as suggested by the word “uni”, which means one. Uni-directional (UD) fabric benefits from great strength as a result of this. UD fabric is not woven, thus there are no crimped or interlaced threads that could compromise the structure. The strength and rigidity are instead increased by continuous fibers. The option to customize the layup with more control for performance traits is another advantage.

(ii) Plain Weave Fabric

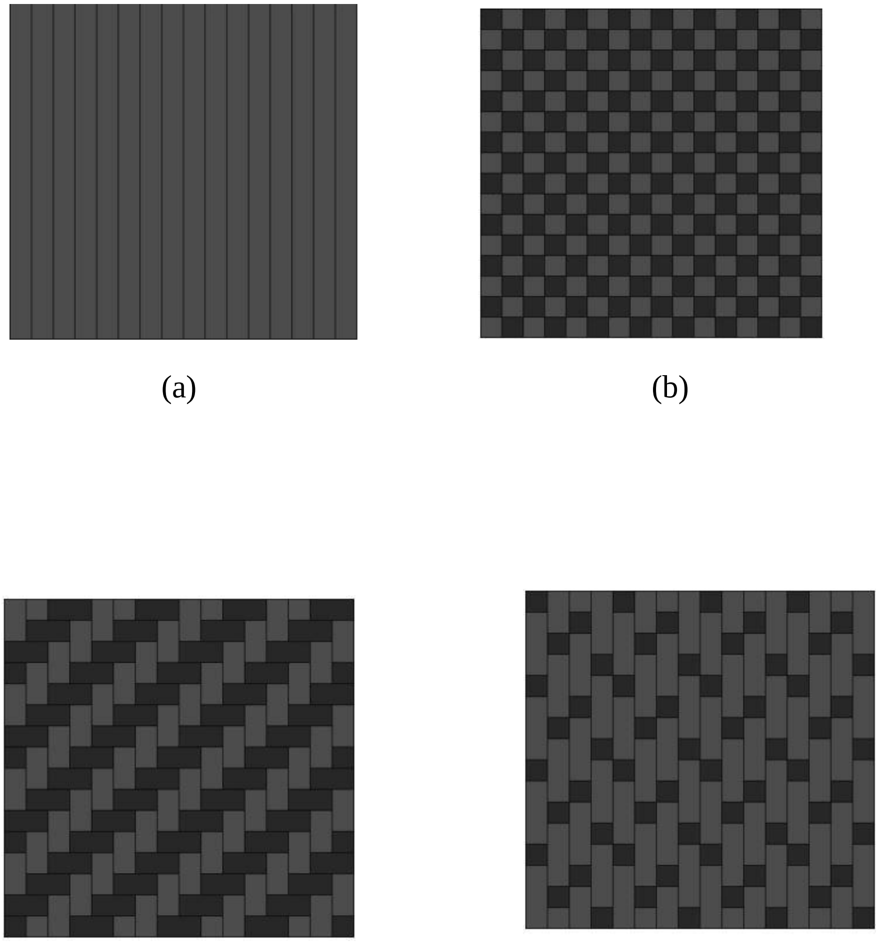
Carbon fiber cloth with a plain weave, often known as a 1x1 weave, has a checkerboard-like symmetry. The tows have closely intertwined stable fibers as it follows an over/under weaving pattern. The ability of a material to hold onto its fiber orientation and weave angle is referred to as fabric stability. Even though it is simpler to handle without causing fabric distortions, because of its high fabric stability and lack of flexibility, plain weave carbon fiber cloth is not ideal for complex curves, whereas it is effective for two-dimensional curves, tubes, and flat sheets.

(iii) Twill Weave Fabric

The most well-known variety of carbon fiber cloth is the twill weave, which has a 2x2 or 4x4 pattern. Each tow runs over two tows and then under two tows in a 2x2 weave. Therefore, it makes sense that each tow in a 4x4 weave crosses over four other tows before going below another four. This woven pattern generates a distinctive diagonal pattern by going over and under a set of tows. In a twill weave, the spacing between the two interlaces is greater than in a plain weave. The flexibility and capacity to conform to intricate shapes of the twill weave along with maintaining good stability are appreciable. To prevent introducing distortions to the weave, it must be handled with more care than a fabric with a plain weave.

(iv) Harness Satin Weave Fabric

Since ancient times, satin weaves have been employed to give silk fabric its lovely drape while still making the fabric smooth and seamless. Satin weaves translate to an ability to easily form around intricate curves when utilized for carbon fiber composites. This demonstrates that satin weaves are less stable than other weaves. A 4HS weave, for instance, entails three tows crossed over, followed by one passed under. As the satin weave number increases the formability will increase while the fiber stability is decreased.



(a) (b)

(c) (d)

Fig.3.4. Different weaves of carbon fabric (a) Unidirectional fabric (b) Plain weave (c) 2X2 twill weave (d) 4HS weave

Since the orientation of fibers plays an important role in determining the strength of composites, many studies have been conducted using unidirectional carbon fibers which is easier for numerical analysis and stress analysis. Here, twill weave carbon fabrics that exhibit orthotropic properties (different properties in different directions) are selected to study how the mechanical properties vary accordingly. The properties of carbon fabric being used is given below in table 3.2.

Table 3.2 Properties of Carbon fibers

Sl. No.	Parameters	Specifications
1	Fabric type	3K genuine carbon fiber fabric cloth
2	Dimension	100cm×30 cm
3	Weight of the fabric	220g/m^2
4	Weave pattern	2×2 twill weave
5	Tensile Elongation at Break	52.2 %
6	Izod impact strength	612 J/m

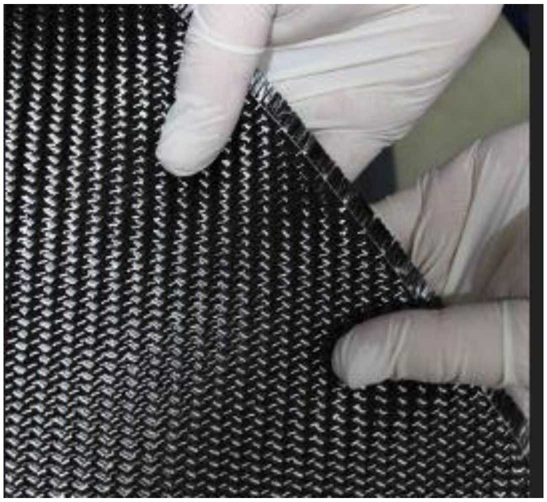


Fig 3.5. Twill weave carbon fiber

3.1.3. Graphene Oxide

Commonly, the oxidation reaction of graphene, sodium nitrate, sulfuric acid, and potassium permanganate results in graphene oxide. GO is made up of a single-atom-thick sheet with connections to hydroxyl and epoxide groups along its basal plane. Its structure makes it hydrophilic. And GO can easily combine with a variety of polymers, including CMC and PVC, to create nanocomposites. To improve the mechanical qualities of the original polymer, such as heat stability, tensile strength, and elastic modulus, many researchers utilized GO as filler.

Additionally, due to its excellent electrical conductivity in areas like solar cells and chemical sensors, GO can be employed as conductive films deposited on specific substrates. Additionally, GO can be antimicrobial materials; for instance, it can stop E. coli bacteria from growing. Various investigations have been conducted to analyze the effect of Graphene Oxide on the performance of CFRPs, whereas a chemical modification on Graphene oxide itself is rarely studied.

Fig. 3.6. Graphene Oxide

3.1.4. 3-Aminopropyltriethoxysilane

One way for improving the interfacial interaction between GO and PMC is to chemically functionalize the GO in order to produce functional groups on its surface. In order to be used in this experiment, the functional groups link with polymers and strengthen the interfacial bond between GO and PMC. To improve the interfacial adhesion, silanization of functionalized GO using 3-Aminopropyltriethoxysilane (3-APTES) is the favored technique. For years, 3-APTES has been utilized to modify the surface of some materials, such as nanotubes**.** The structure of 3-APTES is shown in fig.3.6.

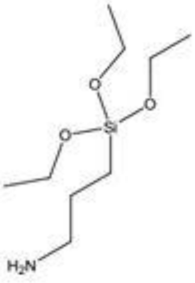


Fig. 3.7. Chemical structure of 3-APTES

In a previous study, 3-APTES was taken into consideration as a silane agent to interact with nanotubes. According to reports, aminosilane has been used in a variety of applications, including nylon, phenolic, and epoxy-based composites. The hydrolyzable alkoxy groups, such as trimethoxy $(OCH_3)_3$ and triethoxy $(OC_2H_5)_3$, are represented by the formula "NH_2-R-$(CH_2)_n$-Si $(OR')_3$," where the value of n is between 1 and 3. These groups can be hydrolyzed to produce trisilanol. In this experiment, the -NH_2 functional organic group of the R group was chosen. Covalent bonds are quickly formed when this group interacts with the hydroxyl groups of GO on the GO surface. The 3-APTES modified GO can significantly improve its coupling with other polymers, such as PMC, by covalent bonding.

(a) (b)

Fig.3.8. (a) Hardener TH 7301 (b) 3-APTES

The details of all the raw materials purchased are formulated as a table below: -

Table.3.3. Details of the raw materials required and
their suppliers

Sl. No.	Material	Specification and Suppliers
1	Carbon Fiber Fabric Cloth	3K genuine, 220g/m^2, 2x2 Twill Weave, Manufacturer Part No. CBC24030, Carbon black Composites, India.
2	Epoxy Resin	Diglycidyl ether of bisphenol A (DGEBA) (YD 128), epoxide equivalent weight (EEW) of 185 to 194g/eq.
3	Hardener	Modified cyclo-aliphatic amine (TH 7301), Aditya Birla Chemicals Limited, Thailand.
4	Silane	3-Aminopropyltriethoxysilane (3-APTES*)* – Thermo Fischer Scientific
5	Graphene Oxide	Platonic Nanotech Private Limited, India.

3.2. FABRICATION OF COMPOSITE PANELS

3.2.1. Preparation Of Carbon Fabric

Epoxide coatings are applied to carbon fibers during manufacturing process; these coatings must be removed before applying any treatments. Therefore, there is a need to desize carbon fiber in a heating furnace at 120^{o}C for two hours. The carbon fiber sheets were then carefully cleaned in acetone to get rid of the dirt and grease. The EPD process was then set up, using stainless steel plates as electrodes and carbon fiber sheets supported by wooden frames as cathodes. When voltage is supplied, charged silanized graphene particles will adhere to the cathodic carbon fiber sheets.

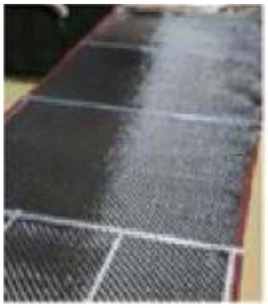


Fig.3.9. Desized carbon fabric

3.2.2. Functionalization Of GO

The dry GO was ground into powder form. Graphene oxide (1.5gm) is dispersed in a 4% silane solution containing 3-APTES in deionized water. This solution is mixed with 900ml of ethanol: water (95:5) solution. The resulting mixture was mixed well using a magnetic agitator for 2 hours at a temperature of 70°C. Finally, the Silanized Graphene Oxide was filtered from the deionized and ethanol solution. The resultant SGO powder was dried at 90°C for about 12 hours.

3.2.3. Preparation Of SGO Coated Carbon Fiber (CF) Via EPD Process

(i) Electrophoretic Deposition (EPD)

A colloidal method called electrophoretic deposition (EPD) can be used to coat fibers or fabrics. The simplicity and affordable cost of EPD is its clear advantages. Additionally, it has been suggested that vacuum infiltration and dip coating cannot provide consistent coatings when utilizing the same graphite suspension. Electrical forces play a major role in the penetration of graphene oxide particles on the carbon fibers. In this method, colloidal particles suspended within a liquid medium move and are deposited on an electrode through a process known as electrophoresis when subjected to an electric field. In the EPD method, any colloidal particle that can carry a charge and be employed to create stable suspensions can be used. The method can be used to coat materials to any electrically conductive surface. The actual processing conditions and possible equipment depend heavily on the materials that are being deposited. The schematic diagram of the EPD method employed for this study is shown in the figure.

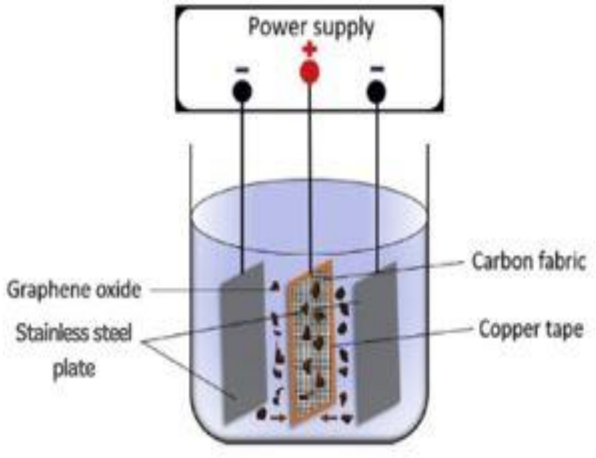


Fig.3.10. Schematic diagram of EPD technique to coat SGO on CF

(ii) Coating SGO On Carbon Fabric

The consumables required for coating SGO on CF are listed below

- Stainless steel plates
- Wooden frames to hold carbon fibers
- Sonicator
- EPD Bath container
- Copper ribbon
- Conducting electric wires
- Power source

Desized carbon fiber was affixed to a wooden frame that serves as a cathode and counter electrodes are made of 216-grade stainless steel plates (25mm x 10mm x 3mm). The suspension for the EPD bath was made by sonicating silanized graphene oxide (SGO) (0.5g/L, 1g/L, and 1.5g/L) with deionized water for an hour in a sonicator (POWER SONIC410). The carbon fiber sheet and stainless steel plates were placed in alternating rows and then submerged in SGO-suspended deionized water with the entire setup being placed within an ultrasonicator. After that, the EPD procedure was carried out using sonication at a constant voltage of 30 V for 20 min, which helped disseminate the nanofillers in the deionized water efficiently and break up bubble formations that may otherwise prevent the deposition of nanoparticles. To ensure a uniform electric field across the entire carbon fiber sheet, a conductive copper ribbon was looped around the material. The carbon fiber sheets were removed after deposition and left to air dry for 24 hours at room temperature. The sheets were then cleaned in acetone and dried once more for two hours in a heating oven set at 150 °C. Following the same procedure 3 concentrations of SGO coated CF were prepared. The details of the 3 compositions and its representation are given in the table below.

Table 3.4. Sample Compositions

Sl. No.	Sample Compositions	Representation
1	CF + Epoxy + Hardener	Neat
2	SGO (0.5g/L) + Epoxy + Hardener	1.5 SGO
3	SGO (1g/L) + Epoxy + Hardener	3 SGO
4	SGO (1.5g/L) + Epoxy + Hardener	4.5 SGO

Fig. 3.11. Experimental setup for the EPD process

3.2.4. Fabrication Of SGO-Modified CFRP Panels

The most used technique for low-pressure closed mold reinforced composite molding is probably vacuum-assisted resin transfer molding (VARTM). It is most appropriately used to describe the vacuum infusion method, which involves molding a composite utilizing a stiff mold to provide component geometry and a thin, flexible film over the fiber. The fiber is compressed tightly against the rigid mold surface by the outside air pressure. Over the past 20 years, the VARTM technique has been refined for efficient utilization. This closed-mold method can create a variety of high-performance composites, including fiber-reinforced polymer structures, for a reasonable price. The procedure entails arranging the fibers or fabric in the required configuration**.** Since the chosen epoxy is having lesser viscosity VARTM technique can be employed with ease**.** The schematic diagram of VARTM is as shown in the figure. For effective implementation of VARTM the following materials are required: -

- Vacuum bagging film
- Vacuum pump
- Peel ply fabric
- Infusion mesh
- Resin infusion connector
- Hose pipe
- Glass plates

Initially, the glass plates of dimension $30cm \times 30\ cm \times 1cm$ were cleaned with acetone to remove any dirt in the plates. Here glass plates act as a molding surface and to ensure surface finish of the composite panels. After cleaning the glass plates, it is coated with wax to prevent the sticking of fabric on the mold. A layer of infusion mesh is placed above the glass plates for easy removal of the composite panel from the mold. Peel ply fabrics are laid over the infusion mesh to facilitate the wetting of Epoxy resin. Then, the peel ply cloth is covered with 12 layers of

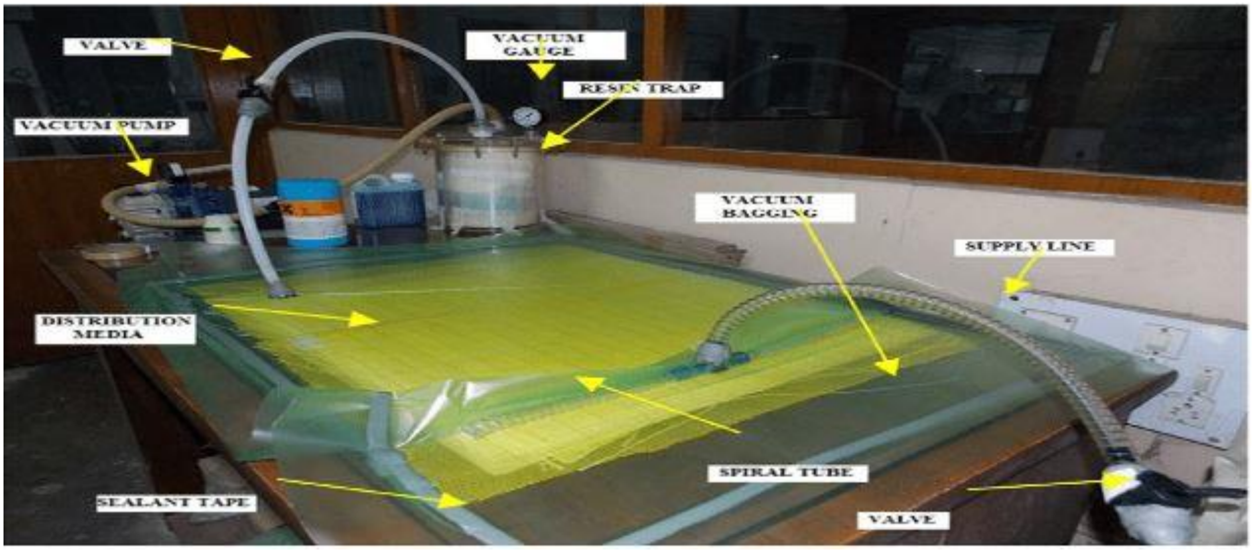


Fig 3.12. Experimental setup for VARTM

twill weave carbon fiber sheet that have been trimmed to 7.5 cm x7.5 cm in size. were stacked one above the other. Once more, the stalked carbon fiber sheets are positioned over the peel ply fabric and infusion mesh to cover the fabric.

Resin infusion connectors are positioned in the proper places to make it easier for resin to enter the mold (inlet) and to exit the mold (outlet). A vacuum bagging film is then placed over the entire arrangement. The vacuum bagging sheet is adhered to the glass surface using sealant tapes to ensure a precise vacuum. Meanwhile Epoxy and hardener were combined in a 2:1 weight ratio. To eliminate the air bubbles from the epoxy/hardener combination, a degassing chamber to remove all the entrapped bubbles formed while mixing the resin and the hardener was employed so that the final composite panel is of good quality and free from voids.

The resin pot and infusion connector are connected via hose pipes, allowing resin to flow to the mold more easily. To produce the vacuum inside the completely sealed bag, the vacuum pump is connected to the second infusion connector via hose tubing. Turn on the vacuum pump for a brief period of time before turning it off to check for leaks. After making sure there are no leaks and the resin is flowing, inlet pipes are then submerged in the resin.

To regulate the resin flow rate and guarantee that the carbon fiber sheets are completely wet, gate valves on the outflow line are controlled. The resin begins to flow to the outflow pipes after thoroughly moistening the carbon sheets, and the gate valve is then shut fully. To prevent gas from leaking into the sealed bag, clamps are put on the inlet and outlet ports, and the vacuum pump is turned off. The created composite after it is demolded after one overnight of curing. Similarly, laminates of all sample compositions (0.5 g/L, 1.0 g/L, and 1.5 g/L) are fabricated. After sufficient curing, these laminates are cut into the required dimensions.

CHAPTER 4

TESTS AND CHARACTERIZATION

4.1. FTIR

The most popular kind of infrared spectroscopy is labeled as "Fourier transform infrared," or FTIR. All infrared spectroscopies operate under the same notion that some Infra-Red energy is absorbed by the material to be tested when it is allowed to pass through the material. It is noted which radiation enters the sample. The spectra emitted by the material can be used to recognize and differentiate between molecules, since different molecules, due to their various structures, emit various spectra. FTIR is the commonly chosen spectroscopy technique, since it is highly accurate and sensitive, available in affordable rates, as well as it does not destroy the sample. It is done using a Michelson Interferometer which acts as the source for IR radiation and Data Acquisition Systems are used for the Fourier Transform operation. A mathematical operation known as the Fourier transform breaks down waves and then calculates the frequency of the waveform based on time. The "output" of the interferometer is a graph called an "interferogram," not the spectroscopic spectrum we employ. The interferogram is transformed by the Fourier transform operation into the familiar and useful infrared spectroscopy spectrum graph. The schematic diagram of FTIR Spectrometer is as shown in the figure. This analysis is done for a variety of applications, including monitoring processes, identifying molecules, conforming certain bonds, and figuring out the constituents of a combination.

The different molecules in a compound will absorb different ranges of the radiation and emit the retaining part of the radiation. The atoms in the compound determine the sort of vibration whether it is stretching or bending of bonds is caused by the infrared radiation. The transmittance trend of different molecule and functional group is unique for the same, it serves as DNA sequence for each compound. Thus, a range of transmitted wavenumbers are obtained and a graph is plotted with wavenumber (cm^{-1}) on X-axis and the % Transmittance on the Y-axis.

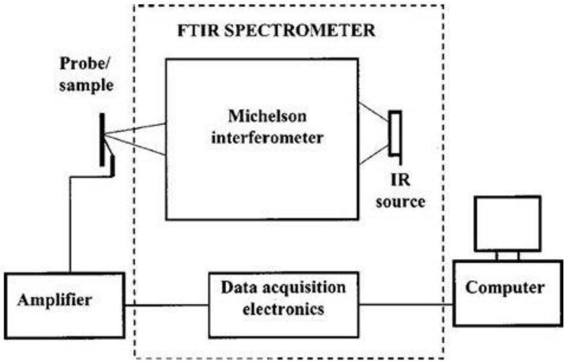


Fig.4.1. Schematic diagram of FTIR spectrometer

The resulting graph contains many peaks, in which each peak refers to a specific bond. The obtained graph is cross-matched with the already existing huge database of the transmittance patterns of different bonds and molecules.

4.2.THERMOGRAVIMETRIC ANALYSIS

A notable method for characterising materials utilised in many petrochemical, culinary, pharmaceutical, and environmental applications is the thermogravimetric analysis (TGA). TGA analyses the products' composition, purity, decomposition processes, decomposition temperature, amount of absorbed moisture etc. TGA analysis enables one to comprehend how a material's mass changes with respect to both time and temperature. The sample is heated in this procedure from room temperature to 1000 degrees in nitrogen or oxygen rich air, after which the weight loss that results from semi-volatile chemicals, polymer breakdown, ash content, carbon black, and moisture is measured. The measurements are performed in environments with controlled oxygen levels and humidity levels to identify interactions with the materials, between substances, and between active ingredients and excipients or packaging materials.

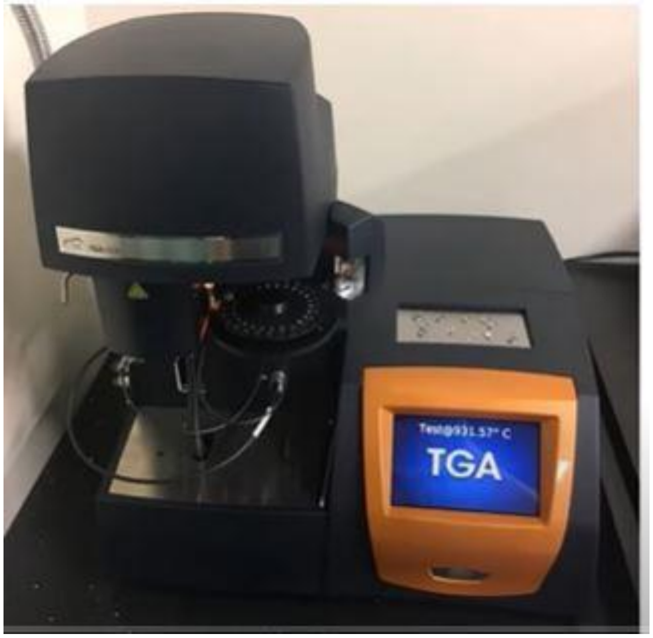


Fig. 4.2. TGA equipment

In reaction to the sample's physical changes (loss/gain) in response to the present temperature, heating rate, and environment, the apparatus offers quantitative and qualitative information. TGA is used as a secondary method of material identification and can quantify the main constituents of the substances, analyse decomposition, and thermal stability.The equipment consists of a closed chamber with an inbuilt furnace for heating the sample, a small pan to hold the sample, and thermocouple to measure the temperature.

In this test, a sample is heated from the ambient temperature to a higher temperature (upto which temperature varies according to the material) for various materials—at a predetermined rate. The apparatus repeatedly measures the sample's weight and temperature every second. This logs the weight change over time or as a function of temperature, along with the weight change rate

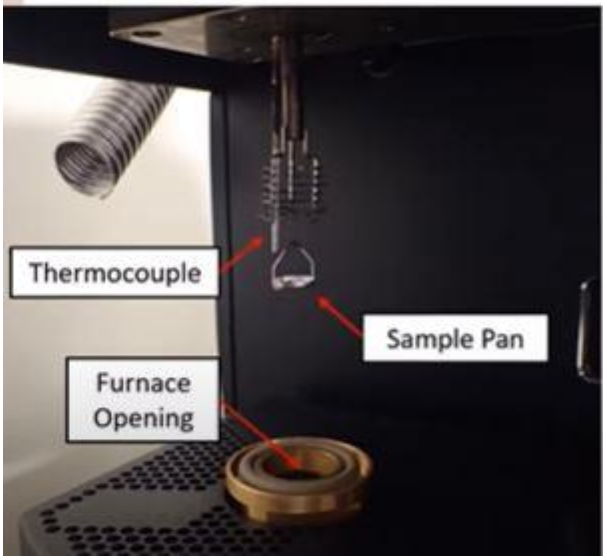


Fig.4.3. Different parts in a TGA equipment

Following TGA tests, the Weight % Curve and Derivative Curve are the two main curves that can be acquired. Temperature is plotted on the X-axis in the weight % curve, while the weight loss % is plotted along the Y-axis. The fraction of weight changes at each stage of the sample's decomposition and the quantity of inorganic residue remaining after testing are calculated using this curve. The TGA results are mainly depended on three factors which includes the heating rate, the Maximum temperature that have been achieved during testing duration, and the furnace atmosphere.

The derivative graph exhibits different peaks which refers to the decomposition of certain compound from the sample. The various informations that can be gathered are the decomposition tempearature and the maximum decomposition rate. In the weight % curve, one point will be selected prior to the visible weight loss and another point just after the weight loss is identified. The difference in the weight % between the starting and ending points is the weight change for that particular decomposition. The % of materials that is left on the sample pan after completion of the experiment is reffered to as the residue of that sample. After completion of the tests, the residue can include fillers such as talc, carbon black, as well as any trace of inorganic elements in the sample.For most polymer materials a significant degradation will occur significantly just prior to the decomposition.

In our study, TGA is done to study the thermal stability of the SGO-modifie CFRP at different temperatures is done. The test is done using a SETARAM Labsys Evo instrument at a heating rate of 10^{O}C/minute between a temperature range of 22^{O}C to 600^{O}C. The test is carried out by taking each samples of about 30mg-45mg. The test is done at Sophisticated Testing Facility, National Institute of Technology, Thiruchirapalli.

4.3. DIFFERENTIAL SCANNING CALORIMETRY

The major thermo-analytical technique which measures physical and chemical changes within a material in response to temperature is differential scanning calorimetry (DSC). The equipment provides quantitative and qualitative information about the endothermic and exothermic processes or the changes in the heat capacity. The differential scanning calorimetry is a dynamic process in contrast to classic calorimetry, in which places a sample inside an enclosed chamber to track its heat absorption and release during an isothermal experiment.

To counteract the impacts of the DSC machine's internal components, DSC equipment exports information on the temperature and heat flow through the sample, the heat flow from the sample is compared to the heat flow from an empty reference pan and subtracted. The information obtained as a consequence shows how much energy the polymeric sample has received or released as well as how the sample's temperature has changed.

Fig.4.4. DSC equipment

In our study DSC test is done to identify the specific heat capacity of the SGO- modified CFRP. It is performed on specimens of weight 20mg- 35 mg. The test is carried out using SETARAM DSC SETLINE instrument with a heating rate of 10^{O}C/minute from a temperature range of -30^{O}C to 300^{O}C. The test is done at Sophisticated Testing Facility, National Institute of Technology, Thiruchirapalli.

4.4. TENSILE TEST

The force necessary to break a polymer composite specimen and the extent to which the specimen stretches or elongates to that breaking point are measured using ASTM D3039 tensile testing. A stress-strain diagram generated by tensile tests is used to calculate the tensile modulus. The information is frequently used as a material specification, to design parts that can bear application force, and as a material quality control check. It is occasionally appropriate to test materials at temperatures that mimic the intended end use environment because the physical properties of many materials can change depending on the ambient temperature.

Fig. 4.5. Universal Testing Machine

At a predetermined grip separation, specimens are loaded into the grips of a universal test machine and pulled till failure. The time to failure or the material specification can be used to establish the test speed for ASTM D3039 (1 to 10 minutes). Standard test specimens are typically run at a pace of 2 mm/min (0.05 in/min). The measurement of elongation and tensile modulus is done with an extensometer or strain gauge. Testing in multiple orientations may be required, depending on the reinforcement and kind.

A universal test machine has a thermal chamber added. The chamber is constructed such that the test mounts from the Universal Tester's base and crosshead can pass through its top and bottom. Standard test equipments are mounted within the chamber, and testing is carried out there in a thermally controlled environment much like it would be outdoors. For higher temperatures, the chamber has internal electric heaters; for lower temperatures, liquid nitrogen or carbon dioxide gas is used as a coolant from the outside.

The most typical ASTM D3039 specimen is a continuous rectangular cross section that is 250 mm (10 mm) long and 25 mm (1 in) broad. To avoid gripping damage, optional tabs can be attached to the specimen's ends.

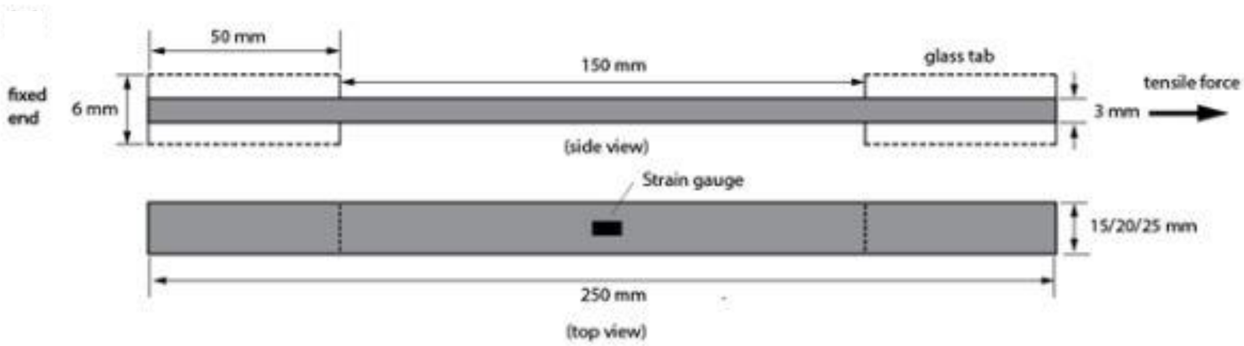


Fig.4.6. Tensile test specimen ASTM standard D-3039 dimensions

4.5. CHARPY IMPACT TEST

Charpy impact test is a single point test that measures the resistance to the impact from a swinging pendulum. Charpy impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. The values obtained can be used for quality control or to differentiate general toughness. Using standardized pendulum-type hammers installed on standardized machines. The machines with pendulum-type hammers have been standardized in that they are required to adhere to a number of specifications, such as a fixed height of hammer fall, which results in a virtually fixed velocity of the hammer at the moment of impact. The specimens for this test technique may have a machined notch or some may not have a notch. The stress concentration caused by the notch encourages brittle fractures rather than ductile fractures. The outcomes of this test procedure are presented as the amount of energy absorbed per unit of specimen width.

Fig.4.7. Charpy Impact testing machine

The Charpy impact energy of neat and SGO modified samples are studied using Charpy Impact test according to ASTM D6110 standards. The standard specimen size for Charpy impact test is 64mm x 11mm x 3.5mm are cut from the prepared composite panels and impact properties are tested for untreated samples as well as the cryo-treated samples. For testing of cryo-treated samples, the samples were immersed in a cryo-bath of Liquid Nitrogen for about 20 minutes. Such cryo-treated samples were tested immediately, so that the alteration induced by the cryogenic treatment is utilized effectively.

4.6. THREE-POINT FLEXURAL TEST

The flexural test is done to determine the flexural characteristics of polymer matrix composite materials under the specified conditions, such as flexural strength, stiffness, and load/deflection behaviour. According to ASTM D-7264 standards, three- point bending test is one type of flexural tests which includes central loading on a simply supported beam. This test procedure was created for continuous-fiber reinforced polymer matrix composites to use to their full potential. The schematic diagram of three-point bending test is as depicted in the figure.

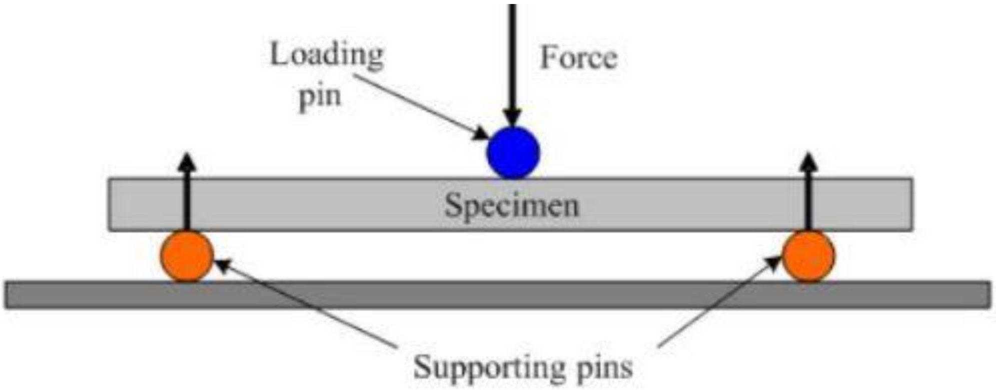


Fig. 4.8. Schematic diagram of three-point bending test

Since no laminate is fully symmetric (even when full symmetry is intended), flexural characteristics may alter depending on which surface of the specimen is under compression; these variations may shift the neutral axis and will be further impacted by even slight asymmetry in the laminate. Usually, static or rotating loading noses are used to evaluate composites. Because non-rolling twin supports on either the compression or tension side of the specimen create tiny longitudinal forces and resistive moments on the beam that superimpose with the desired loading, the kind of loading nose can have an impact on the results. Additionally, the specimen should be evenly touched across its width by the loading noses. Lack of uniform contact can have an impact on flexural characteristics by causing crushing damage and unevenly loading the beam. To ensure uniform loading the supporting rollers are also cylindrical with a radius of 3.0 mm. The standard support span-to-thickness ratio for flexural strength is designed such that failure occurs at the specimens' outer surface and is solely caused by the bending moment. The standard specimen length is about 20% longer than the support span, with the standard specimen thickness being 4 mm and the standard specimen width being 13 mm. The standard span-to-thickness ratio is 32:1.

Fig. 4.9. Experimental set up for 3-point bending test

CHAPTER 5

RESULTS AND DISCUSSION

For characterization analysis which include FTIR, TGGA, and DSC were done on samples at room or ambient conditions since all tests involve heating of the specimen. Whereas the tests done to determine the mechanical properties like Tensile strength, Charpy impact Energy, and flexural strength were done on two sets of samples. One among them is samples at room conditions which is represented as “untreated” (UT) samples, while the samples which are cryo-dipped are labelled as “cryo-treated” (CT). The cryo-treated samples were obtained by soaking or immersing the samples in a cryo- bath containing sufficient amount of LN_2. The tests were conducted immediately after taking the samples from the cryo-bath. All the tests mentioned in the previous chapter has been successfully carried out and results of all the test are analyzed and inferred in the following sections.

5.1. FOURIER TRANSFORM INFRA RED SPECTROSCOPY ANALYSIS

FTIR analysis is done for all the samples to confirm whether any reaction occurred between the silane and the graphene. FTIR analysis is done on PERKIN ELMER SPECTRUM TWO FT-IR SPECTROMETER which measures in the range of 400-4000cm^{-1}. The FTIR spectra for all concentrations including 0.5g/L, 1g/L, and 1.5 g/L are obtained. The figure shows the offset graph of all three compositions in which the transmittance value is taken as the offset value, since wavenumber is the unique code to analyze different bonds.

Peaks in the spectrum near 3400cm^{-1}, 2924 cm^{-1}, 1606 cm^{-1}, and 1237 cm^{-1} confirmed the presence of epoxide groups, hydroxyl groups and carboxyl groups on the surface of graphene. The FTIR spectra of SGO indicated that a reaction between Silane and Graphene particles was occurring since specific peaks from pristine Graphene nanoparticles varied. There was a doublet peak at 2932 cm^{-1} and 2880 cm^{-1}. This is in coherence with the vibrations of both symmetric and asymmetric alkyl groups. Silane moieties can be thought of as the cause of this.

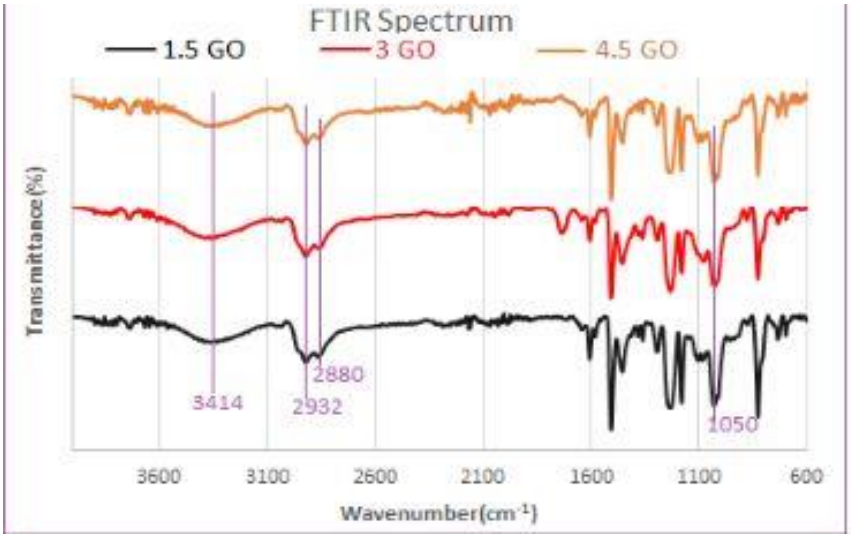


Fig. 5.1. Overlay of FTIR spectra of SGO-modified CFRP

Peaks at approximately 1055 cm^{-1}, 1225 cm^{-1} , 1627 cm^{-1} , and 3414 cm^{-1} confirmed the presence of the vibration of C-O bonds of alkoxy groups, C-O-C bond extending the vibration of epoxy groups, stretching vibration of aromatic C=C bonds, stretching vibrations of OH groups attached to the graphene surface, respectively. The occurrence of doublet peaks at 1108 cm $^{-1}$ and 1050 cm $^{-1}$, further supported the existence of Si-O-Si and Si-O-C bonds respectively. We have validated that graphene can be successfully functionalized by silanizing agents with the help of FTIR results, which have been mentioned in numerous journals.

5.2. THERMOGRAVIMETRIC ANALYSIS

The TGA curve showing the weight % loss is plotted for neat CFRP as well as SGO-modified CFRP sample. Due to better performance in mechanical tests, 1- SGO modified CFRP is chosen for TGA test. The TGA curves of neat and 3-SGO modified sample is shown in fig.5.2.

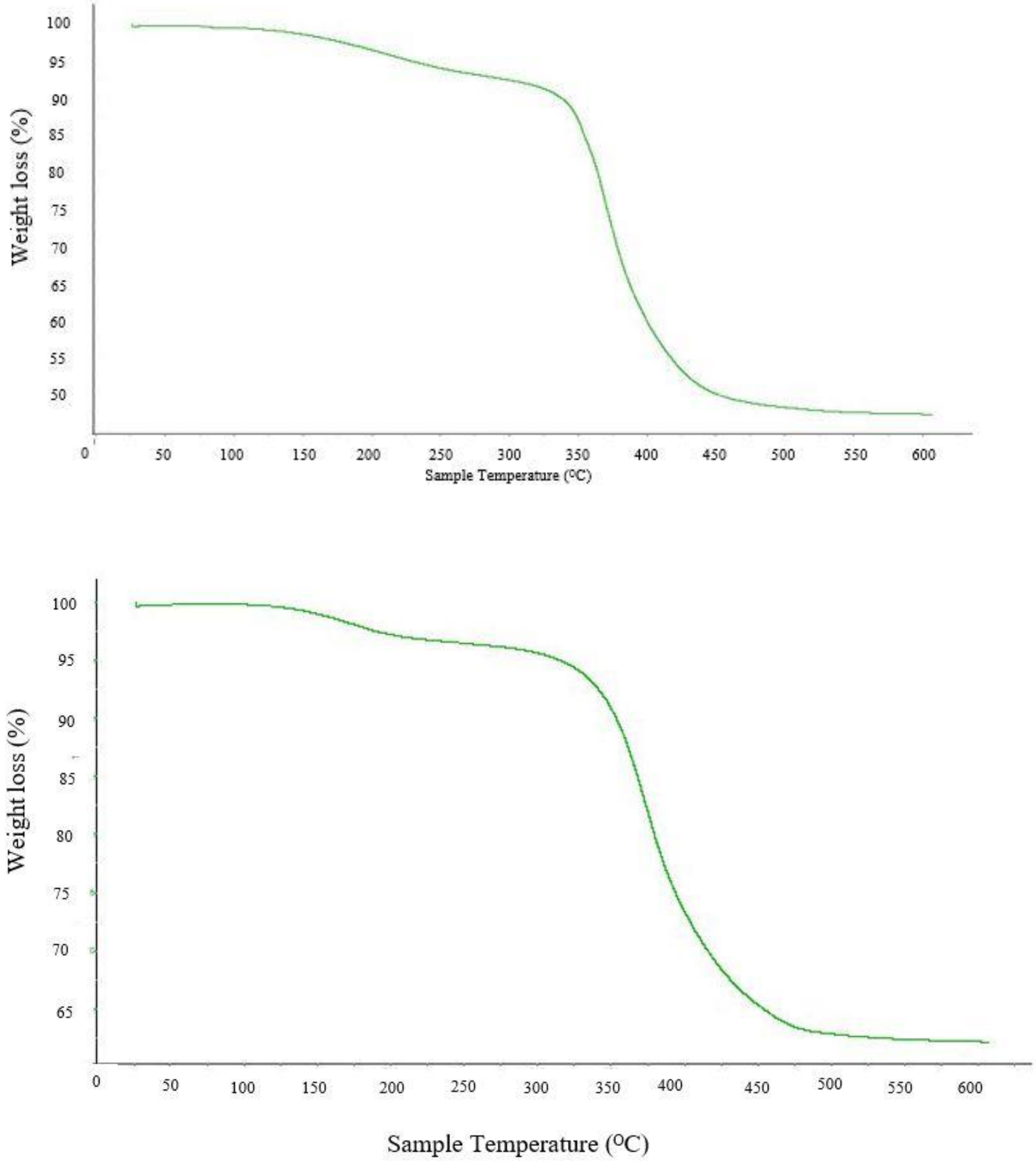


Fig. 5.2. TGA curve showing the loss in weight % of (a) SGO-modified CFRP (b) Neat CFRP

The thermal stability of both samples can be inferred from this curve. The overlay graph of both samples is plotted and it is identified that till 211^{O}C the SGO-modified CFRP sample is more thermally stable than the neat sample since the red curve is slightly above the black curve. This indicates that SGO -modified CFRP is better performing than neat CFRP.

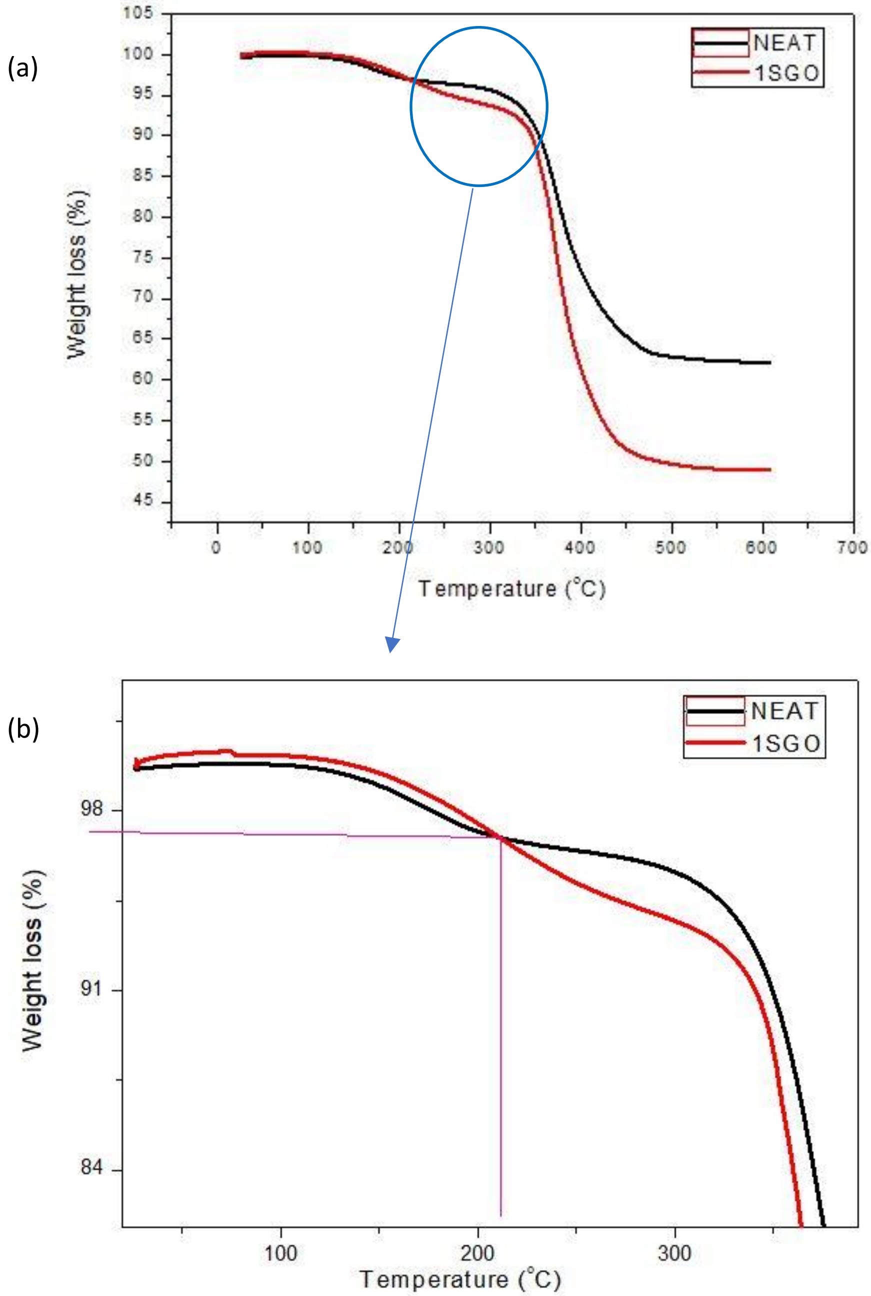


Fig. 5.3 (a) overlay of 1-SGO modified sample and neat sample (b) zoomed view of marked portion.

The improvement in the thermal stability of SGO -modified CFRP can be associated with the fact that the tendency of the dispersed GO to carry the thermal load. The graph is compared with the TGA-DTG curve of Graphene Oxide and it is identified that the first drop of the GO occurs at around 200^{O}C [35].The drop refers to degradation of the GO, hence the performance of SGO-modified CFRP drastically reduces after 211^{O}C. The addition of silanizing agent has increased the temperature of degradation by around $8\text{-}10^{O}$C. From the figure it is clear that after 211^{O}C the curve drops suddenly for SGO modified CFRP which indicates the thermal decomposition happening in the sample. This depriciation is mainly due to the degradation of the functional groups and reduction of GO. Also, the SGO forms flexible -Si-O-Si- bond which is confirmed in FTIR tests, reduces the rigidity of the epoxy matrix. Thus, the reduction in bond strength may result in the increased thermal degradation.

At 51% mass loss the curve transforms into a stable trend denoting the residue after the TGA test. The residue will contain Carbon and graphene as char, since all other compounds are degraded in response to the temperature increase.

5.3. DIFFERENTIAL SCANNING CALORIMETRY

Different Scanning Calorimetry analysis is done to determine the specific heat capacity of all the modified samples. Specific heat capacity value is a property of material which varies with respect to temperature as well as the state of matter. Three curve method is being used for the determination of C_P value of all samples. The final DSC curve of all the modified samples and neat sample is shown below from fig.5.4 to fig. 5.7. All the samples have expressed a similar trend which is confirmed by the offset graph of DSC curves of all the samples. 4.5 SGO modified CFRP has showed an anomalous behaviour that can be attributed to the agglomeration of SGO particles.

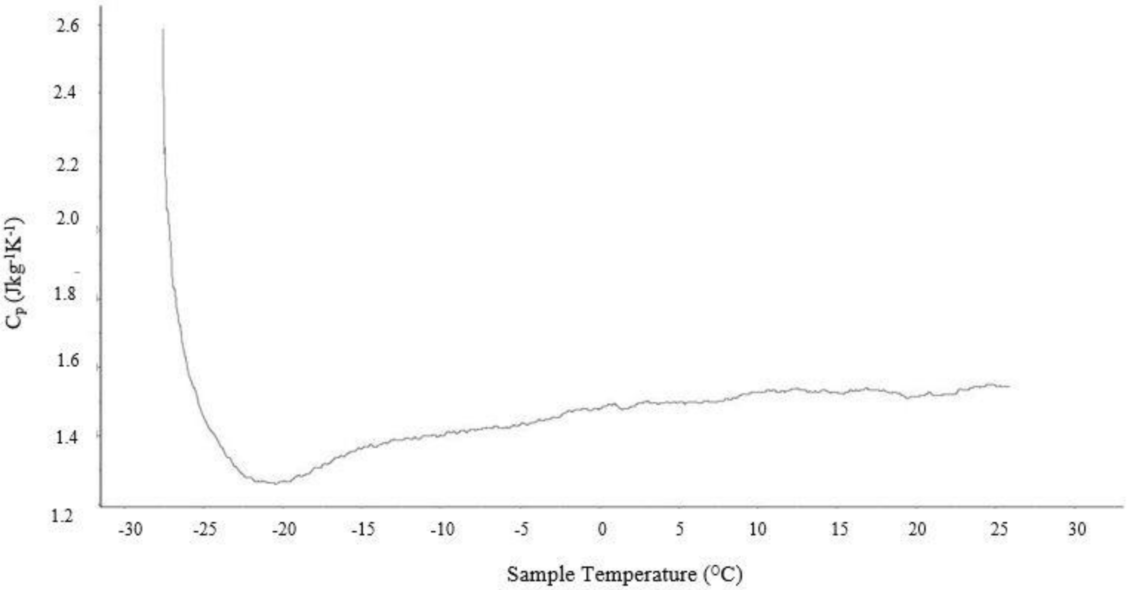


Fig. 5.4. DSC curve of neat sample

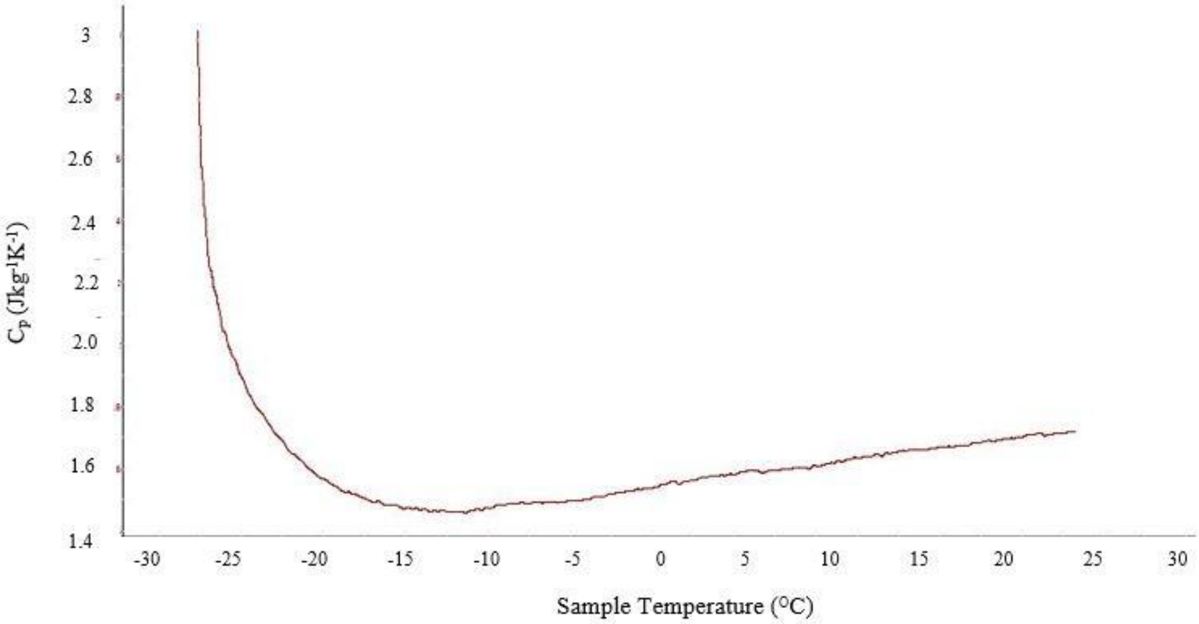


Fig. 5.5. DSC curve 0.5g/L SGO-modified CFRP

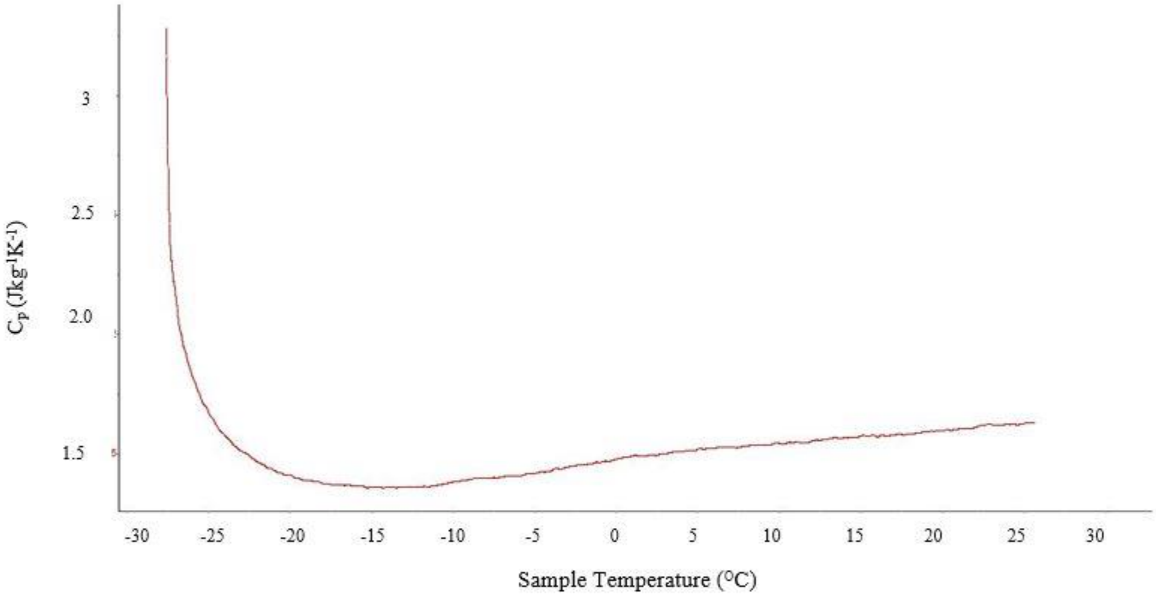


Fig. 5.6 DSC curve of 1g/L-SGO -modified CFRP

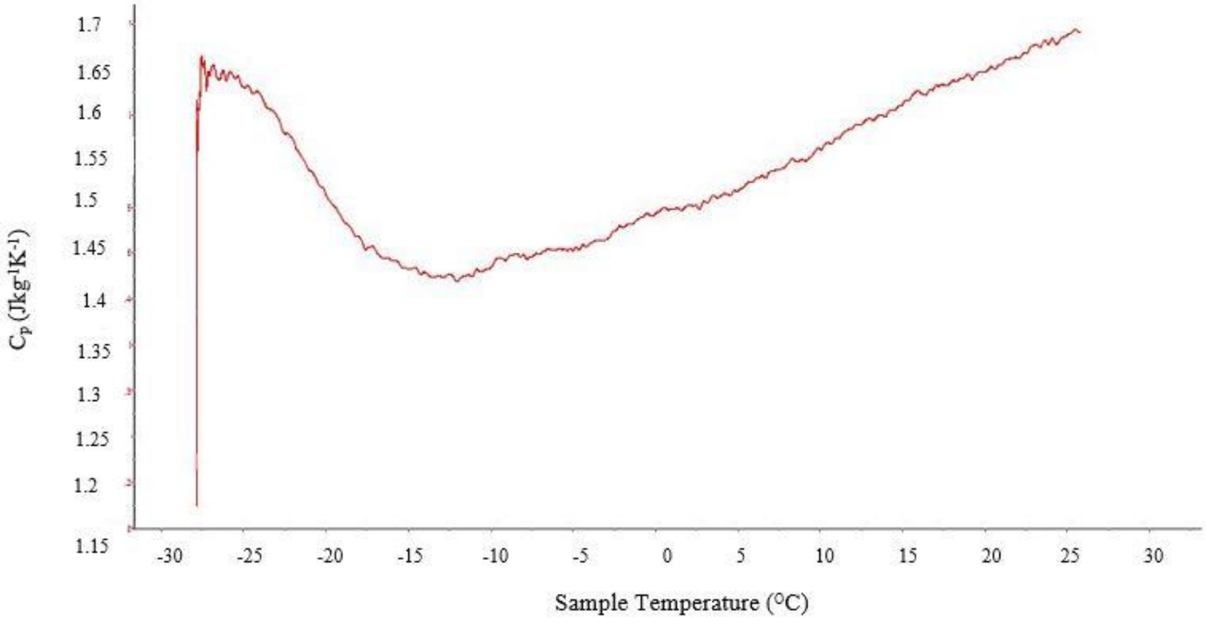


Fig.5.7. DSC curve of 1.5g/L-SGO -modified CFRP

Since the specific capacity is a temperature dependent property, part of the graph marked as (a), (b), (c) and (d) from the fig.5.8 were identified on the actual curve to determine the C_p value of neat, 0.5SGO modified CFRP, 1.0SGO modified CFRP, 1.5 SGO modified CFRP samples respectively at two temperatures 25^{O}C and 20^{O}C and plotted as a bar graph in fig. 5.9.

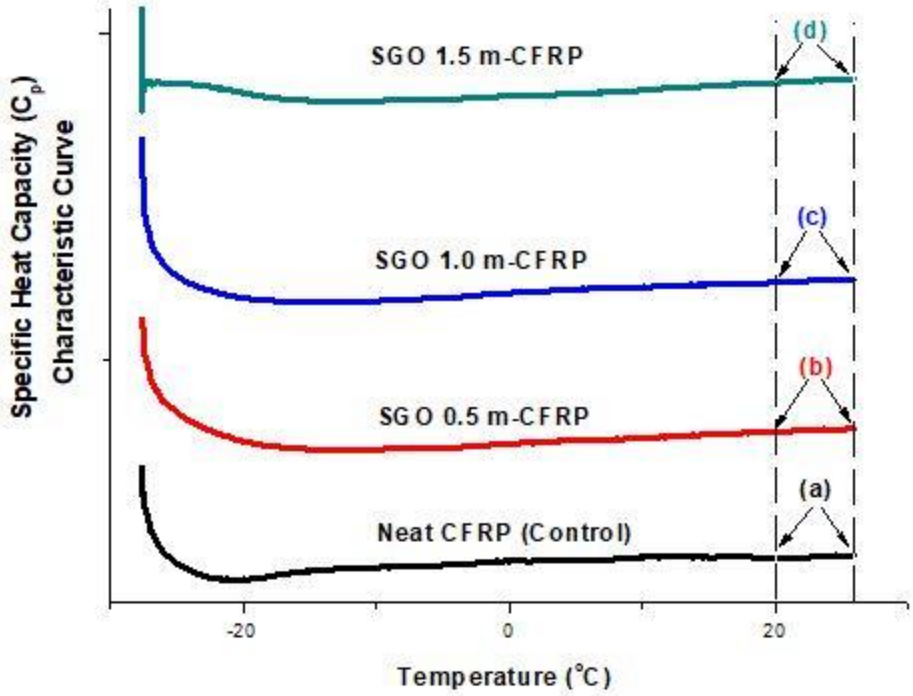


Fig 5.8. Overlay of DSC curves of all samples

From the bar graph it is clear the 0.5SGO modified CFRP exhibits highest specific heat value 1.682 Jkg^{-1} K^{-1} and 1.71 Jkg^{-1} K^{-1} at 20^{O}C and 25^{O}C respectively. The C_p values of neat, 1.0SGO modified CFRP, 1.5 SGO modified CFRP samples at 20^{O}C were 1.51 Jkg^{-1} K^{-1}, 1.59 Jkg^{-1} K^{-1}, and 1.64 Jkg^{-1} K^{-1} respectively. Similarly, the C_p values of neat, 1.0SGO modified CFRP, 1.5 SGO modified CFRP samples at 25^{O}C were 1.54 Jkg^{-1} K^{-1}, 1.62 Jkg^{-1} K^{-1}, 1.68 Jkg^{-1} K^{-1} respectively. By comparing the values of modified CFRP's C_P values with neat samples there is a slight increase being exhibited which is due to the addition of SGO particles.

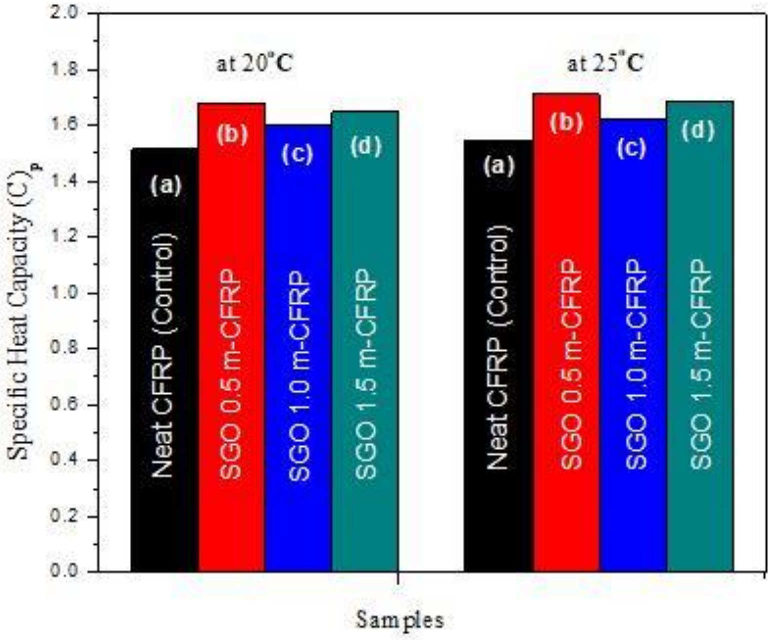


Fig. 5.9. C_p values of all samples at 20^{O}C and 25^{O}C

5.4. TENSILE TEST

Tensile strength of the SGO modified samples and neat samples were obtained by conducting tensile test in an UTM, in accordance with the ASTM D3039 standards. The tests were done for samples at room temperature as well as for the cryo-treated samples. The tensile strength values of untreated (UT) and cryo- treated (CT) samples are shown in the Table 5.1.

Table 5.1. Tensile strength values of untreated and cryo-treated samples

Sl. No.	Sample Composition	Tensile Strength (UT) MPa	Tensile Strength (CT) MPa
1	NEAT	357	323
2	0.5 SGO modified CFRP	379	344
3	1 SGO modified CFRP	404	372
4	1.5 SGO modified CFRP	362.5	336

The SGO modified CFRP has exhibited improved tensile strength when compared with the neat samples. Among all the samples 1 SGO has portrayed significant increase in the tensile strength i.e., a 13.61 % increase is observed which confirms the positive effect of the introduction of SGO particles. But there is a decline in the tensile strength value of 1.5SGO modified CFRP which is attributed to the agglomeration of SGO particles in the carbon -epoxy interface. Due to the clusters of GO particles, it may not act as bridging the gap between epoxy and fibers, instead it will act as crack initiation sites and cause failure. The overlay graph of stress- strain curve for all samples in both the conditions is given below.

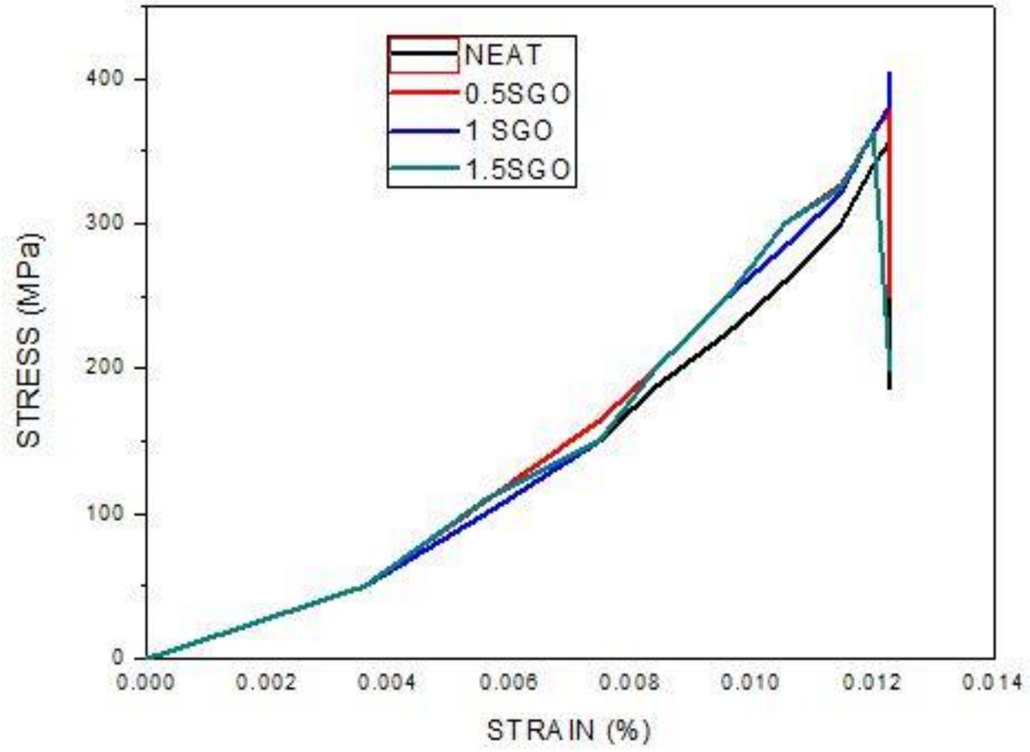


Fig 5.10. Stress- strain curve of samples at room conditions

The same tests conducted for cryo-treated samples have also showcased an enhancement in the tensile strength value when compared to the neat samples. The improvement percentage also increased for cryo-treated samples, i.e., 1SGO modified CFRP has exhibited an increase of 15.17% with respect to neat sample. The addition SGO in CFRP can contribute better performing samples at cryogenic temperature. After cryogenic treatment the Si-O-Si- bond may slightly loose its flexibility. But it acts as bridge between the contracted epoxy and expanded fibers thus reducing the thermal stress induced during cryo-treatment.

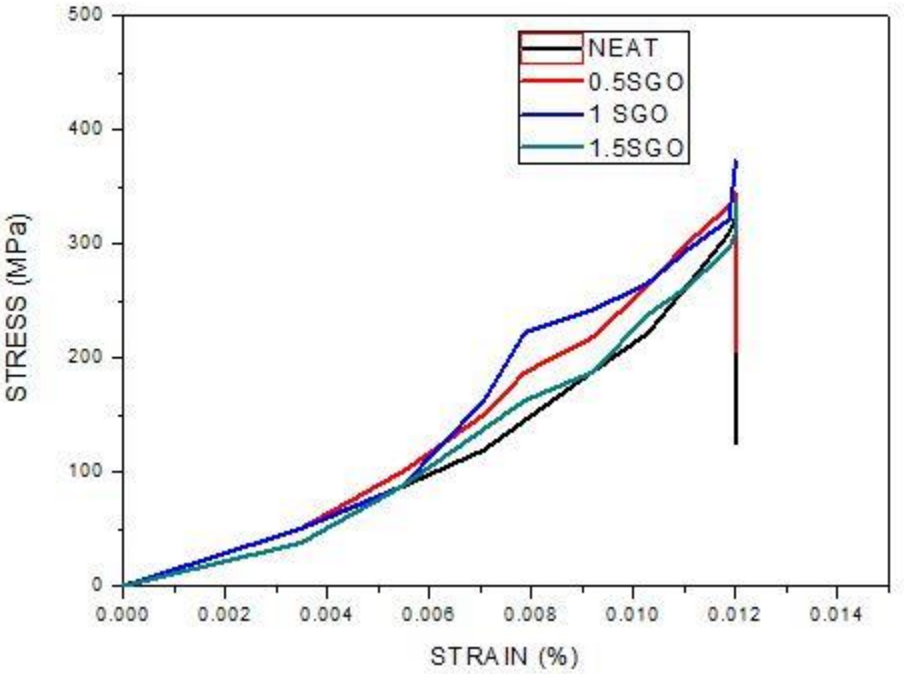


Fig.5.11 Stress-strain curve of cryo-treated samples

The tensile strengths of all the untreated and cryo-treated samples are plotted as a bar graph for better comparative analysis. The fractured surface has been thoroughly analyzed after the test. Inference from the fracture morphology has thrown light on the nature of failure of untreated and cryo-treated SGO modified CFRP and neat CFRP samples. The samples at room conditions have exhibited evident fiber breakage which is visible in (a), (b), (c), and (d) of Fig 5.13. Whereas for cryo-treated samples, the failure appears to be more brittle with less fiber breakage.

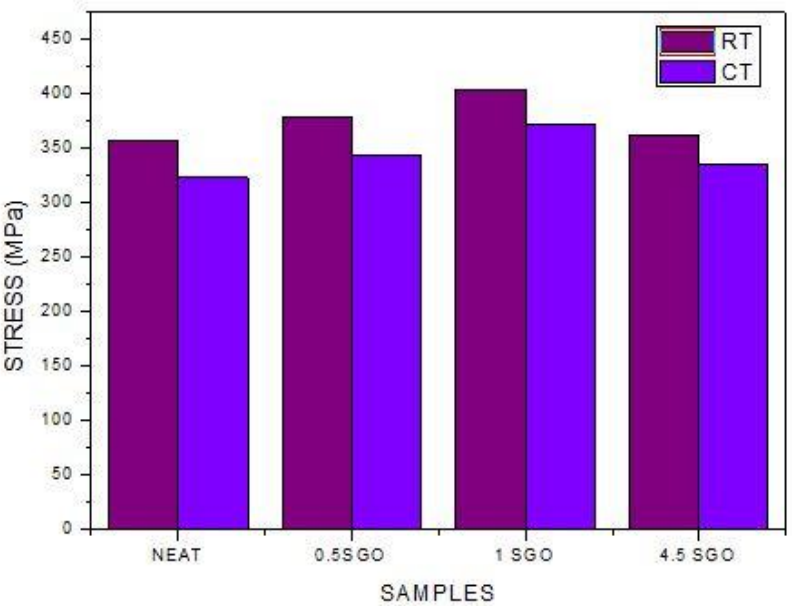


Fig 5.12. Bar graph showing tensile strength of all samples

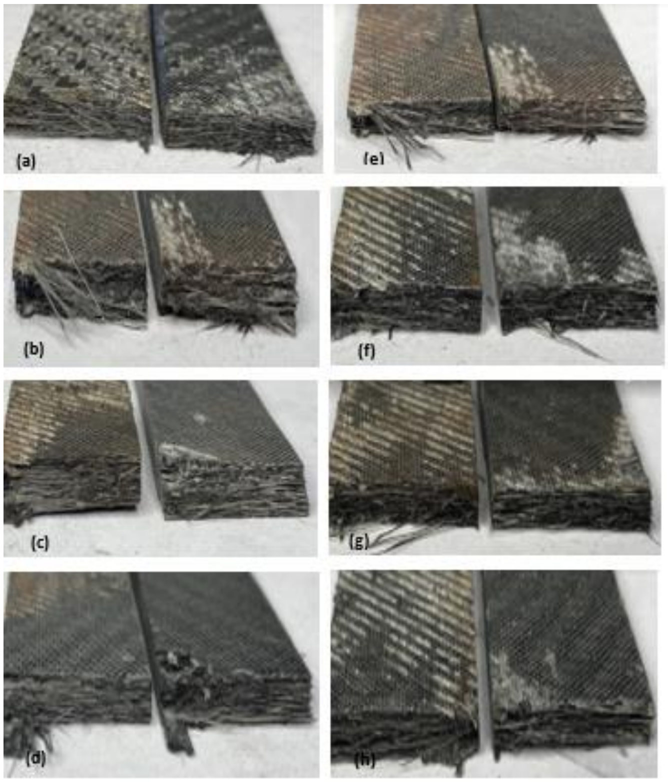


Fig.5.13. Macroscopic images of fractured surface of untreated (a-neat, b-0.5g/L ,c-1g/L, d- 1.5g/L) and cryo-treated samples (e-neat, f-0.5g/L, g-1g/L, h-1.5g/L).

5.5. CHARPY IMPACT TEST

Charpy impact test were done to determine the impact strength of neat and SGO modified sample. A conventional pendulum impact system is used for the test. The average values of impact energy (kJ/m^2) were obtained after testing of 5 samples of each composition. The impact energy values of neat CFRP, 0.5 SGO modified CFRP, 1.SGO modified CFRP, and 1.5 SGO modified CFRP at room conditions were obtained as 114 kJ/m^2, 125 kJ/m^2, 130 kJ/m^2, 124 kJ/m^2 respectively. The cryo-treated samples have exhibited a decline in the impact energy. The values of impact energy of cryo-treated neat CFRP, 0.5 SGO modified CFRP, 1.SGO modified CFRP, and 1.5 SGO modified CFRP samples are 108 kJ/m^2, 122 kJ/m^2, 127 kJ/m^2, 117 kJ/m^2 respectively. The reduction % of impact energy cryo-treated with untreated samples has reduced upon modifying the CFRP with SGO. Whereas the cryo-treated 1.5 SGO modified CFRP exhibits drastic decline in the value. Due to the increased concentration, agglomeration effect can come into play. Furthermore, after cryo- treatment, these clusters of SGO may act as crack initiation sites which may result in reduced impact energy.

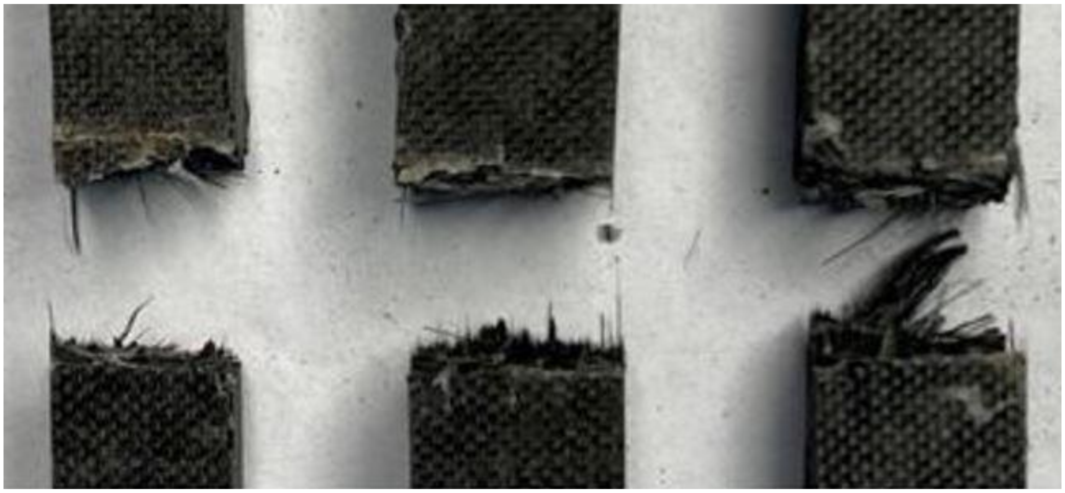
Fig.5.14. Bar graph showing impact energy of all samples

All composite fracture mechanisms were related to carbon fibre breaking, bending failure followed matrix cracking, and rupture occurred (prevalent at 1.5 SG), which could be attributable to agglomeration and a low-quality link between Silanized Graphene and epoxy surface. The fractured surface of the neat sample at room conditions is shown in figure.5.15 which evidently shows the shearing of carbon fiber because decreased absorbing energy translates to CF failure. While for SGO-modified samples the fiber breakage was considerably less as compared to the neat samples. When Silanized Graphene Oxide was introduced the fracture mechanisms were drastically altered which is shown in the fig.5.16.

Fig.5.15 Fractured surface of neat sample in ambient condition

The fiber breaking in the SGO-modified samples is not due to shear, as shown in the neat sample. The maximum strength was demonstrated by 1g/L samples with the most uneven surfaces and carbon fiber fracture, which accounted for the dissipation of the majority of the impact energy. Furthermore, rough fracture surfaces cause crack path deflection, which deviates the direction of crack propagation from its real path, increasing the area of the crack. The toughness of the carbon fibre matrix interphase increased as the bond strength soared up due to the creation of flexible -Si-O-Si- linkages, as evidenced by fracture morphology.

(a)

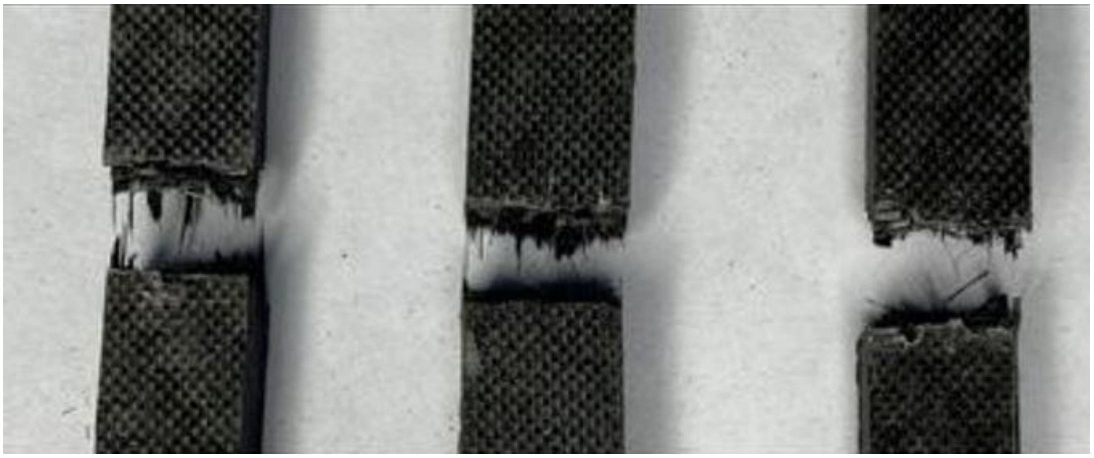


0.5g/L SGO modified CFRP

1.0g/L SGO modified CFRP

1.5g/L SGO modified CFRP

(b)



0.5g/L SGO modified

1.0g/L SGO modified CFRP

1.5g/L SGO modified CFRP

Fig. 5.16. Fractured surface of SGO modified samples (a) Room temperature (b) after cryo-treatment

5.6. THREE-POINT FLEXURAL TEST

The three point bending test is conducted to determine the bending or flexural strength of the SGO modified CFRP samples and neat samples. The bending strength is obtained by considering the maximum tensile stress at which the specimen commences to break. By the addition of SGO in CFRP the bending strength has enhanced. The stress- strain curve of all the samples at room temperature is plotted in figure 5.15 using ORIGIN. From the graph it is clear that the SGO modification has definitely improved the extent of the flexibility of the specimens. It is due to the formation of flexible -Si-O-Si- bonds formed which is confirmed by FTIR results. Moreover 1.5 SGO modified CFRP exhibits highest flexural strength which is about 24.18%. But, in tensile test 1.5SGO modified CFRP sample showed a decline in the tensile strength. The enhancement in the bending strength can be attributed to the improved flexibility of -Si-O-Si- bond.

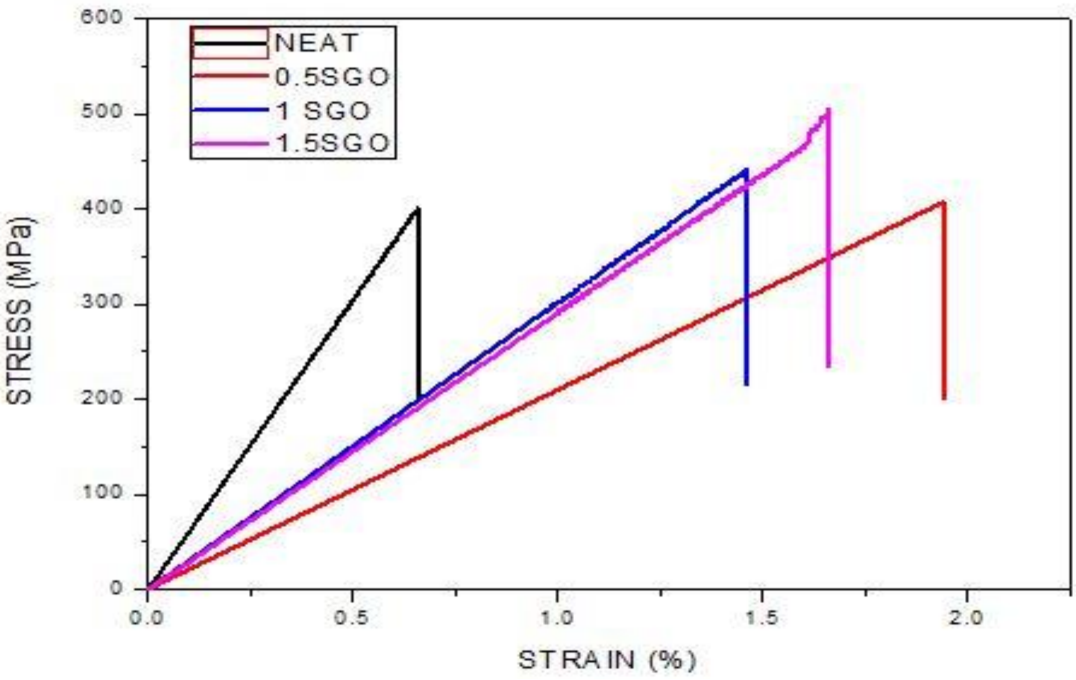


Fig.5.17. Stress-strain curve of all samples at ambient conditions.

While analyzing the results of cryo-treated samples, the 1 SGO modified CFRP exhibited the maximum flexural strength of 506MPa which is about 35.29%. This anomalous behaviour can be due to the reduction in the flexibility of silane bond. Also, after cryo- treatment the freezing of agglomerated SGO clusters will act as an initiator for the cracks. Hence a lesser concentration with sufficient flexibility for bridging the thermally stressed epoxy and carbon fibers showcased a significant improvement. Contrastingly at room temperature increased concentration of SGO have resulted in enhanced flexural strength for 1.5 SGO modified CFRP sample.

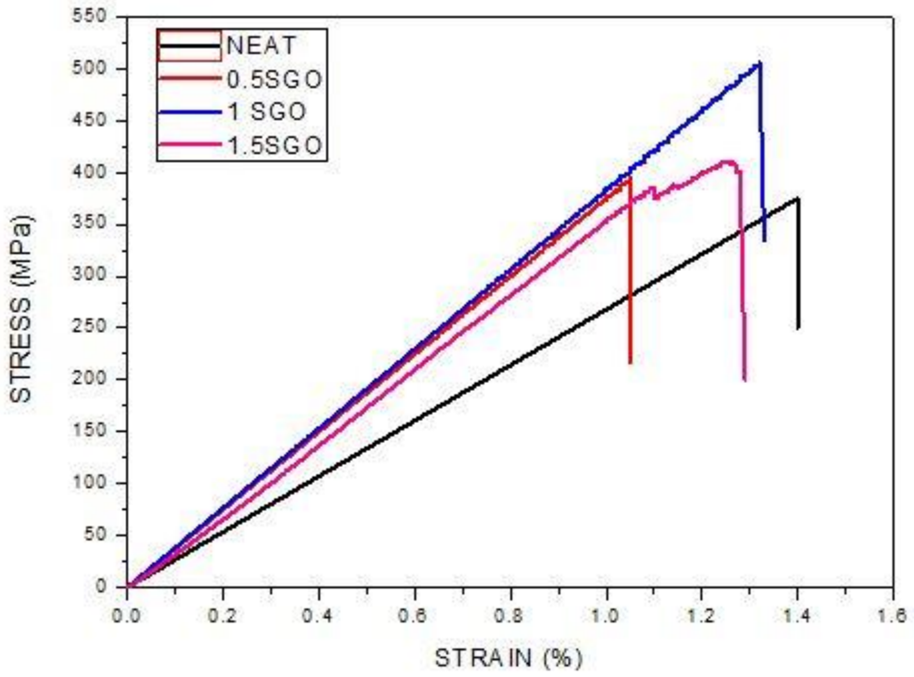


Fig.5.18. Stress-strain curve of cryo-treated samples.

CHAPTER 6

CONCLUSION

In this work, the role of Silanized Graphene oxide coating on the carbon fibers in improving the properties of CFRP has been studied. Electrophoretic Deposition technique was adopted to modify the carbon fibers. This has resulted in ionic bond formation between the SGO and carbon fibers, which is stronger than covalent bonding. Due to the ionization of GO particles during EPD process the dispersion of SGO on the carbon fabric is uniform. A favorable voltage of 30V was used for coating SGO on the CF. Increased voltage and time may result in deterioration of the properties as well as agglomeration of GO particles. FTIR analysis was conducted to identify the bonds formed after the SGO modification. It was confirmed by the presence of peaks at 1108cm^{-1} and 1050 cm^{-1} that -Si-O-Si- bonds and -Si-C- bonds were formed. To analyze the behaviour of SGO modified CFRP in cryogenic environment, samples of all the concentration were cryo-treated by immersing them in LN_2 for about 20 minutes and tested immediately after taking them out of the cryo-bath. The tensile strength of SGO modified samples was greater than neat samples, among which 1g/L SGO-modified CFRP exhibited an increase by 13.16%. The enhancement of tensile strength for cryo-treated samples were further increased by 15.17%. Both the enhancements are attributed to the formation of flexible -Si-O-Si- bond and reduction in the thermal stress induced during cryo treatment. The impact energy of SGO modified samples were slightly greater than neat samples, the samples at room conditions achieved an increase of 14.03% whereas the cryo-treated samples showed an increase of 17.59% when compared with neat samples. But cryo treatment has slightly deteriorated the ability of the SGO-modified CFRP to withstand this sudden impact. While considering the three-point flexural test, 1.5g/L SGO-modified CFRP outperformed all other samples with an enhancement of 24.18% whereas 1g/L SGO-modified CFRP portrayed an increase of 35.29 %. Since 1g/L is better performing its thermal stability is analyzed by TGA test which has confirmed that 1g/L SGO-modified CFRP is more thermally stable than neat sample. DSC analysis is also conducted to determine the specific heat capacity of SGO-modified samples, in which 0.5g/L SGO modified CFRP possess highest specific heat capacity of 1.682 $Jkg^{-1} K^{-1}$ and 1.71 $Jkg^{-1} K^{-1}$ at $20^{O}C$ and $25^{O}C$ respectively. Thus, from all the tests and its result analysis it is evident that modification using Silanized Graphene Oxide has improved the mechanical and thermal stability of CFRP.

There is large scope for a detailed study in the future. Since the modification resulted in successful enhancement of properties, a detailed study on thermal properties such as thermal conductivity, thermal diffusivity etc. can be done in future. Along with the thermal properties electrical properties can also be investigated which has more scope since, EPD method is used for coating CF there can be a tendency for improvement in the electrical properties as well. All these mechanical tests can be done in a cryogenic environment to study its effect.

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LIST OF PUBLICATIONS

1. **Manu M, K E Reby Roy** et al. (2022) Review on development of effective carbon fiber based cryogenic storage tank materials for space applications, ICAME 2021 TKM COLLEGE OF ENGINEERING