THERMAL CHARACTERISATION OF NANOCOMPOSITES

A PROJECT REPORT

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BONAFIDE CERTIFICATE

Certified that this project report titled **"THERMAL CHARACTERISATION OF NANOCOMPOSITES"** is the bonafide work of **"R HEMA PRIYA (18103033), S JANANI (18103041) AND P ESTHER NIRMALA (18103068)"** who carried out the project work under my supervision. Certified further that to the best of my knowledge that work reported here does not form part of any other project / research work on the basis of which a degree or award was conferred on an earlier occasion on this or any other candidate.

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LIST OF ABBREVIATIONS

S NO	SYMBOLS / ABBREVIATION	DESCRIPTION
1	ASTM	American Society for Testing and Materials
2	TGA	Thermogravimetric Analysis
3	DMA	Dynamic Mechanical Analysis
4	TiO_2	Titanium Dioxide
5	$E^{'}$	Storage Modulus
6	$E^{''}$	Loss Modulus
7	MPa	Mega Pascal
8	kN	Kilo Newton
9	mm	Millimeter
10	GPa	Giga Pascal

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ABSTRACT

The aim of this project is to study the effect of Titanium dioxide (TiO_2) and Graphene nano-filler content on the thermal properties of the glass fibre/epoxy composite. For the study, samples of TiO_2 in combination with Graphene simultaneously 0%, 1%, 2%, 3% and 4% were dispersed in the epoxy matrix. The thermal characterization of the nanocomposite samples was done through Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA). From the values obtained from the TGA, the weight percentage and thermal decomposition with the addition of the nano-fillers is studied and from DMA variation in the values of storage modulus, loss modulus, tan δ are studied. DMA and TGA results showed a considerate effect on the thermal decomposition and thermal stability of the glass fibre/epoxy composite with the addition of TiO_2 and Graphene nano-fillers. The results obtained provided an effective solution for glass fibre/epoxy nanocomposite with better thermal properties. These findings open a way to develop high-performance composites at higher temperatures for various potential applications especially in the aerospace industry.

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CHAPTER 1

INTRODUCTION

1.1 Introduction to Composites

Composite materials have found its way to all the industries in the past decade. All metals, non-metals and other materials will soon be replaced with composites because of their unique features. The usage of composites has become integral with our daily life. From packaging to aerospace industries composite is widely used for different reasons. Aircrafts and Spacecrafts use composites in various components because its light in weight, has high fatigue strength and high corrossion resistance. Usage and development of composite has created more curiosity and more experiments in the industries. Various studies are being conducted on composites to try and enhance their properties. The most widely used are carbon fibre, glass fibre and aramid fibre reinforced epoxy composites.

There are three different types of composites. They are:

I. Fibre based reinforced composites

II. Particulate based composites

III. Structure-based or hybrid composites

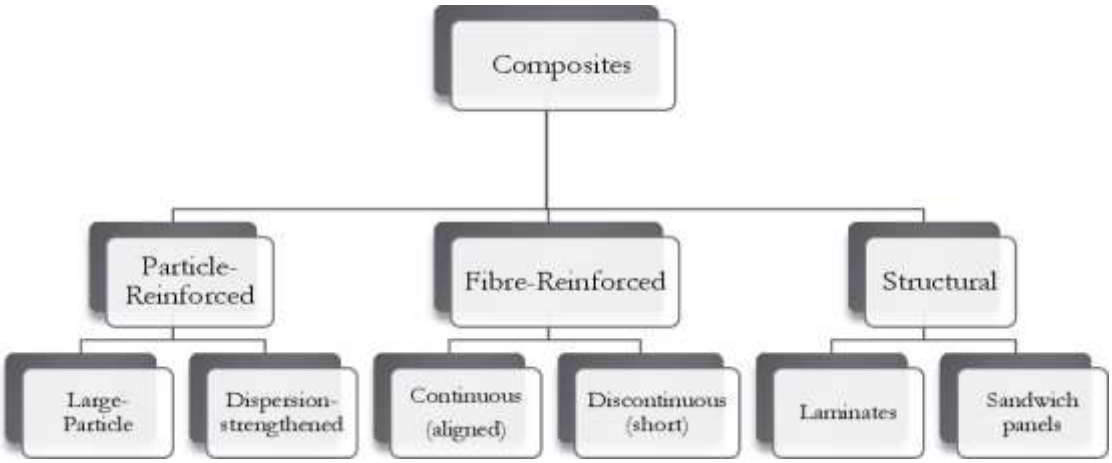


Fig 1.1 Classification of Composite materials

Different types of Composites based on Matrix are:

I. Metal Matrix Composites (MMC)
II. Ceramic Matrix Composites (CMC)
III. Polymer Matrix Composites (PMC)

Composites generally have fiber or particle stage which is more stiffer and is stronger than the continuous matrix phase and also act as the primary load carrying members. The matrix is a load transfer medium between fibers, and in some cases they also bear load. The matrix is more ductile when compared fibers and therefore acts as a source of composite toughness and also protects the fibers from environmental damages.Fibres generally have more length when compared to its dimension and the aspect ratio which length with respect to diameter of fibre vary for a continous fibre the aspect ratio is higher and for discontinous fibre which has random orientation the aspect ratio is less.

1.1.1 Fibre based Composites

Fibre reinforced composites are composed of fibre and a matrix. Fibers or reinforcement is the part of composite that provide strength to composite whereas the matrix helps in bonding of all the fibres and provide shape to the composite and also transfer loads.

1.1.2 Particulate based Composites

A particulate composite is defined as being composed of particles which are generally suspended in a matrix. Particles may have any type of geometry, size or configuration. Particles that are generally used reinforcement include ceramics and small particles generally minerals,metals or amorphous solids. Polymer composite materials has created huge interest in various engineering fields, particularly in aerospace applications.

1.1.3 Structure based or Hybrid Composite

Hybrid composites is the most advanced composites when compared to conventional composites. Hybird composites either have one reinforcing and matrix phase or multiple reinforcing and matrix phases. The mechanical properties of a hybrid composite can be varied by changing their volume ratio and stacking sequence of different plies.

1.1.4 Metal Matrix Composite

Metal matrix composites (MMC) consist group of materials (which includes metals, alloys and other compounds) that is incorporated with different reinforcement or fibre phases, like particulates, whiskers or continuous fibres. They are of lightweight and also have high-specific strength therefore has wide range of industrial applications particularly in automotive, aerospace and thermal management industries.

1.1.5 Ceramic Matrix Composite

Ceramic matrix composites (CMCs) is a type of composite in which both the reinforcement of fibre phase and matrix phase consist of ceramic materials.

1.1.6 Polymer Matrix Composite

Polymer matrix composites are materials made up of fibres which are embedded in an organic polymer matrix. The fibres enhances the properties from the conventional materials[1] .One of the main advantage of using polymer matrix composite is their strength and stiffness. Polymer matrix composites are limited to operating temperatures below 600° F (316° C), at temperatures higher than 316 degree celsius ,the polymers start to degrade [2].

1.2 Background to the project

The extent of our task is to fabricate the glass/epoxy composite by Compression moulding with Titanium oxide and Graphene as nano fillers. The improvement

of different morphologies of nanocomposites essentially relies on a superficial level treatment of the nanoparticles and explicit scattering or handling strategies.[3] The composite is then cut into samples of required dimensions for the analysis. Thermogravimetric analysis and dynamic mechanical analysis are conducted on the samples to note the variation in the properties of composite.

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate. Dynamic Mechanical analysis (DMA), is a technique where a small deformation is applied to a sample in a cyclic manner which allows the materials response to stress, temperature, frequency and other values to be studied. The expansive field of use for this class of material is fundamentally owing to its out-standing qualities with respect to strength and and rigidity and its suitability for lightweight construction.[3]

Glass fibre reinforced polymers have unique properties such as lightweight, high strength and modulus, good availability, recyclability, high strength and toughness, and ease of processing. Glass fibres are the most frequently used reinforcement for polymeric matrix to prepare its composites. It is transparent and has very little shrinkage. In addition, epoxy resin has extremely high bond strengths as adhesives. the qualities of composites are largely underneath the strength of resin because of non-uniform molecule size circulation and molecule aggregation.[4] Moreover, it is inert and also has excellent resistance to heat, which make them ideal for electronics and electrical systems as well as other industrial applications.

1.3 Objective of the project

The project aims to study the influence of TiO_2 and Graphene nano-filler content on thermal decomposition characteristics and thermal stability of glass/epoxy

composite. To study and tabulate the variation in properties of the composite sample for different calculated amounts of nano-filler added. The thermal analysis considered: Thermogravimetric analysis and Dynamic mechanical analysis.

1.4 Scope of the project

The project includes an overview of the previous studies, research on Glass fibre reinforced polymer with various percentages of nanofillers and attempts to find a solution for glass fibre/epoxy composite with better thermal properties like thermal stability and thermal decomposition using the thermal characterization methods, Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA).

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This section gives a quick overview of the projects done before related to the study on thermal properties of the composites and polymers by the addition of nano- fillers through the published journals and research papers. In order to add more precision to our project, we have done a study on these papers as references.

2.2 LITERATURE SURVEY

Mat Yazik, M.H et al (2021). In this study, MWCNT and MMT (montmorillonite) were used as filler materials to study their effect on the dynamic mechanical and thermal properties of SMEP (Shape Memory Epoxies). Shape memory epoxies (SMEP) are covalently cross-linked networks that have their glass transition temperature as transformation temperature. Their permanent shape is dictated by the cross-linked network that is formed during curing and their temporary shape is due to mechanical deformation above glass transition temperature.[5] Dynamic mechanical and thermal properties were evaluated via dynamic mechanical analysis (DMA) which measures the storage modulus (E'), loss modulus (E"), and damping factor (tan δ), which are temperature dependent properties, and thermogravimetric analysis (TGA) through which decomposition temperature and rate of decomposition can be obtained.[5] The MMT amounts used were 1%, 3%, and 5% weight percentage of the mixture and MWCNT amounts used were 0.5%, 1%, and 1.5% weight percentage of the mixture. DMA and TGA analysis show that the incorporation of 1%, 3%, and 5 wt.% of MMT, in combination with 0.5, 1, and 1.5 wt.% MWCNT, can lead to an enhancement or deterioration of the thermal properties of SMEP nanocomposites. Finally, the paper concluded that the hybridization of 3 wt.% MMT and 1 wt.% MWCNT in

SMEP leads to considerably better thermal properties, thermal stability, decomposition temperature and viscoelastic performance, compared to other formulations.[5] However, additional investigation is necessary to assess the performance of hybrid filler loaded SMEP nanocomposite in terms of shape memory effect, especially shape fixity and shape recovery.

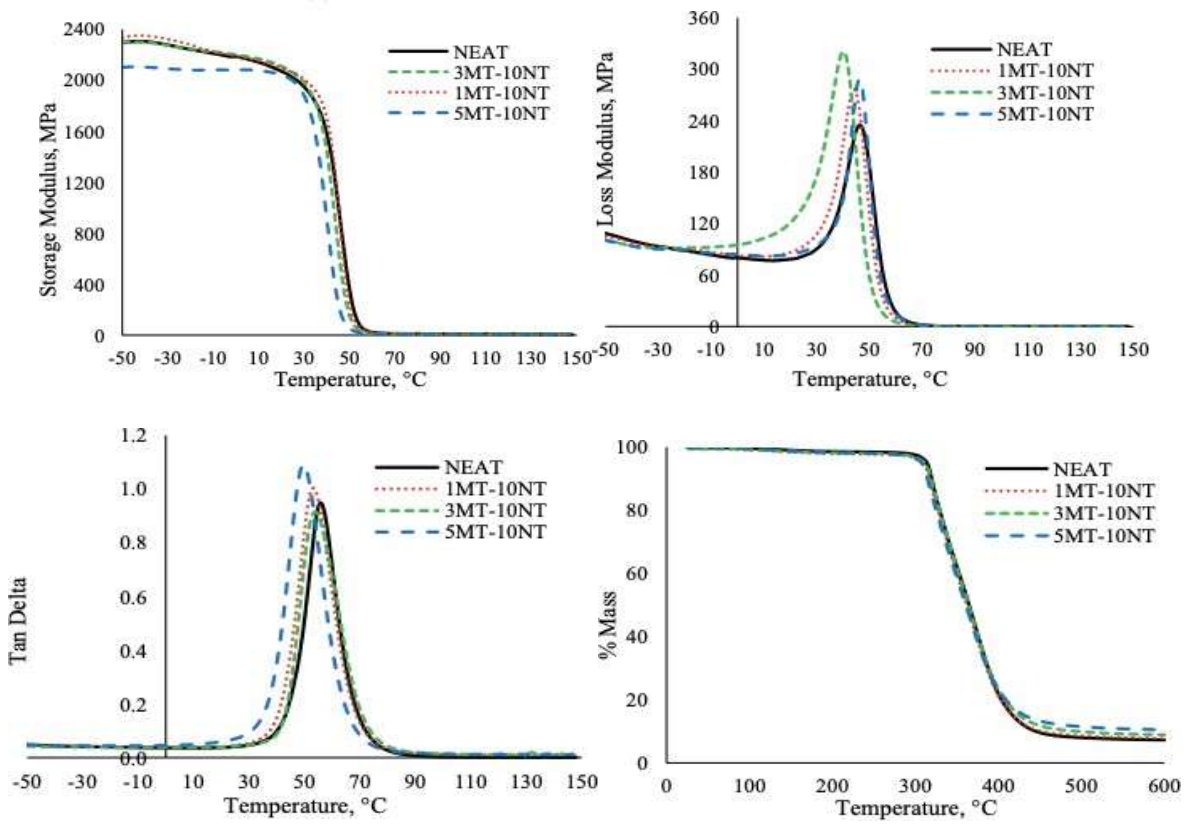


Fig 2.1 Graphs showing DMA of composite with MWCNT and MMT as nanofillers

Manap et al (2020). In this paper, the effect on thermal properties by the incorporation TiO_2 in the carbon-based TPU matrix (TiO_2/MWCNT/TPU), without inclusion of costly chemical treatments has been studied. Titanium Dioxide (KEMOX RC 800 PG), Multi- walled Carbon Nanotubes (KNT-M12), Thermoplastic Polyurethane (DESMOPAN 359X DPS300) are the materials used with dimensions being MWCNT 10nm - 20nm diameter, 10µm length; TiO_2- 0.19µm average particle diameter. Thermogravimetric Analysis (TGA) is used to study the properties such as loss of moisture and residual weight %. DMA is used to evaluate the thermo-mechanical characteristics of the composite.[6]

DMA analysis confirmed that MWCNT acts as an excellent heat conductor, and TPU is a good heat insulator. The low tan δ properties of the TiO_2/MWCNT/TPU composite shows that the composite is an excellent electrical insulator. The high glass transition temperature in TiO_2/MWCNT/TPU shows that the composite can sustain its rigidity of its molecular structure at high temperature. TGA also confirmed that MWCNT/TPU showed higher weight loss (beyond 360 °C) due to the tendency of degradation of MWCNT in an oxygenated environment and low superheating effect.

Table 2.1 Material composition of the samples P1, P2 and P3

SAMPLES	TPU (%)	MWCNT (%)	TiO_2 (%)
P1 – Pure TPU	100	0	0
P2 – TPU/MWCNT	97.8	2.2	0
P3 – TPU/MWCNT/TiO_2	94.5	2.2	3.3

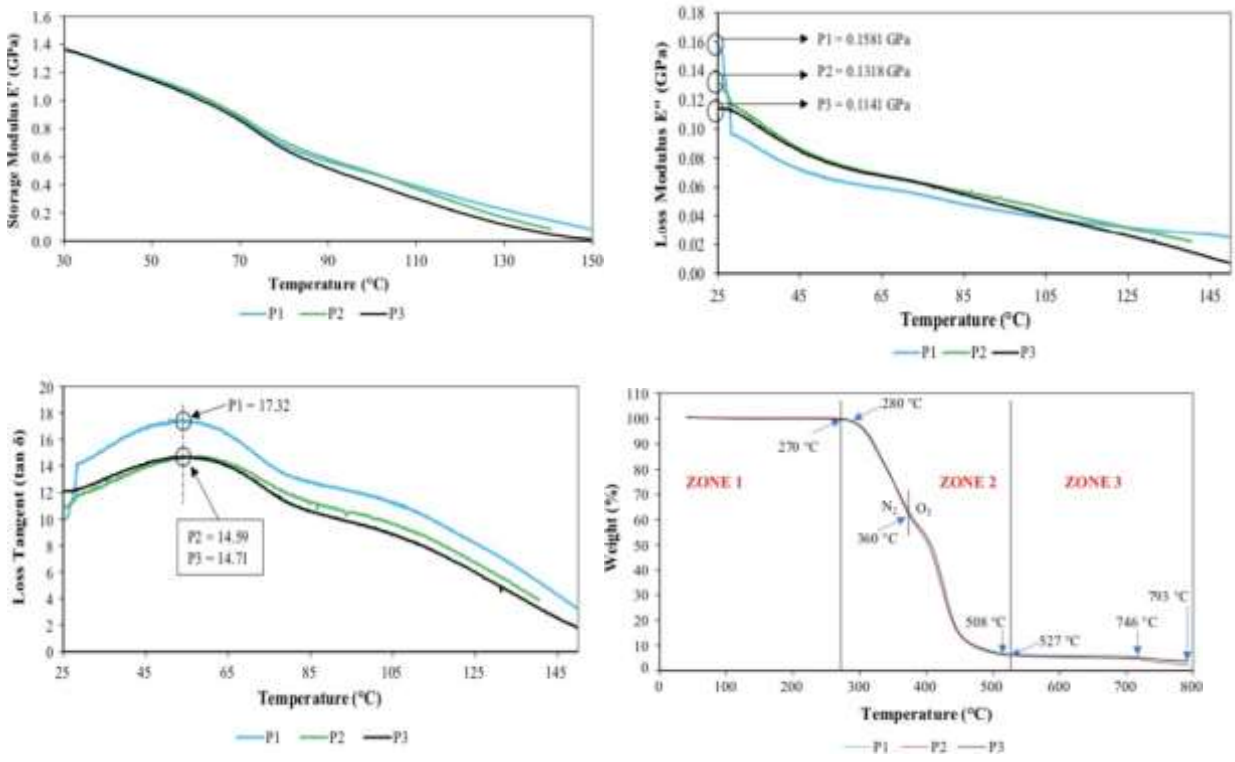
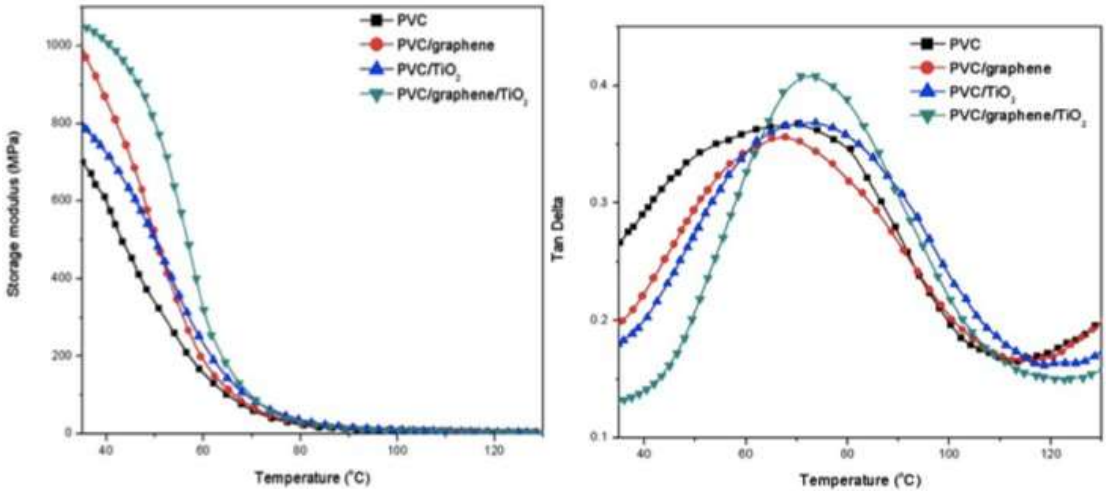


Fig 2.2 Graphs showing DMA of thermoplastic polyurethane composite with MWCNT and TiO_2

Xiaming Feng et al (2015). This paper describes about adding TiO_2 to graphene nanosheet to enhance the thermal properties of PVC. One more primary reason to add TiO_2 is that it supress the emission of harmful substances that are emitted during combustion of PVC. Graphite oxide was prepared according to Hummers method. In preparation of graphene/TiO_2, graphite oxide was dispersed in a mixture of H_2O and ethanol under ultra-sonication to get a homogenous suspension of exfoliated graphene oxide.And some amount $Ti(OiPr)_4$ was added to the graphene oxide suspension and it was ultra-sonicated this resultant mixture was then transferred to a Teflon-sealed autoclave and was kept in oven at 150 °C for 12 hour. The final product was isolated by centrifugation, rinsed thoroughly with deionised water and ethanol, and was finally dried in vacuum.[10] Thermogravimetric analysis (TGA) was carried out using a Q5000 IR thermoanalyzer instrument under an air flow of 25 ml/min. In each case, the samples (about 5 mg) were heated from room temperature (30 °C) to 600 °C at a linear heating 4 rate of 20 °C/min.The changes of the fire behavior were primarily attributed to the synergistic effects of graphene/TiO_2 hybrids: the adsorption and barrier effect of fillers slow down the thermal degradation of polymer, and restrain the heat transfer and the flammable or toxic gaseous products release.



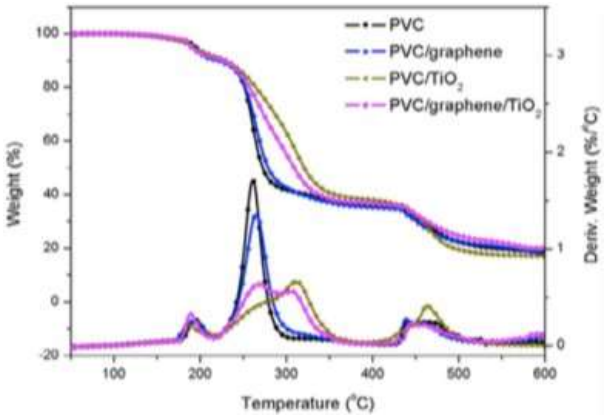


Fig 2.3 Graphs showing DMA of PVC with fillers Graphene and TiO_2

Aswathnarayan et al (2020). Synergistic effect of nano graphene on the mechanical behaviour of glass-epoxy polymer composites. Materials Today: Proceedings, 20, 177-184. In this study the material frameworks chose for the review are perfect epoxy (EP), 1 wt percent Nano Graphene filled glass-epoxy (1GE) and 2 wt % filled glass-epoxy nanocomposites (2GE) and these were created utilizing vacuum sack shaping procedure. The potential fillers, for example, PTFE, SiC, TiO2, MoS2 and Alumina in small size have demonstrated their best during mechanical execution when utilized with polymer composite. The trial and error method has been done to concentrate on the conduct of epoxy based nanocomposites. The mechanical and sliding wear conduct of epoxy nanocomposites has been contemplated affected by room temperature according to ASTM Strategies.

The outcomes uncovered that the impact of nano graphene filler expansion into glass texture supported epoxy composites fundamentally worked on both mechanical behaviour of composites considered.[7] The XRD designs were considered and are dissected. These examples recommend nano particles are available in composite organization. This assists with concentrating on the impact of these fillers on the properties of the composites examined. At first, the rate diversion of perfect epoxy was 3.3. However, at that point expansion of 1 wt % nano graphene into texture built up epoxy has upgraded the redirection conduct

of the composites contemplated. Further, expansion in composition of nano graphene declined the redirection conduct of composites considered. This might be because of diminishing in synergism between the fillers and sap in bowing.

The graphs in fig 2.4 show the effect of nano graphene on mechanical behaviour of the composites in each wt%. The technique for test to decide the strength limits accounts a ton in assessing the strength behaviour of composites. The impact of nano filler expansion has further developed the effect strength of the composites contemplated.

The effect strength of flawless epoxy was 19.45 J/mm^2. However, the addition of 1 wt percent nano filler has further developed the effect strength of glass epoxy composites to 45 J/mm^2 which is 13.1% increment over the flawless epoxy. Further incorporation of nano graphene further improved the effect strength of the glass epoxy composites. This is might be because of pliable nature of texture which is the foundation of the composites. This might be credited to the shortfall of agglomeration of nano fillers and uniform conveyance of nano graphene filler in composites. The nano graphene was utilized as the best filler for working on the mechanical and tribological conduct of glass texture supported epoxy composites.

The X-beam diffraction design investigation showed that the example top were concentrated and sharp demonstrating the glasslike idea of nano composites. The elasticity of glass epoxy composites has been significantly worked on because of progress give expansion of nano graphene (up to 2 wt percent). The pliable conduct in pressure has been worked on because of consideration of nano graphene filler in to glass epoxy composites. The flexural conduct of glass epoxy composites has been adequately worked on because of expansion of nano graphene. The great reaction as far as effect strength has been displayed by the glass epoxy composites because of incorporation of Graphene nano filler. It is seen that the improvement in mechanical conduct of these nano composites is

because of the compelling support of glass texture and interfacial communication of nano graphene with epoxy composites.

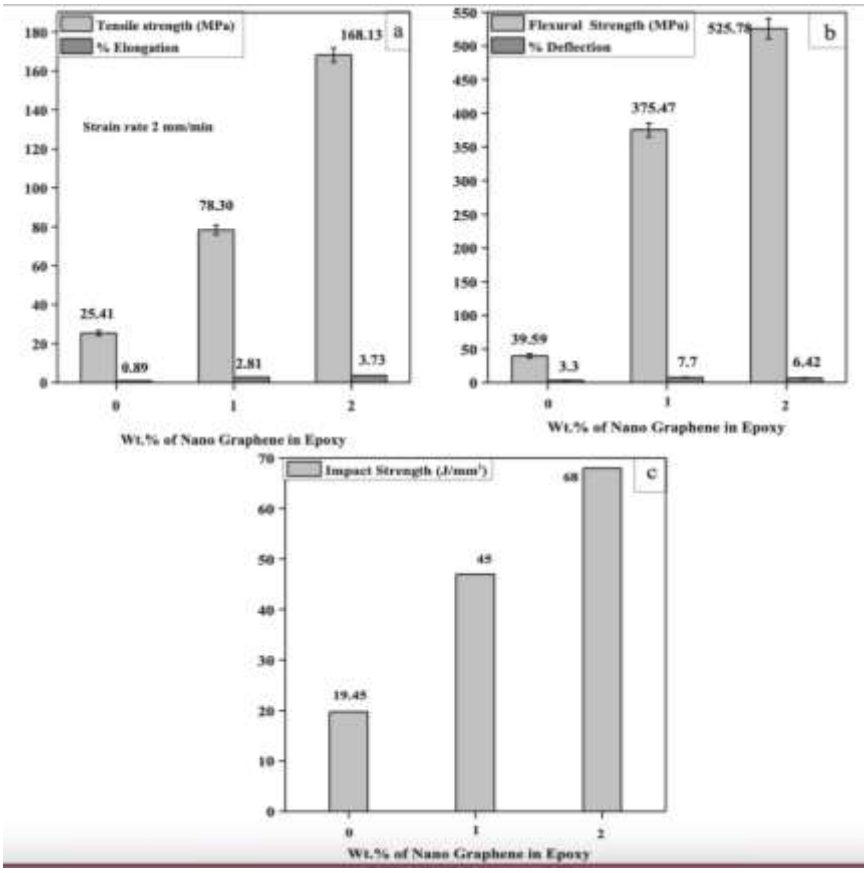


Fig 2.4 Graphs showing the effect of Nano Graphene on Mechanical behaviour of Glass–Epoxy Nano composites: a) Tensile behaviour, b) Flexural behaviour and c) Impact strength

Gantayat et al (2018). Thermogravimetric examination showed a moving of the decomposition temperature towards higher worth with expanding VGCNF. This demonstrates that the consolidation of VGCNFs into epoxy offered a settling impact. Integrated nanocomposites by filling the epoxy tar lattice with various loadings of u-CNFs (untreated) and s-CNF (silanized CNF). The outcomes got shown higher tensile strength and lower Young's modulus for s-CNF/epoxy nanocomposites than the u-CNF/epoxy nanocomposites.Moreover, the TGA examination demonstrated that the s-CNF/epoxy nanocomposites are more thermally stable than virgin epoxy and u-CNF based nanocomposites.[8] This

moving of decomposition temperature proposes the improvement of thermal stability of epoxy because of the insertion of VGCNF. Examined the impact of various MWCNTs on the warm properties of amino functionalized MWCNT/epoxy sap nanocomposites by thermo gravimetric examination. From the noticed changes in TGA bends, they proposed that the higher items in MWCNTs make air pockets and agglomeration in the matrix giving moderately weak dispersion coming about certain imperfections in epoxy matrix which revives the thermal decomposition rate.

Thomason, J. L. (1995). In this study, the wide scope of utilizations for composite materials guarantees a practically inescapable contact with fluids and fumes, either natural or watery, which can influence both the quick and the drawn-out presentation of the material. The instruments of water assimilation, the plasticizing impact of retained dampness and the bringing down of the glass-elastic progress temperature are notable cycles which have been generally considered in polymeric materials. Water ingestion has been displayed to prompt an overall decrease in the mechanical properties of composites and this has been ascribed, to a limited extent, to debasement of the fiber-framework interfacial bond. Composites were ready with an ostensible 65 voP/0 fiber content utilizing a scope of business Eglass rovings accepted to have distinctive restrictive surface coatings. Three examples, length 10 mm and width 12 mm, were cut from the unidirectional glass-supported epoxy composite poles for water ingestion measurements. The cut examples were first dried under vacuum at 105 °C for per week. Estimations were made at 230°C and a general dampness of 100 %. The examples were presented distinctly to water fume to limit weight reduction because of draining. Water ingestion in polymers is frequently broke down as far as Fickian diffusion, which necessitates that the outcomes are plotted as weight gain (as a level of dry weight) versus square foundation of time. Examination of water retention ordinarily requires the utilization of chunks of test material with

the goal that the straightforward one-layered Fickian dispersion model can be utilized to work out a dissemination coefficient from the example dimensions, the underlying incline and balance esteems from the water take-up versus time plots.[9] The main consideration impacting water take-up in glass fiber-supported epoxy composites was viewed as the composite void substance. The kind of grid framework, for example the idea of the relieving specialist, and specifically the epoxy sap/restoring specialist proportion, was likewise found to importantly affect water take-up. To a lot lesser degree, the interfacial strength and the fiber surface covering additionally have some impact. An amazing outcome was that expulsion of the fiber surface covering had no clear impact on the energy of 6 water ingestion, notwithstanding the enormous unfavourable impact on the interfacial strength. The water assimilation results additionally demonstrate that the thickness of the grid is brought down by the presence of the glass strands, maybe due to the development of an interphase locale. Regardless of the maybe natural conspicuousness of the impact of voids on composite water assimilation, these outcomes are the first, as far as anyone is concerned, which efficiently show the greatness of the impact.

Saha et al (2016). Different nanoparticles have been included polymer grid to upgrade the mechanical, warm, electrical, and attractive properties of polymer nanocomposites. Expansion of little grouping of graphene in polymer grid shows an improvement in mechanical, electrical, and warm properties. Be that as it may, it will in general shape totals in polymer grid because of solid van der Waals powers of fascination in the middle the graphene nanosheets. To defeat these solid vanderWaals powers two methodologies were by and large utilized viz. covalent alteration and non-covalent adjustment of graphene. Graphene oxide and graphene were additionally portrayed utilizing UV-vis-NIR spectroscopy. About 0.1 mg/ml of graphene oxide and graphene were broken down in DMF and test

sonicated for 15 min. UV-vis-NIR spectroscopy of these sonicated arrangements was completed.

Optical absorbance spectra show a trademark ingestion top at 232 nm which affirms the development of graphene oxide. While, optical retention spectra of graphene showing a top at 272 nm demonstrates the decrease of graphene oxide. The change in glass progress temperature (Tg) gives significant knowledge about the polymer chain elements at polymer nano fortifications interface.[6] Tg esteem diminishes if the communication between the polymer and nanoparticles is appalling, and increments if the cooperation between the polymer and nanoparticles is appealing. Also, the very much scattered nanoparticle in polymer network diminishes the Tg esteem extensively; while total nanoparticle scattering in polymer grid prompts more modest melancholy in Tg.

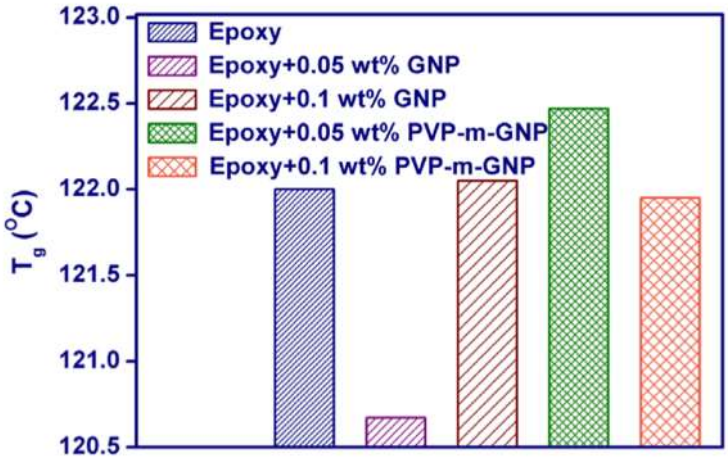


Fig 2.5 Glass transition temperature of epoxy, epoxy/graphene, and epoxy/pvp-modified graphene nanocomposites.

Due to improved scattering of graphene nanosheets in epoxy framework, huge surface area of graphene nanosheets is in touch with epoxy lattice which brings about a productive burden move from epoxy grid to graphene nanosheets and subsequently expanding the properties of nanocomposites. At 0.1 and 0.2 wt percent of graphene in epoxy network, the reduction in flexural modulus and flexural strength is because of amassed scattering of graphene in epoxy

framework, and in this way works with the helpless burden move from graphene nanosheets to epoxy matrix. The most noteworthy upgrade in mechanical properties was accomplished at 0.05 wt percent of PVP-altered graphene nanosheets-built up 7 epoxy nanocomposites. This is because of better scattering of PVP-adjusted graphene nanosheets in epoxy framework and a cooperation among PVP and epoxy grid. At higher focus mechanical properties diminishes because of total of PVP-changed graphene nanosheets.

Tg of PVP-adjusted graphene epoxy nanocomposites increments because of the communication among PVP and epoxy matrix. Flexural modulus is anticipated hypothetically utilizing altered standards of blends and it is contrasted and tentatively determined flexural modulus. PVP-changed graphene epoxy nanocomposites show upgraded reinforcing factor when contrasted with graphene epoxy nanocomposites. Higher fortifying component portrays improved pressure move across the support lattice interface. Warm steadiness of epoxy nanocomposites increments by expansion of lower convergence of graphene nanosheets in epoxy framework. Fractography study uncovers the limited bendable break because of expansion of graphene in epoxy lattice. Crack beginnings at collected destinations of graphene area in light of higher pressure fixation. The proportion of graphene: PVA should be investigated further.

Bashir et al (2021). Dynamic mechanical analysis (DMA) is likewise among the scientific strategies vigorously utilized by specialists to describe the interfacial connections of filled polymer systems. DMA can be considered as standard hardware for the estimation of dynamic mechanical properties of filled polymers. In a regular DMA analyse, an oscillating force is applied to a sample at a given temperature and frequency, and the material's reaction to this force is estimated. The applied power is known as the pressure (σ), and the deformation in the sample is known as the strain (γ). For viscoelastic materials, like polymers, the

size of the material's reaction to the applied 4 oscillating force is moved by a phase angle δ.

In this paper the variety of different polymers and fillers, it is apparent that the interfacial interactions exist between the polymer matrix and the filler particles and DMA are a significant scientific instrument for exploring and understanding the interphase district of filled polymers. Acrylic resin based coatings showed an expansion in Tg (and capacity moduli), which was not exactly that seen in alkyd resin based coatings under comparative circumstances.

The authors ascribed this outcome to the way that the substance crosslinking in the alkyd resin was sped up and reinitiated during maturing tests at 60 ◦C, causing an expansion in Tg. The acquired outcomes were not examined as for the interfacial associations between the binders utilized and the NFC filler. The vast majority of the studies including a variety of polymers and fillers recommend that in the event of a solid interfacial interaction between the matrix and the filler, the peak value of tan δ lessens, while a critical expansion in Tg of the composite isn't seen all the time. In view of trial and displaying work, there additionally exists dependable proof appearance that the decrease in the peak value of tan δ of filled polymers is connected to the higher rubbery storage modulus and not to the interfacial interactions between the polymer grid and the filler particles.

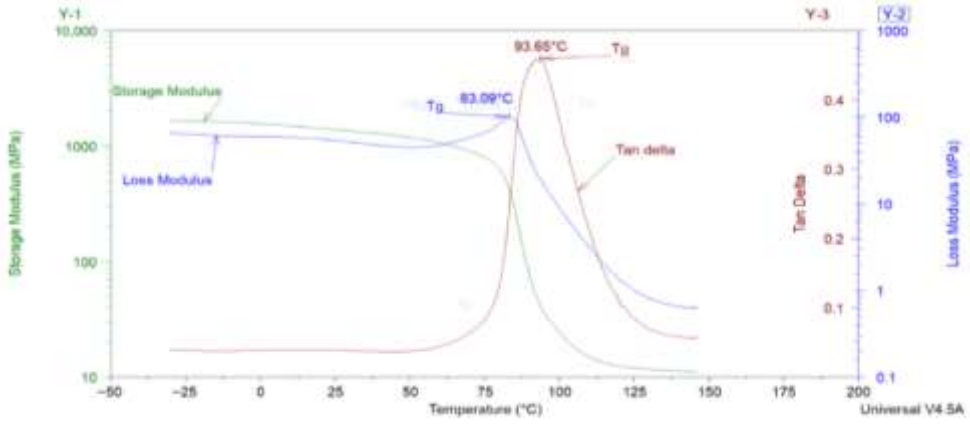


Fig 2.6 Storage modulus, loss modulus, and tan δ results of a sample analyzed in tension mode in DMA.

At last, it ought to be featured that in commercial items, a scope of various added substances are utilized, and the impact of such added substances on the interfacial interactions is moderately less understood. In this way, there is critical space for additional information and precise examinations about understanding the interfacial interactions in the filled polymers utilizing flexible insightful instruments like DMA.

2.3 SUMMARY

From the literature survey, the process of fabrication and thermal analysis with different nano fillers were studied. Graphene and TiO_2 have good thermal characterization as nanofillers in PVC. Nanographene with Glass fibre reinforced with epoxy has also been researched previously in some studies. The effect of nano fillers like Graphene and TiO_2 in glass fibre reinforced with epoxy however, the synergistic effect of Graphene and TiO_2 have not been studied extensively.

Thus, in our project the thermal properties of Glass/epoxy composite with various compositions of hybrid nano fillers like TiO_2 and Graphene are explored and implemented based on our requirements. In contrast to traditional filled polymer frameworks, nanocomposites require moderately low dispersant loadings to accomplish critical property upgrades, which cause them a vital possibility for aviation applications in which a portion of these upgrade to incorporate expanded modulus, further developed gas obstruction properties and atomic oxygen resistance, and better thermal and ablative performance. [10]

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

The methodology involves selection of materials, Fabrication and testing of samples.

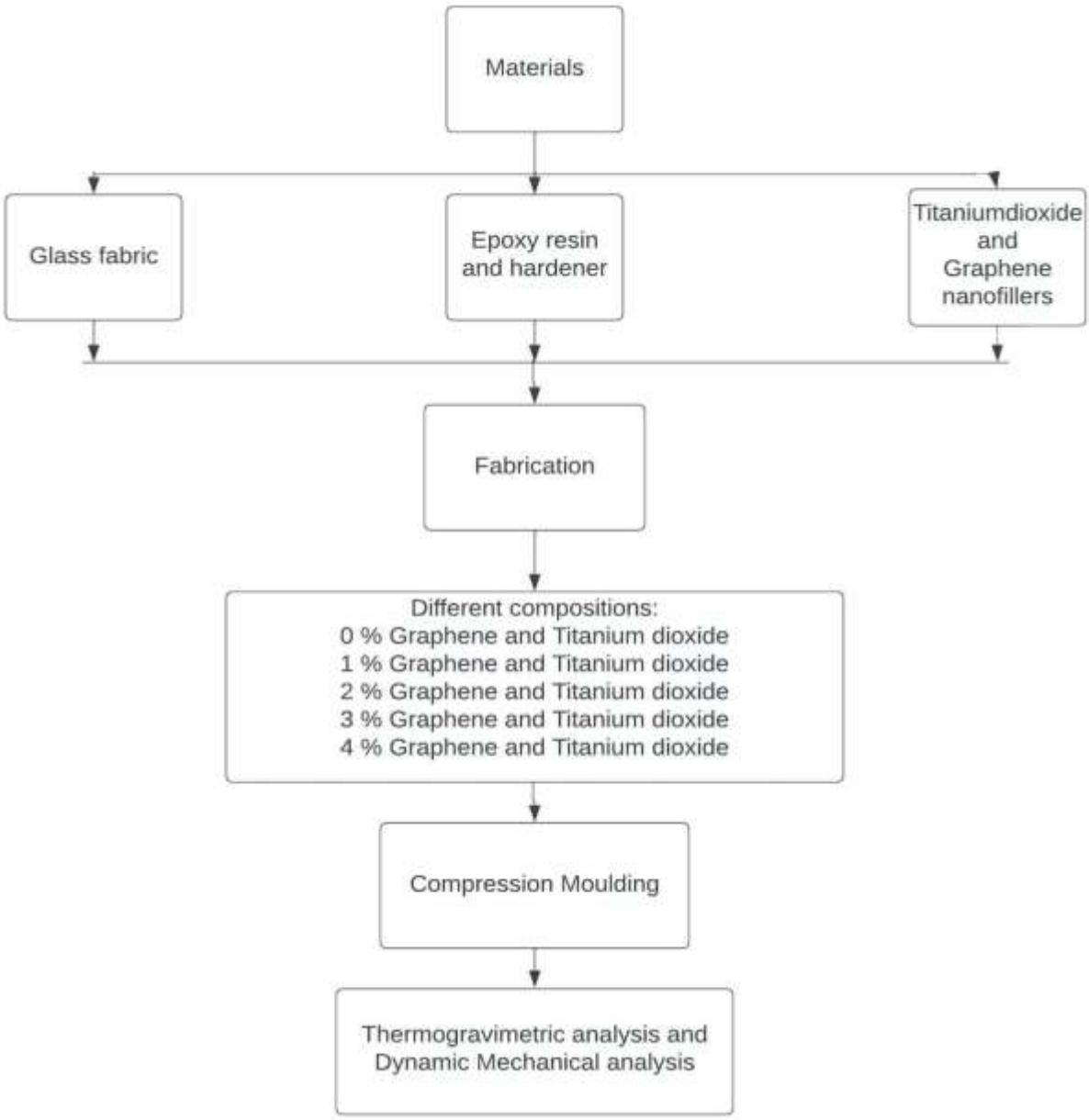


Fig 3.1 Flowchart of Methodology

3.2 MATERIALS

3.2.1 Selection of Fibre

For this study, glass fabric is selected. Mechanical properties of the glass fibre are roughly comparable to rest of the fibres such as carbon fibre and polymers. These fibres are much cheaper and less brittle but not as rigid as carbon fibre. Glass fibre acts as reinforcing agent to form a strong and relatively lightweight fibre reinforced polymer (FRP) composite material called Glass-reinforced plastic (GRP) also known as 'fibreglass'. Due to these properties of the glass fibre it is widely used in the industry today. Glass fabric of type E; 400 GSM were purchased from Sakthi Fibre Glass, Chennai. The density of glass fibre is 2.54 g/cm^3 and the tensile strength of the fibre is in the range of 1.7 - 3.5 GPa.

3.2.2 Selection of Resin

Epoxy resin is one of the most used thermoset polymers due to its excellent properties such as good interface, low curing time, high stiffness, better mechanical properties and lower moisture absorption. HY951 is used as a hardener. This hardener has better encapsulation with epoxy resin LY556. It has better coherence with epoxy resin, it is selected for fabricating composite laminates. Epoxy resin LY556 with HY951 hardener was acquired from Javanthee Enterprises, Chennai. Mixing and usage of resin and hardener reduce the formation of voids and it should be placed under cold conditions. It takes 24 hours to cure at 25 degrees centigrade and for complete curing, it should be cured at 40 degrees centigrade.

3.2.3 Selection of Nanofillers

Titanium Dioxide

Reinforcement of titanium dioxide, among the inorganic nano-fillers, has been extensively studied. TiO_2 is a good heat insulator and highly resistant towards fire. Studies explained that the incorporation of TiO_2 nanoparticles in the epoxy matrix improved the thermal properties such as glass transition temperature and storage modulus, and also prevents the re-stacking of the nano sheets. R-960 type research grade Titanium Dioxide is used and is purchased from Go Green fibre, Chennai.

Table 3.1 Properties of Titanium dioxide

Material	Titanium dioxide
Formula	TiO_2
Molar mass (g/ mol)	79.866
Density (kg/m^3)	4.23
Melting point (deg celsius)	1843
Boiling point (deg celsius)	2972

Graphene

Graphene is a material composed of carbon atoms that are grouped hexagonally. This arrangement results in monolayers of an atom thick. Graphene is known for its outstanding properties. Few properties of graphene are high thermal conductivity, high electrical conductivity, high elasticity and high density. Shilpent Graphene Powder research grade is used in this project and is brought from Go Green fibre, Chennai. These properties of Graphene make it suitable to be ued as a nano-filler.

Table 3.2 Properties of Graphene

Material	Graphene
Formula	C
Molar mass (g/ mol)	12.01
Density (kg/m^3)	2.267
Melting point (deg celsius)	3652 -3697
Boiling point (deg celsius)	4200

3.3 FABRICATION OF COMPOSITE

Fabrication of composite can be done in different set of process. Some of those processes are;

i) Open moulding

ii) Closed moulding

iii) Cast polymer moulding

The fabrication process that is followed to manufacture the composite is Compression moulding. The reason to choose compression moulding is this strategy is used to rapidly fix enormous amounts of complex fibreglass-supported polymer parts. Compression moulding features quick moulding cycles and high part consistency. The interaction can be robotised. Moreover, work costs are low and it gives plan adaptability and pleasant surface completions.

3.3.1 Safety measures

The following are the security measures to be attempted while creating composite laminates,

• Hand gloves, Face mask and Safety glass is compulsory security gear required while doing hand lay-up measure.

• Proper blending of resin and hardener should to be finished.

• Flammable should not be available close to the resin mixing area.

• Resin should to be utilised promptly whenever it is blended in with hardener.

• Should manufacture in a decent ventilated area.

3.3.2 Fabrication process

The materials that are required for fabrication are kept prepared and before starting fabrication of composite. The top and the base plates of the silicon mould are to be cleaned impeccably with thinner. Then the Polyester sheet should be cut according to the size of 300mm*300mm. Cut the Polyester sheet more than recommended, so over abundance resin will not pour out from the sheet. Stick the silicon rubber at the edges of the Polyester sheet with the height of 4 mm for preventing the over flow of resin. The resin is prepared using Epoxy resin (LY556) and hardener (HY951) in the ratio of 10:1. Graphene and titanium dioxide is added to the resin mixture and is mixed using mechanical stirrer gradually at 500 RPM for 30 minutes in room temperature for uniformity. Glass fabric is placed on the mould and resin mixture is applied all over the fibre and all air bubbles are removed through the roller. The same process is repeated. Reinforcement and matrix are arranged alternatively for 5 layers. The composite is placed in compression moulding setup under 5 bar pressure and the curing time is about 4 to 5 hours.

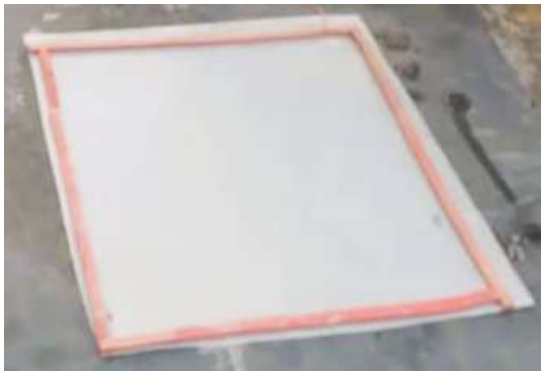


Fig 3.2 Silicone mould for preparation

Fig 3.3 Glass fibre of 400 GSM

Fig 3.4 Adding Resin and nanofillers

Fig 3.5 Composite plate

Fig 3.6 Composite is cut using high speed axesaw

CHAPTER 4

EXPERIMENTAL TEST

4.1 INTRODUCTION

In this project two thermal analysis were carried out. The following tests are conducted on the composites containing 0%, 1% ,2%, 3% and 4% hybrid nano-fillers such as Titanium Dioxide and Graphene to compare the thermal properties of the composites.

The testing methods used for these laminates are

- Thermogravimetric Analysis
- Dynamic Mechanical Analysis

Before testing the samples were cut in cutting machine according to ASTM standards.

4.2 TESTING PROCEDURE

4.2.1 Thermogravimetric analysis

For this test, the sample was crushed into fine powder by making sure it contains no impurities. The test was carried out on each sample, in the nitrogen atmosphere. TGA testing for the samples was performed in the TA TGA55 instrument according to ASTM E1131. The test was performed in the temperature range from 30°C to 950°C with a constant heating rate of 10°C /min and the frequency was set to 1 Hz. There-fore, TGA is mainly used for understanding certain thermal events such as absorption, adsorption, desorption, vaporization, sublimation, decompo- sition, oxidation, and reduction. [5] The characteristics of the material are taken in the form of the plot between weight loss % with the change in temperature,

called the TG curve and also the derivative of this curve called as DTG curve.

The following characteristics can be obtained from this test method,

- Residual Weight %
- Inflection Point Temperature

Fig 4.1 Thermogravimetric analyser

Fig 4.2 Powder form of Sample

4.2.2 Dynamic Mechanical Analysis

DMA in the three point bending mode was carried out as per the ASTM D4065 utilizing SII (DMS 6100) instrument with a specimen size of 60×12.5×3 mm3, at temperature from 35°C to 180°C at the rate of 5°C min−1 at a frequency of 1Hz.This method covers the thermal characteristics of the samples cut out from the composite materials. The characterisation is done using the properties such as storage modulus (E'), loss modulus (E''), and tan δ plotted against the temperature. the storage moduli are found to decrease with increase in temperature. This is due to loss in stiffness of fibres at high temperature.[4]

The peak E', peak E'', Tg for E'', peak tan δ, Tg for tan δ are analysed and determined.

Fig 4.3 DMA Analyser

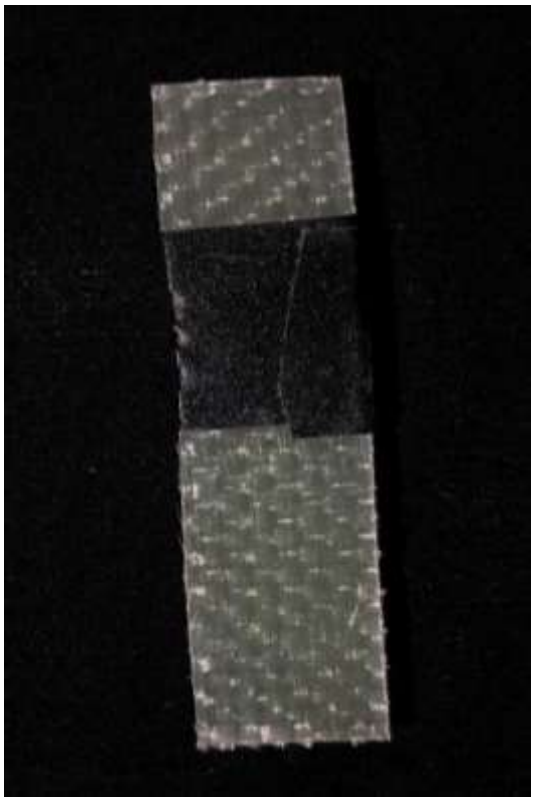


Fig 4.4 DMA sample

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 INTRODUCTION

The results for all the specimen such as storage modulus, loss modulus, tan δ and residual weight % from thermogravimetric analysis and dynamic mechanical analysis are tabulated.

5.2 COMPARISON OF DMA RESULTS

Storage Modulus- The storage modulus (E') represents the stiffness of a viscoelastic material and is proportional to the energy stored during a loading cycle.

The Fig 5.1 shows the graph comparing the storage modulus vs temperature values of all the samples. Specimen S3 (3% TiO2 and 3% graphene) is the highest with significant difference in E' values which indicates that it has the highest energy storing capacity followed by S0, which is the neat GFRP. The trend of the specimen S3 shows a two-stage energy absorption. The values of the remaining specimens are quite similar.

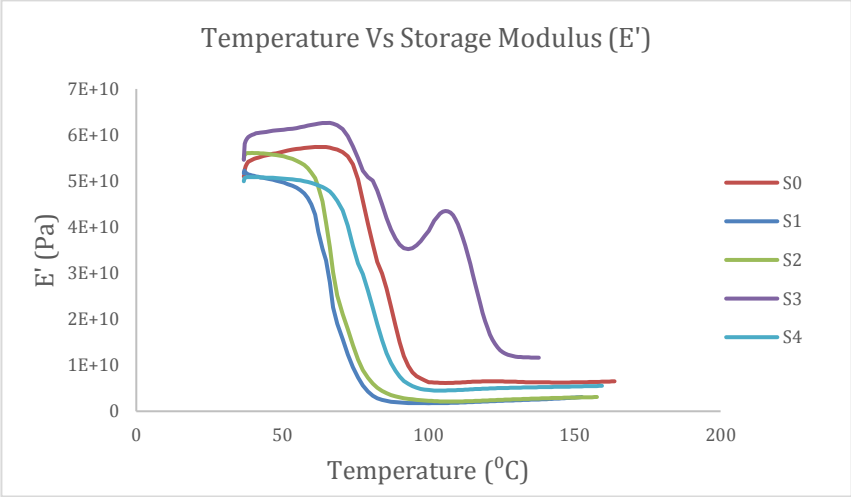


Fig 5.1 Storage modulus Vs Temperature

Loss modulus- Loss modulus (E'') is the energy dissipated during one loading cycle.

The loss modulus values of all the specimens except specimen S3 (3% TiO2 and 3% graphene) have reduced compared to the neat GFRP values. Specimen S2 (2% TiO2 and 2% graphene) has the lowest loss modulus values which indicates the least loss of energy. The graph comparing the trends of Loss modulus vs temperature for all the samples is shown in fig 5.2.

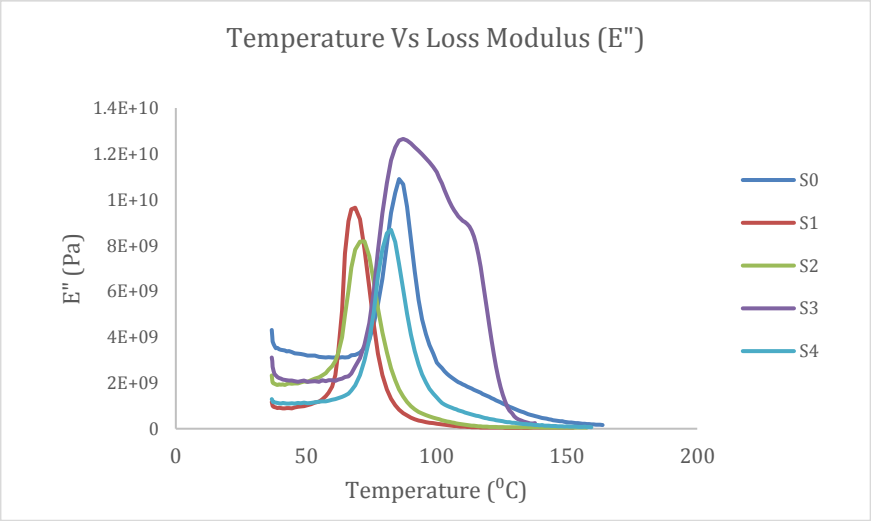


Fig 5.2 Loss modulus vs Temperature

Tan δ - It is the ratio of loss modulus to storage modulus and also called loss factor.

From the graph shown in Fig 5.3, it is found that the specimen S3 (3% TiO_2 and 3% graphene) has the lowest tan δ values which indicates that it has elastic strain component. The peak value for specimen S3 is 0.347. Whereas, specimen S1 (1% TiO_2 and 1% graphene) has the highest value of 0.644 which indicates that it has high non-elastic strain component. The peak values of the remaining three samples are quite close which is specified in the Table 5.1.

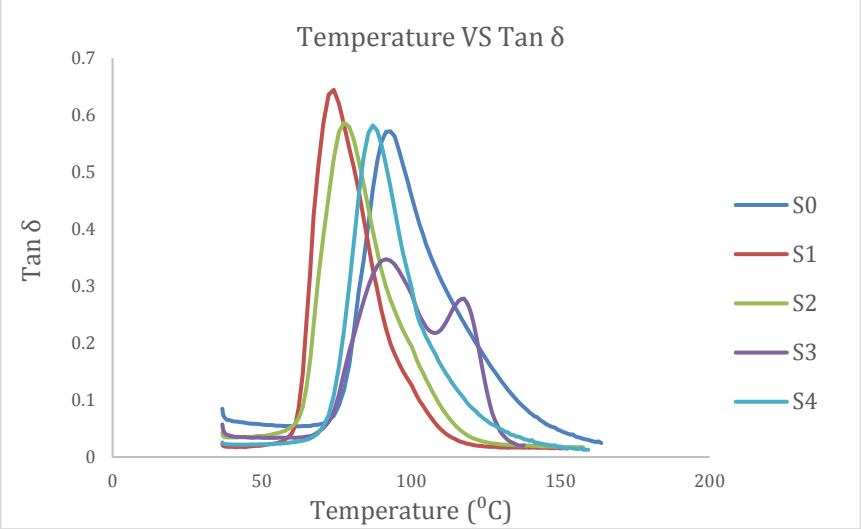


Fig 5.3 Tan delta vs Temperature

Table 5.1 Peak Storage modulus, Loss modulus, Tg, Tan delta and temperature at tan delta

Composite	Peak storage modulus (Pa)	Peak loss modulus (Pa)	Peak tan delta	Temperature at Peak tan delta (°C)
S0	$5.74*10^{10}$	$1.09 * 10^{10}$	0.571	91.69
S1	$5.23 * 10^{10}$	$9.65 * 10^{10}$	0.644	84.71
S2	$5.61 * 10^{10}$	$8.18 * 10^{9}$	0.580	82.20
S3	$6.26 * 10^{10}$	$9.92 * 10^{9}$	0.347	96.98
S4	$5.08 * 10^{10}$	$8.68 * 10^{9}$	0.582	88.19

5.4 COMPARISON OF TGA RESULTS

The thermogram and derivative thermogram of the nanocomposite is plotted and the values of all the samples are compared.

From the graphs in Fig 5.4 and Fig 5.5, its seen that the composites have two stage degradation and the onset and inflection are almost the same for all compositions but specimen S3 has the minimum weight loss percent with

42.047% in stage 1 and 4.751% in stage 2. The values for weight percentage, inflection point, onset and endset temperature values are specified in Table 5.2.

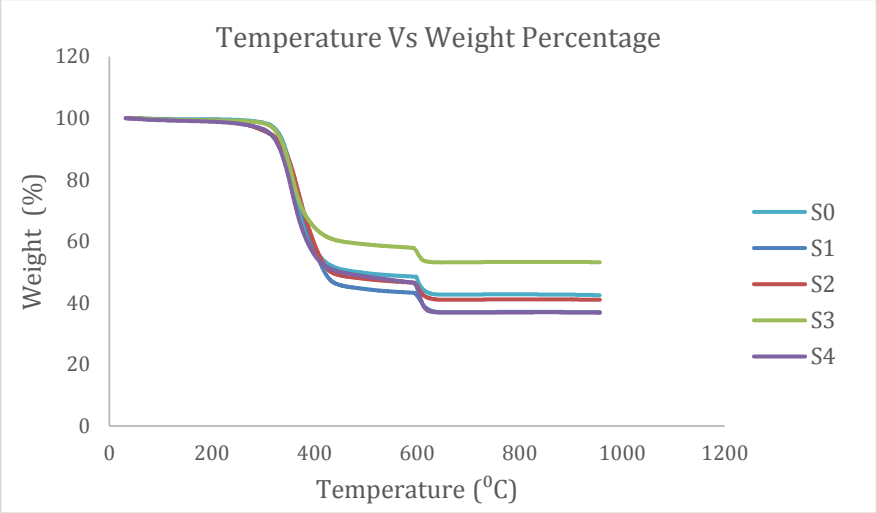


Fig 5.4 Weight loss percentage vs Temperature

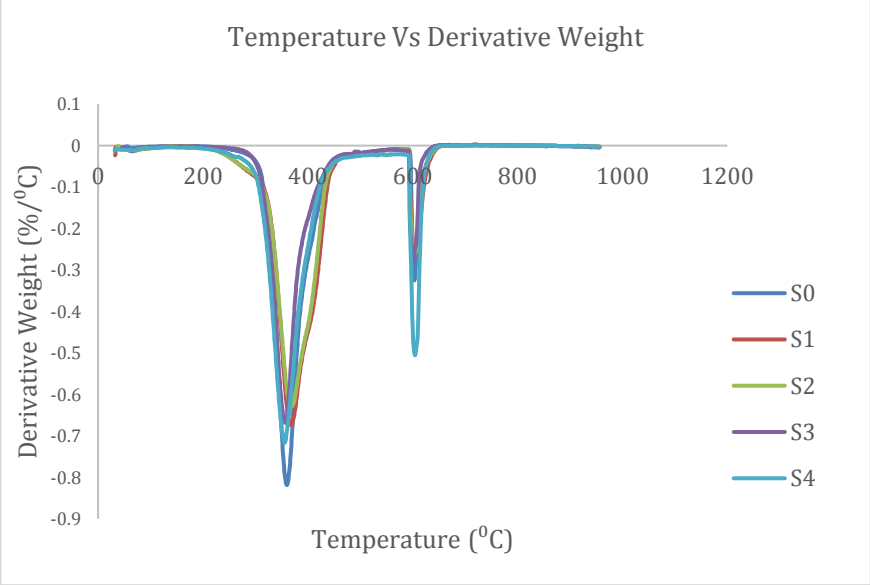


Fig 5.5 Derivative weight percentage vs Temperature

Table 5.2 Onset, Endset, inflection temperature and weight loss%

Composite	Onset temperature (°C)	Inflection temperature (°C)	Endset temperature (°C)	Stage 1 Max weight loss (%)	Stage 2 Max weight loss (%)
S0	277.79	359.64	459.94	51.36	6.122
S1	203.40	368.66	463.02	56.68	6.409
S2	212.88	369.55	458.89	53.358	5.644
S3	263.27	357.17	460.01	42.047	4.751
S4	264.34	355.76	458.08	53.316	9.839

5.5 SUMMARY

Specimen S3 (3 % Graphene and 3 % Titanium dioxide) has minimum weight loss percentage, lowest tan δ value and has the highest storage modulus when compared to the neat GFRP and other samples. However, it has the highest loss modulus values.

CONCLUSION

Graphene and TiO_2 were added to the epoxy matrix in different amounts, to reinforce a glass fibre/ epoxy nanocomposite. Thermal characterization by TGA and DMA were conducted to obtain data regarding the storage modulus (E'), loss modulus (E") and the thermal degradation properties of the nanocomposite samples.

- A significant increase in storage modulus (E') was obtained after the incorporation of 3% Graphene and 3% TiO_2 (specimen S3) while the other percentages of nano-fillers reduce E'. This indicates higher stiffness compared to neat GFRP.
- Specimen S3 had the highest loss modulus (E") values. The values of other specimens were similar to that of neat GFRP.
- Specimen S3 had the lowest tan δ values compared to the other specimens.
- The thermal decomposition of the nanocomposite showed a two-stage decomposition. Specimen S3 showed minimum weight loss percentage.

Overall, it can be concluded that the combination of 3% TiO_2 and 3% Graphene in glass fibre/epoxy composite leads to considerably better thermal properties, thermal stability and viscoelastic performance compared to other formulations. However, additional investigation is necessary to assess the performance of the nano-filler loaded GFRP nanocomposite.

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