Department of Mechanical Engineering

Faculty of Engineering and Science

Experimental Determination of Mechanical and Wear Performance of Glass Fiber Reinforced Polymer Nanocomposites

Kandasamy Prabhakar

0000-0003-1291-8567

This thesis is presented for the Degree of

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of

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Declaration

To the best of my knowledge and belief this thesis entitled "Experimental Determination of Mechanical and Wear Performance of Glass Fiber Reinforced Polymer Nanocomposites" contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature :

Name : Kandasamy Prabhakar

Date : 30th June 2020

Thesis Committee

Chairperson   : A/Prof. Dr. Perumal Kumar

Supervisor   : A/Prof. Dr. Sujan Debnath

Co-Supervisor   : Dr. Mahmood Anwar

Associate Supervisor   : Dr. K.Palanikumar

<div style="text-align: right">30th June 2020</div>

The Chairperson

Department of Mechanical Engineering,

Curtin University,

CDT 250, 98009 Miri,

Sarawak, Malaysia.

Dear Sir,

I submit this thesis entitled "Experimental Determination of Mechanical and Wear Performance of Glass Fiber Reinforced Polymer Nanocomposites" for the fulfilment of the Doctor of Philosophy in Mechanical Engineering.

Yours sincerely

Kandasamy Prabhakar

Student ID: 18772601

Acknowledgements

List of Publications

Conference Publications

I.   K. Prabhakar, Sujan Debnath, Rajamohan Ganesan and K. Palanikumar. "A Review of Mechanical and Tribological Behavior of Polymer Composite Materials", *Materials Science and Engineering 344 (2018) 012015*.

II. K. Prabhakar, Sujan Debnath, Mahmood Anwar and K. Palanikumar. "A Review of Surface Treatment, Nanoparticle Dispersion and Interfacial Bonding Characteristics of Glass Fiber Reinforced Polymer Composites", *OCPC 2018*.

III. K. Prabhakar, Sujan Debnath, Mahmood Anwar and K. Palanikumar. "Experimental Analysis on the Effect of Surface Treatment of Glass Fibers and Nanoclay on Mechanical Properties of Glass Fiber Reinforced Polymer Nanocomposites", *Materials Science and Engineering 495 (2019) 012091*.

Journal Publications

I.   K. Prabhakar, Mahmood Anwar and Sujan Debnath. "Nanoclay Concentration Influence on Interfacial Bonding Behavior of Glass Fiber Reinforced Polymer Nanocomposites", *European Polymer Journal (2020) (Elsevier) (In-Progress)*.

II. K. Prabhakar, Mahmood Anwar and Sujan Debnath. "Plastics in high wear resistant Application", *Encyclopaedia of Materials: Plastics and Polymers (2020) (Elsevier) (In-Progress)*.

Abstract

Polymer nanocomposite materials are increasingly preferred in recent years because of their lightweight and mass manufacturing aspects. However, tribological behaviour of polymer nanocomposites is not substantial due to the lack of proper interfacial bonding between fibre/filler reinforcement and matrix. Eventually this leads to further compromise in its mechanical performance. It is evident that addition of nanoparticles as a filler material between fibre and polymer composites is one of the solutions to enhance the bonding i.e. provide improvement in tribological and mechanical properties of the composite. Therefore, in this research glass fibers reinforced epoxy polymer nanocomposite with nanoclay was studied for tribological and mechanical performance. Nanoclay particles were incorporated in the composite as a potential interfacial bonding enhancer. The bonding characteristics between the composite matrix and nano particles were analysed through various surface treatments for glass fibers (i.e. silane treatment, acid treatment and untreated) and nanoclay (i.e. trimethyl stearyl ammonium modified and untreated) with the variation of nanoclay concentration between 0-6 wt.%. Subsequently, the diffusion behavior of nano particles into the epoxy system has been analysed through various dispersion techniques. These included mechanical stirrer with speed variation between 125-2000 rpm and ultrasonication with amplitude variation between 20-100%. Followingly, effect of curing temperature and curing time on mechanical and wear properties were analysed with the variation of curing temperature ranging between 25-125°C as well as curing time between 30-480 minutes. Finally, tribological performance of the effective parameters was validated through Pin-On-Disc wear rate testing. The mechanical performance of the composites was evaluated through tensile, flexural, impact and micro-hardness tests. The characterizations were analysed through the SEM, EDX, FTIR and XRD analysis. It was found that silane treated glass fiber with 1 wt.% of nanoclay concentration was the most effective in terms of hardness with the improvement achieved 45.5% increment. Conversely, found that with further addition of nanoclay had shown reduction in hardness properties. Interestingly, EDX analysis revealed that the interfacial bonding between the glass fiber and epoxy matrix was significantly influenced through sodium suppression with nanoclay concentration. Such behaviour was further conformed with FTIR and XRD analysis. Such behavior contributed that the appropriate nanoclay concentration enhanced the silane coupling agent by interacting with the functional groups in the resin and the fiber. Eventually, this aid the formation of intercalation structure of the composite which implied strong interfacial bonding between the polymer matrix and the glass fiber, hence, resulted increase in surface hardness of the nanocomposite i.e. enhanced wear performance. This research work is expected to contribute towards improved performance of glass fiber reinforced polymer nanocomposite for high wear resistant application such as piping and marine industries.

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ABBREVIATIONS

NC   - Nanoclay

MNC   - Surface Modified Nanoclay

UNC   - Unmodified Nanoclay

UGF   - Untreated Glass Fiber

AGF   - Acid treated Glass Fiber

SGF   - Silane treated Glass Fiber

PMC   - Polymer Matrix Composites

FRP   - Fiber Reinforced Polymer

GFRP - Glass Fiber Reinforced Polymer

MMT   - Montmorillonite

SEM   - Scanning Electron Microscope

FTIR   - Fourier Transform Infrared Spectroscopy

XRD   - X-Ray Diffraction

EDX   - Energy Dispersive X-Ray

HV   - Vickers Hardness

ASTM- American Society for Testing and Materials

Na   - Sodium

CHAPTER 1

INTRODUCTION

1.1 Overview/Background

Composite materials are finding increased applications in various engineering fields such as the aerospace, marine and automotive sectors etc. They are also finding many applications in sporting goods and other industrial applications. Polymer nanocomposites have superior properties if constructed properly. A nanocomposite is a matrix to which nanoparticles are added to improve the mechanical performance of the original material. The improved properties of nanocomposites have caused researchers and industries to consider using these materials in several fields.

In the area of nanotechnology, polymer matrix-based nanocomposites have generated a significant amount of attention in the recent literature. The structural components produced using nanocomposites will exhibit a high strength-to-weight ratio. For example, an epoxy containing carbon nanotubes can be used to produce wind turbine blades which results in a strong but light weight material, which in turn allows for longer windmill blades. Practically, these longer blades increase the amount of electricity generated by each wind turbine [1]. A typical polymer nano-system is represented in Figure 1.1 where phase changes occur when a natural or surface modified nanoparticle is added to the polymer resin using appropriate dispersion technique which is further reinforced with glass, carbon, aramid or natural fibers. Finally, it is cured using resin transfer molding (RTM) to a polymer nanocomposite.
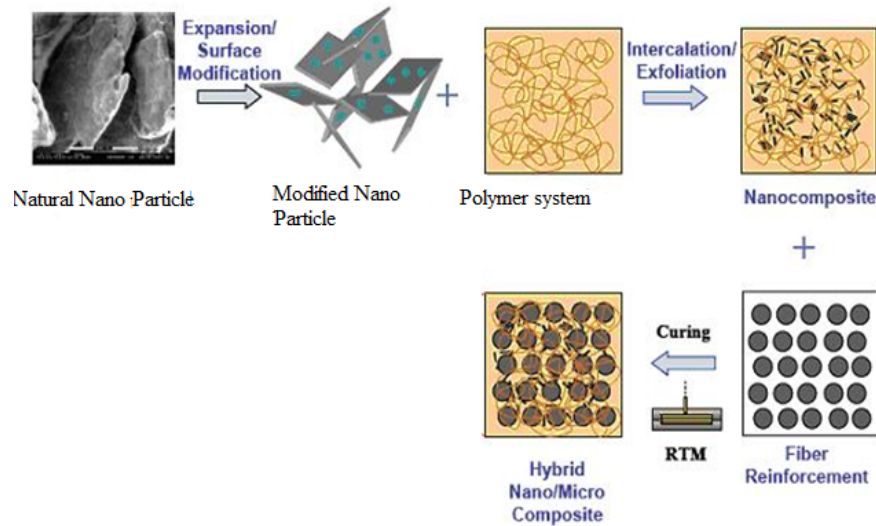
Figure 1.1 Typical Polymer Nano system [2]

1.1.1 Nanocomposites: Nanocomposite is basically a multiphased solid material where one of the manufacturing phases has at least one dimension less than 100 nm. In recent years, nano-reinforcements have recieved significant attention as a result of intense research and development. The main advantages of nanocomposites is its ability to achieve a desirable mechanical strength, toughness, increased wear resistance properties as well as improved electrical and thermal conductivity by the addition of nanoparticles in as small a volume as 1-5% of weight [3]. Based on the matrix used, material composites are classified as Polymer matrix composites, Metal matrix composites and Ceramic matrix composites.

1.1.2 Nanoparticles: Polymer nanocomposites are being increasingly used as engineering materials in which tribological properties are of considerable importance. Fillers such as glass, carbon and textile fibers are incorporated within many polymers to improve their tribological performance. Nanoparticles such as carbon-nanotube, nanoclay, titanium oxide (TiO_2) and silicon carbide (SiC) are added in volumes of 1-5% by weight which, in turn enhances the mechanical properties. The reduction in wear is mainly due to preferential load support or the load bearing capacity of the reinforcement components, by which the action of abrasive mechanism to the wear of the materials are highly suppressed. Figure 1.2 shows microscopic images of nanotubes, nanographite, nanoclay and nanosilica for visualization of those microstructures.
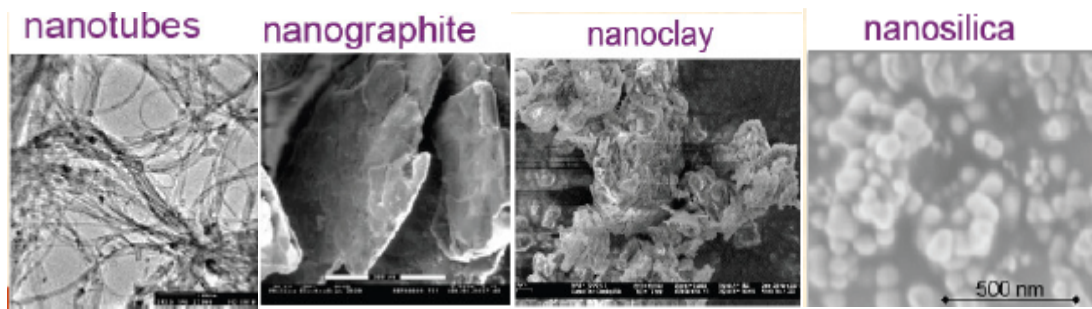
Figure 1.2: Typical Nanoparticles used for Polymer Nanocomposites [4]

1.1.3 Polymer Nanocomposites: When nanoparticles are embedded in the polymer, the resulting composite material is known as a polymer nanocomposite. Polymer nanocomposites consist of a polymeric materials (e.g. thermoplastics, thermosets or elastomers) having nanoparticles or nano-fillers dispersed in the polymer matrix which may be of different shapes (e.g. fibers, spheroids or platelets) with at least one of the dimensions less than 100 nm.

1.1.4 Mechanical Properties of Epoxy Resin/Glass Fiber and Nanoclay

The different mechanical properties of the constituents of common polymer resins are listed in Table 1.1.

Table 1.1: Mechanical Properties of Epoxy Resin/Glass Fiber and Nanoclay

Properties	Epoxy Resin	Glass Fiber	Nanoclay
Tensile Strength	85 MPa	2000-3500 MPa	101 MPa
Density	1.23 gram/cm^3	2.55 gram/cm^3	1.77 gram/cm^3
Elongation	0.8 %	2.5-3.0 %	8 %
Specific Gravity	1.19	2.6	1.77
Young's Modulus	10.5 GPa	70.0 GPa	4.657 GPa

1.1.5 Applications of Polymer Nanocomposites: Table 1.2 shows the summary of applications, types of polymer matrix composites and the advantages of polymer matrix composites.

Table 1.2: Advantages and Applications of Polymer Nanocomposites

Industry	Type of PMC	Advantages of PMC	Areas of Application
Aerospace	CFRP	-Weight reduction for high speed and increased payload. -Energy saving in terms of fuel consumption. - High stiffness to weight ratio.	-Wings, Central torsion box, rear pressure bulk-head, tail, fuselage, helicopter rotor blades etc.
Automotive	CFRP/GFRP	-Weight reduction. -Light weight for gaining higher fuel economy.	-Rear leaf springs, drive shafts and wheels. -Major body, chasis, interior and suspension components.
Sporting equipment	CFRP/GFRP	-Increased safety, lighter weight and greater strength.	-Skis, boots, poles, gloves, rackets, fishing rods, bicycle frames etc.
Marine	CFRP/GFRP	-Greater strength to weight ratio. -High modulus to weight ratio.	-Sail boats, fishing boats, life boats, Yachts, Naval ships in decks, hull,masts, propulsion shafts etc.
Infrastructure	CFRP/GFRP	-Corrosion resistance. -Lower maintenance cost. -Lighter weight. -Higher stiffness and greater strength to weight ratio.	-Replacing steel in bridges, buildings, highway overpasses. -Gas and sewage lines.

1.1.6 Classification of Polymers

There are three main classes of solid polymers: thermoplastics, thermosets and elastomers. These classifications relate to the mechanical properties and thermal performance. All three types of materials can be used as solids. However, thermoplastics can be solidified by cooling and can be remelted by heating. Examples include polystyrene and polyethylene. The cooling and heating cycles can be repeated many times with little loss in properties. Thermosets preserve their shape in the course of cooling and heating cycles. They are cross-linked, so post polymerization heating softens the solid but does not permit the material to flow. Examples include phenolic resins, urea-formaldehyde resins, epoxies, cross-linked polyesters and many polyurethanes. Elastomers have elastic properties: they deform readily with applied force and can recover their original shape after the force is withdrawn. The term rubber is generally used for elastomers from natural sources, while elastomers may refer to material from synthetic sources.

1.1.7 Advantages and Disadvantages of Polymer Nanocomposites

The addition of nanoparticles increases the strength to volume ratio which in turn dramatically changes the properties of the nanocomposites [5]. The advantages and disadvantages of polymer nanocomposites are listed below:

Advantages:
- Improved mechanical properties (tensile strength, stiffness and toughness)
- Synergistic flame retardant additive
- Improved dimensional stability
- Improved thermal conductivity, thermal expansion properties
- Greater strength/stiffness to weight ratio

Disadvantages :
- Limiting process ability due to increased viscosity
- Dispersion difficulties
- Sedimentation
- Black color when different carbon containing nanoparticles are added

1.1.8 Wear Behaviour of Glass Fiber Reinforced Polymer Nanocomposites

The utilization of nanoparticles in polymers for tribological performance started around mid-1990s and this area has become quite promising for the future as newer nanomaterials are being economically and routinely fabricated. In most of the cases, mechanical properties of a polymer nanocomposite rely on the high interface area between the filler (nanoparticles or nanofibers) and the matrix (polymer). Good interfacial bonding between the two phases leads to a better strength and toughness properties over unfilled polymer. For all the polymer/nanoparticle systems, there is an optimal amount of nanoparticles beyond which there will be a reduction in the toughness as the stiffness and strength increases [3].

Recently, many attempts have been made to develop nanoparticle-filled polymeric composites for tribological applications. The tribology of nanoparticle-filled polymers

is of significant interest because of the ability of nanoparticles in altering the properties of the matrix and the surfaces involved while keeping many intrinsic merits of pure polymers. Despite these efforts, the influence of nanoparticle fillers on friction and wear behaviour of polymers is not yet thoroughly understood. In this research work, the influence of nanoparticles on the hardness properties and wear behaviour of polymer matrices were evaluated based on the experimental investigation.

The inorganic filler particles can enhance mechanical and tribological properties of polymers, which is a renowned fact. The effectivity of the reinforcement is determined by several factors such as the basic properties of the composite matrix, microstructure of the composite, filler size and shape, homogeneity of particle distribution and the quality of the filler–matrix interface. The processing methods including curing temperature and time also have significant influence in the improvement of mechanical and tribological performance of the composite material. Moreover, a suitable surface pre-treatment of the nanoparticles can lead to less filler agglomeration and thus better bonding between the nanoparticles and the matrix [5].

Among the above factors, the interfacial bonding between the filler and matrix plays a critical role for the ultimate nanocomposite's performance. The quality of the filler–matrix interface may to some extent be affected by the filler's size and shape because of different specific surface areas and surface reactivity. Unfortunately, these aspects have not yet been extensively investigated.

Various types of surface modification techniques (for instance, covalently grafting of an organic precursor on the nanoparticle or nitric acid treatment of CNTs) for the nanoparticles and nanofibers are other areas that need to be focused. The surface modification of the fillers will enhance the interfacial bonding strength between the filler and the matrix. Agglomeration of nanoparticles is a dominant practical problem that could be effectively minimized by surface chemical treatment or high shear mechanical mixing [5]. To prevent agglomeration, surface treatment of nanoclay as well as ultrasonication process and mechanical stirrer for addition of nanoclay into the epoxy matrix were adopted in this research work.

1.2 Problem Statement

The review of published literature reveals that the effects of fiber/filler reinforcement on the tribological behaviour of polymer nanocomposites are not substantial due to lack of proper interfacial bonding. Addition of nanoparticles as a filler material between fiber and polymer composites would be one of the solutions to enhance the bonding i.e. provide improvement in mechanical and tribological properties of the composite. However, diffusion of nanoparticles in the matrix hamper the formation of the well performed composite mainly due to agglomeration of nanoparticles and interfacial bonding between epoxy system and glass fibers. Quantitative characterization of interfacial adhesion strength can help in evaluating the mechanical behaviour and capabilities of composite materials. The interfacial bonding quality ultimately dictates the mechanical and wear performance of glass fiber reinforced polymer composites.

1.3 Objectives

The specific objectives of this research work are as follows:

1. To identify the influence of surface treatment for glass fibers and nanoclay on the interfacial bonding between glass fibers, epoxy matrix and nanoclay.
2. To identify the effective nanoclay concentration in the glass fiber epoxy system by varying the nanoclay percentage and analysing the wear performance.
3. To enhance the dispersion performance of nanoparticles in the glass fiber epoxy matrix system for improved wear and mechanical performance by using mechanical stirrer and ultrasonication.
4. To identify the impact of curing temperature and time in the glass fiber epoxy system by varying the curing temperature and curing time for improved wear and mechanical performance.
5. To understand the mechanism of wear performance of the developed glass fiber reinforced polymer nanocomposite (SEM, EDX, FTIR, XRD) and validate using pin on disc wear test.

1.4 Scope of Study

The scope of this study are as follows:

1. This study focused on the determination of effective surface treatment of glass fibers and nanoclay, nanoclay concentration, dispersion mechanism, curing temperature and curing time.
2. This study also observed a coherent relation between the nanoclay concentration and sodium suppression influence significantly on the interfacial bonding strength in terms of radical variation in surface hardness.

1.5 Research Significance

The research significance of this research work are as follows:

1. Identify the key parameters that influence the interfacial bonding between the matrix and the filler.
2. Evaluate the mechanical and wear performances of the composite material by incorporating proper surface treatment and more evenly dispersed nanoparticles in the epoxy-glass fiber composite.
3. Provide significant reference for future researchers, scientists and material engineers to continue developing enhanced composite materials with improved properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Glass fiber Reinforced Polymer Nanocomposite

Polymer Matrix Composites (PMCs) constitute a major category of composite materials with a wide range of industrial applications. In PMCs, fibers or any other reinforcing agent is embedded in the polymer matrix. They offer very attractive properties which can be tailored to the specific requirements by proper selection of fiber, matrix, fiber configuration (short, long, straight, woven, braided, laminated etc.) and fiber surface treatment along the direction of reinforcing fiber. PMCs are lightweight material coupled with high stiffness and strength. They also exhibit dimensional stability, temperature and chemical resistance with relatively easy processing. Advanced PMCs are replacing metal components in many applications, particularly in aerospace and automotive industries.

Fibers as reinforcing materials offer two advantages. Firstly, the bulk material is always stronger when produced as small diameter fibers due to the natural exclusion of large-scale defects. Secondly, the fiber configuration allows the tailoring of properties in the specific directions. Fibers added to the resin system provide strength to the finished part. According to the desired properties required in the finished product, reinforcing material are selected. Various forms of fibers such as yarns, rovings, chopped strands, woven fabric and mats are used in the advanced composite. Each of these has its own specific application. Yarns and rovings are used in processes such as filament winding or pultrusion. When preforms are used in parts manufacture, woven fabric ormats are required. Four basic types of fiber as reinforcing materials namely glass, carbon, aramid and boron are used in the advanced composite industries.

Glass fibers consist of $(-SiO_4-)_n$ tetrahedra units in the backbone and are amorphous in nature. It is the most common reinforcing material for PMCs, as they offer high strength at relatively low cost. They are manufactured as continuous and short

fibers. However, they have poor abrasion resistance, poor adhesion to polymer matrix and tendency to absorb moisture. In order to overcome these drawbacks, coupling agents (e.g. silanes) are used. Two types of glass fibers that are most commonly used in the manufacturing industries are E-Glass and S-Glass. The primary material used in glass fibers is silica, which are manufactured by melting the ingredients in a furnace to a temperature of about $1370^{\circ}C$ [5]. E-Glass is the most commonly used glass fiber, which has a useful balance of mechanical, chemical and electrical properties at very moderate cost. Typical strength and stiffness (modulus) levels for the individual filaments of E-Glass are about 3450 MPa tensile strength and 75.8 GPa Young's modulus. Higher-performance, higher-cost S-2 Glass fibers have properties of 4830 MPa tensile strength and a modulus of 96.5 GPa. Generally, glass fibers are better known for their impact toughness, medium modulus, high tensile strength and thermal stability [6].

The glass used for making fibers are classified into five major types. The letter designation is based on the characteristic properties of the glass. A-Glass is a high-alkali glass, it has very good resistance to chemicals, but lower electrical properties. C-Glass is a chemical grade, which offers extremely high chemical resistance. E-Glass has low alkali content which provides good insulation property and strong resistance to water. S-Glass has 33% higher tensile strength than E-Glass. D-Glass has superior electrical properties with low dielectric constant [5].

2.2 Surface Treatment of Glass Fibers and Nanoclay

Surface treatment of glass fibers and nanoclay are widely used to enhance the adhesion between glass fibers and epoxy matrix where nanoclay enhances molecular bridge between the inorganic glass fiber and organic polymer matrix. The mechanical properties of composites increase significantly if the silane coupling agent (SCA) interacts with reinforcement as well as the polymer matrix. Silanes coupling agents have general formula $R\text{-}(CH_2)_n\text{-}Si\text{-}X_3$, where X is a hydrolyzable group which produces silanol and forms siloxane linkages with the inorganic substrate. R is a non-hydrolyzable organic group which interacts or forms bonds with polymer matrix [7]. The treatment of fillers with glycidoxy functional silanes or amine functional silanes are known to improve the dispersibility of fillers in epoxy and improve the mechanical strength of

composites. The surface modification of nanoclays (montmorillonite (MMT) and organically modified montmorillonite (OMMT)) with SCAs can also be performed to improve dispersion of nanoclays in polymers and to achieve better mechanical properties of nanocomposites [8].

Hyeong et al. [9] studied the mechanical behaviour of glass fiber reinforced polydicyclopentadiene resin (p-DCPD) composite where the glass fibers were treated with norbornene bases silane. The glass fibers were first dried at 200ºC for 4 hours to remove the impurities and moisture in the fibers. The surface treatment solution was prepared with a mixture of silane, ethanol and acetic acid mixed in an appropriate mass ratio of 5:4:1. The solution was added to glass fibers in a mass ratio of 100:1. Finally the treated fibers were further dried at 140ºC for 4 hours before being reinforced with epoxy matrix system. The mechanical testing such as shear, tensile and impact strength were carried out and shear strength was evaluated using the microdroplet pull-out test. The test results concluded that the shear strength of norbornene based silane sample increased by 40% when compared with untreated sample, which was due to the interaction between the silane and surface of the glass fiber. After the surface treatment, norbornene group was formed at the surface of the glass fiber. When the DCPD resin was polymerized by a catalyst, the reaction at the surface occurs with the norbornene moiety. As a result interfacial adhesion between the glass fiber and the resin improved significantly. Cohesive failure was observed for the samples which were surface treated thereby indicating higher interfacial affinity between glass fibers and epoxy matrix. FTIR spectroscopy analysis was performed to observe the quality of surface treatment and it was noted that sufficient surface functionalization was achieved using surface treatment of glass fibers.

Ferreira et al. [10] studied the effect of surface treatment on the mechanical properties such as toughness, stiffness, static and fatigue strength of nanoclay filled polypropylene matrix. Injection moulding was used to prepare composites with a fixed weight of 3% nanoclay. The comparison was made between organomodified nanoclay and nanoclay which was further modified using water mixed with acetic acid. The test results shown that nanoclay enhanced by surface treatment had improved the mechanical properties by 6% on tensile strength and 3% on modulus of elasticity. The fatigue strength of surface treated nanoclay performed as close as neat composite but better than

untreated nanoclay composite. The observation of fractured specimens through scanning electron microscopy indicated that surface treated specimens had shown better clay dispersion, adhesion and no significant agglomeration. It was also observed from the SEM images that surface treatment of nanoclay had contributed to better clay dispersion, smaller particle size and no significant agglomeration leading to improved fatigue resistance.

Mengyuan et al. [11] analysed the enhancement of mechanical performance for glass fiber reinforced polymer composite where the glass fibers were surface treated with polyurethane dispersion (PUD), silane and hybrid combination of silane followed by PUD process. The composites were made using hand lay-up method and the test results revealed that PUD treated glass fiber composite exhibited better tensile strength than the silane coupling treated and hybrid composites. The tensile strength results also revealed that non-treated glass fibers showed the least values owing to insufficient interphase adhesion which was also reconfirmed through SEM analysis. Kutlay et al. [12] studied the effects of mechanical performance in terms of tensile strength, flexural strength, interlaminar shear strength and fracture toughness of silane surface treated glass fibers reinforced polymer composite which was initially modified by heat cleaning and HCL acid treatment. The test results revealed that the silane coating on heat cleaned glass fibers had shown beneficial effect on the interfacial adhesion between the fibers and the matrix whereby increasing the interlaminar shear strength. On the other hand, silane coating on the acid activated glass fibers did not improve the interlaminar shear strength of the composite because of the fiber damage caused by HCL acid solution. The study also highlighted that the silane treatment increased the interfacial mobility through the enhancement of fiber/matrix adhesion which had contributed to the increase in flexural strength. The SEM photographs of the fractured surface for the tensile specimens had shown improved adhesion between glass fiber and epoxy resin through cohesive mode of failure, as large amount of epoxy resin adhered to the fiber surfaces forming a thick layer clearly indicating good interfacial bonding between the fiber and the resin. Somayeh et al. [13] analysed the interfacial adhesion characteristics of the glass fiber reinforcement with epoxy matrix. The glass fibers were heat-cleaned to 450°C for 1.5 hours for sizing and removal of impurities following silane treatment by different combinations of glycidoxypropyltrimethoxysilane (GPS) and tetraethoxysilane (TEOS) (inorganic-organic silane blends). The adhesion properties were studied through the

single fiber microdroplet pull-out test and the load displacement curves from the pull-out test were observed. The test results revealed that specimens containing 75:25 and 50:50 of GPS:TEOS had shown better interfacial adhesion properties between the glass fiber and the matrix. It was observed from the SEM images that the failure mode propagated through textured interphase in more tortuous path resulted in greater degree of energy absorption during the fiber-matrix pull out. This experimentation also demonstrated that silane treatment act as a bridge thereby providing chemical bonding as well as mechanical interlocking between glass fiber and matrix which in turn tailored the mechanical properties of the composite material.

Withers et al. [14] studied the mechanical properties of GFRP reinforced with organomodified nanoclay Cloisite 30B (1nm thickness and 200-300nm in length) concentration of 0,2 and 4 wt.% of the epoxy system. Cloisite 30B can create non-covalent bonding from hydrogen bond or covalent bond through chemical reaction with epoxy resin when moderate heat is applied. E-Glass fiber in bi-directional form [0°/90°] with weave yarns of 1mm wide was used in this experimental work. The test results revealed that mechanical properties such as tensile strength, stiffness and ductility increased with nanoclay addition by strengthening the fiber-matrix interphase with the best results attained at 2 wt.% of nanoclay concentration. It was specified that 2 wt. % of nanoclay addition was sufficient for adequate reinforcement, well dispersion and exfoliation in the epoxy resin. Moreover with further addition of nanoclay, aggregates are postulated that negatively affected the mechanical properties. The study also revealed that the nanoclay reinforced composite can be used for repair work of localised damages in the external surface wall of pipes and vessels installed in process and marine pipelines. Guojun et al. [15] studied the enhancement of mechanical properties such as tensile and impact strength of surface treated glass fiber composites. The glass fibers were treated with film former (GFf) containing certain ratio of Maleic anhydride grafted Polypropylene (MPP) and a kind of β-nucleating agent (TMB-5) through impregnation method with different ratios of 2, 3 and 10 wt.%. It was observed that the mechanical properties such as tensile and impact properties improved dramatically with small amount of 2 wt.% of MPP to glass fibers in the matrix system. Further increase of MPP has resulted in increase of tensile strength but decrease of impact strength. The SEM images also indicated that the film former had enhanced the interfacial adhesion with 2 wt.% of MPP addition by facilitating the formation of β-transcrystal at the interface and

with further addition the interaction between the film former and MPP in the matrix was saturated, thereby interfacial adhesion could not be prominently noticed.

Dinesh et al. [16] analysed the mechanical properties of glass fiber reinforced epoxy composite where the matrix system was reinforced with amino silane treated glass fiber 600 gsm and ferric oxide (Fe_2O_3) particles of 200 nm. The addition of Unsaturated Polyester (UP) into epoxy resin had shown increase in flexural and impact properties but reduction in tensile and thermal properties dramatically. With the addition of reinforcement, the tensile and thermal stability had shown improvement for UP blended epoxy composites. This improvement of mechanical properties was identified mainly due to the formation of interpenetrating polymer network (IPN) structure which created flexible links and reduced degree of cross linking. The morphological characterization had shown that the dispersion of reinforcement is uniform which had led to improvement in mechanical and thermal properties. Gorbatkina et al. [17] studied the effect of interfacial adhesion strength of three different modifiers such as active diluents, thermostable rigid chain thermoplasts and dispersed fillers to glass fibers and epoxy resin. The different mechanism to evaluate the interfacial strength between the epoxy resin and glass fibers were analysed and it was observed that the addition of thermostable thermoplasts were more effective by providing higher interfacial strength at certain concentration level than the other two fillers modification.

Moutushi et al. [18] studied the effect on the interfacial bonding strength of glass fiber and epoxy matrix interphase through the surface modification of silane coupling agent and film former. Single fiber microdroplet test was used to determine the interfacial bonding strength between glass fiber and epoxy matrix. The test results revealed that amino silane sizing with azamide based film former had shown 47% increase in interfacial shear strength when compared to other composites which was achieved through chemical bond formation and by improving the surface roughness of glass fibers. Atomic force microscopy was used to analyse the surface morphology and was found that both silane and film former components affected the failure mode at the interface between glass fibers and the epoxy system. The study also concluded that reactive film formers along with reactive silane coupling agents influenced the interfacial bonding properties between epoxy matrix and glass fibers.

Based on the above, several approaches have been taken to improve the mechanical strength and damage tolerance of glass fiber reinforced composites. The main research for toughened composites includes the control of the fiber–matrix interfacial adhesion, matrix modification and fiber hybridization. Among the various methods, the control of the fiber–matrix interfacial adhesion appears to be very promising since it has a major effect on the bonding strength of the composites. A variety of surface treatment and modification techniques has been developed to control the interfacial properties of glass fiber. The surface treated glass fibers had undergone cohesive failure during mechanical testing, thereby indicating improved interfacial affinity between the glass fibers and epoxy matrix. Furthermore, the surface treatment of nanoclay had led to better dispersion in matrix with reduced agglomeration. The surface treatment of glass fiber as well as nano particles act as a bridge thereby providing mechanical interlocking between the glass fiber, epoxy and nanoparticles which in turn enhanced the interfacial bonding strength. Nevertheless, it was also identified that the dispersion of nanoclay plays a vital role in the interfacial bonding mechanism. The key challenge is to avoid agglomeration and inadequate adhesion of nanoclay between glass fiber and epoxy matrix through adequate dispersion which is discussed in the following section.

2.3 Dispersion Mechanism for Nanoclay Addition in Matrix System

A key component to achieve these improvement of properties lies in the proper dispersion of the nanoparticles in the polymer matrix. Some of the most commonly used methods for dispersing nanoparticles in polymers include mechanical mixing, magnetic stirring and sonication. It has been reported by many researchers that poorly dispersed nanoparticles could degrade the mechanical properties of polymers [19-28]. Depending on the mixing technique used, conventional nanoclay reinforced composites can take the form of phase-separated microcomposite, intercalated nanocomposites or exfoliated nanocomposites. Phase-separated microcomposites offer little improvement in material properties while exfoliated nanocomposites were reported to show the greatest interfacial interaction and phase homogeneity. Therefore, the degree of exfoliation is an important parameter to evaluate the physical properties of polymer-based nanocomposites. Numerous studies have extensively explored many of these mixing

techniques to disperse nanoparticles in polymers with the aim of achieving full exfoliation [19-22].

Hossein et al. [19] analysed the ballistic behaviour by reinforcing the organically modified montmorillonite nanoclay (Cloisite 30B) in glass fiber reinforced polymers (GFRP) at varying range of 0,3,5,7 and 10%. Nanoclay was dispersed in hardener for 60 min with 3000 rpm using shear mixing method. Then the mixed solution was sonicated with 150 kW/cm^2 power and at 5 mm amplitude for 30 min duration. The mixture was stirred for 60 min at 3000 rpm again. Finally, the mixture was stirred with the resin, Epon 828 (difunctional bisphenol A/ epichlorohydrin resin) for 10 min with speed of 100 rpm at 25°C. Based on the experimental results, the highest energy absorbing capacity was observed at 3 wt.% nanoclay at the impact velocity of 134 m/s while the highest energy absorbing capacity was recorded at 10 wt.% nanoclay at the impact velocity of 169 m/s. The results also demonstrated that the energy absorption capacity and mechanical properties were enhanced by addition of nanoparticles through systematic dispersion techniques which in turn enhanced the interfacial strength of the system. The addition of nanoparticles increased the fiber matrix interface bonding at the matrix due to their large surface area whereby varying the mechanical properties through fiber/matrix interface bonding which translated into energy absorption capabilities. At the same time with increase of nanoclay content above 7 wt.%, agglomeration occurs which acts as stress concentrators or crack initiation sites in the matrix which resulted in reduction of composite toughness. Mohammad et al. [20] observed the mechanical properties of epoxy glass fiber polymer reinforced with organically modified montmorillonite nanoclay Cloisite 30B at various range from 0 to 7 wt.% of nano-matrix. The nanoclay particles were directly mixed with the hardener in a 0, 1, 2, 3, 5 and 7 wt.% ratio with respect to the matrix for 2 h with 1800 rpm. The mixture of the clay and the hardener were subjected to sonication using an ultrasonicator at 40°C for 20 min. Nanoclay cannot be added directly to epoxy resin. It forms globular structures. In order to uniformly mix nanoclay with epoxy resin the technique named as sonication is being adopted. Sonication is the act of applying sound (usually ultrasound) energy to agitate particles in a sample for various purposes. This is usually applied using an ultrasonic bath or an ultra-sonic probe, commonly known as sonicator. Then the mixture was mixed with Epon 828 at 40°C for 10 min with 100 rpm and as the hardener had much lower viscosity than the polymer and the homogenous mixing was easier. Vacuum

assisted resin transfer method was used to fabricate the nanocomposite. The mechanical test results and SEM images revealed that quality of adhesion between fiber/epoxy and nanoclay had improved the tensile strength by 13% with 7 wt.% of nanoclay, toughness by 27% with 7 wt.% of nanoclay and flexural strength by 11% with 3 wt.% of nanoclay. During the ultrasonication process, which is accompanied by heat transfer and local heating of modified nanoclay platelets provide temporary physical crosslink with hardener. When post curing was done at elevated temperatures the polymerisation of nano epoxy generates free radicals leading to an increase in cross link density at the interface formed by the nanoclay. The nanoclay and their bundles act as rigid connectors which results in better stress transfer in the system. As a result, the increase in the fracture surface area and better adhesion of fiber, epoxy and nanoclay had increased the modulus, strength and toughness despite the mobility is reduced.

Sivasaravanan et al. [21] analysed the impact properties of E-Glass fiber reinforced composite matrix with nanoclay (Cloisite 20A) of varying ranges from 1 to 5 wt. % of epoxy resin using hand lay-up method. Hand lay-up method is a simple technique being used in small and medium scaled industries. Mold is used for hand lay-up parts unless the composite is to be joined directly to another structure. The mold can be as simple as flat sheet or have infinite curves and edges. The mold is prepared with release agent followed by reinforcing fibers to be laid on the mold. A roller, brush or squeegee can be used to impregnate the fibers with resin. The impact test results revealed that nanocomposite prepared with 5 wt.% of nanoclay had shown the best impact properties and further increase of nanoclay percentage decreased the impact properties and the material became brittle. Karanbir et al. [22] studied the impact properties of untreated/treated polypropylene fibers using silane treatment and maleic anhydride (MAH) grafting which was further reinforced with nanoclay (Cloisite 15A) 1phr (parts per hundred rubber). The neat epoxy sample, predetermined amounts of epoxy and hardener in the weight ratio of 100:34 were uniformly mixed by a mechanical stirrer for 10 min at 500 rpm. The system was then degassed for 30 min. For preparation of epoxy and clay nanocomposites, the nanoclay was dried in an oven at 120ºC for 3 h. The dried clay equivalent to 1 phr was mixed with epoxy by homogenization at 20,000 rpm for 10 min with help of a homogenizer followed by ultrasonication using a probe sonicator. Ultrasonication was done at 80% amplitude for 10 min, with pulse-on time of 40s and pulse-off time of 20s. To prevent rise in temperature during sonication, the beaker was

kept in an ice bath. The epoxy/clay suspension was cooled to 40ºC before the addition of hardener. The test results revealed that impact strength of treated fibers increased by 44% while the tensile and flexural properties decreased. On the other hand, the mechanical properties such as tensile strength, flexural properties as well as impact strength of untreated fibers decreased due to the poor adhesion among the constituents.

Dolati et al. [23] analysed the impact behaviour of glass fiber reinforced epoxy composite reinforced with nanoclay of 0, 0.5, 1.5 and 3 wt.%. Nanoclay was placed in an oven for 1 h at 110ºC to remove any moisture, and it was then added to epoxy resin which was further mixed using a high shear homogenizer at 2000 rpm for 80 min, until a consistent mixture was obtained. The mixture was then subjected to sonication using an ultrasonicator at an ultra-high frequency of 200W for 30 min to further disperse the clay, while resin temperature was maintained cold by using an ice bath. The mixture was degassed in a vacuum oven followed by the addition of curing agent. From the experimental results, it was concluded that specimens with 1.5 wt.% of nanoclay showed least damage extension when compared to specimens with 0.5 and 3 wt.%. The highest damage extension increased by 32.59% for specimen with 3 wt.% of nanoclay concentration. This weak behavior could be attributed to inadequate dispersion of nanoclay leading to agglomeration which attributed to creation of stress concentration at various location in the laminated plates leading to reduction in mechanical performance. Jumahat et al. [24] studied the wear properties of nanoclay filled epoxy polymers and nanoclay filled fiber reinforced polymer (FRP) composites with varying percentage of 1, 3 and 5 wt.% of nanoclay fabricated using vacuum bagging method. The mixture was then milled using high shear three roll mill machines at 12.7 m/s and 60°C. The mixture was then degassed in vacuum oven for 1 h to remove the entrapped air. Finally, the mixture was blended with hardener at ratio of 100:30 for 15 min before it was poured into silicon moulds coated with release agent. The prepared sample was cured for 24 hours at room temperature. The test results revealed that nanoclay/epoxy composites with 3 wt.% of nanoclay had highest wear properties than neat, 1 and 5 wt.% of nanoclay concentration having the effective dispersion in epoxy which in turn improved the load carrying capacity. The main reason for the increase of wear rate in 5 wt. % nanoclay concentration was due to agglomeration leading to easier surface removal and weak interfacial bonding between epoxy, glass fiber and nanoclay particles.

Secondly, nanoclay reinforced FRP composites had shown highest wear properties at 5 wt.% of nanoclay when compared to neat, 1 and 3 wt.% of nanoclay concentration.

Senthil et al. [25] analysed the tribological behaviour of epoxy resin reinforced with nanoclay (Cloisite 25A) ranging from 0 to 8 wt.% with and without glass fiber reinforcement. The epoxy system was heated up to 70°C to maintain the viscosity. Nano clay (Cloisite 25A) in wt.% (2, 4, 6, 8 and 10) was dispersed in solvent acetone separately. Then the dispersed clay was mixed up with epoxy resin using mechanical stirrer. During the entire process, the temperature of the mixture was maintained at 70°C with the assistance of a heating mandrel. The nanoclay/epoxy mixture was further stirred up for 30 min using ultrasonication in order to reduce the agglomeration. Then, degasification was carried out for 30 min to facilitate the removal of bubbles from the clay/epoxy mixture. In conjunction, the hardener (HY 951) was supplemented into the clay/epoxy mixture once the temperature of mixture was cooled down to the room temperature. The experiment was conducted with four variables namely filler content, normal load, sliding velocity and sliding distance. The test results concluded that the fiber reinforcement of laminates has less impact on the wear rate and coefficient of friction when compared to laminates without fiber reinforcement. SEM results indicated that better adhesion and morphological properties were observed for 2 wt.% and 4 wt.% of nanoclay concentration with E-Glass fibers. The SEM images of 8 wt.% and 10 wt.% loading also exhibited appreciable adhereness which could be due to the better attraction between the MMT layers and epoxy. This enhancement might also be due to the superior matrix interface with glass fiber which could lead to reduced impact strength.

Mohan et al. [26] conducted the tribological analysis of glass fiber reinforced epoxy polymer composite reinforced with nanoclay particles of 0,1,2,3,4 to 5 wt.% and with fiber reinforcement of 25, 50 and 75 wt.%. Initially, the resin (without hardener) was heated to 80°C in a temperature-controlled magnetic stirrer and then the desired quantity of clay (with respect to the combined epoxy and hardener weight) was introduced and mixed at 500 rpm for 2 hours. Following this, the resin bath was removed and left to cool at room temperature. When the resin–clay mixture attained room temperature, 30 wt.% of hardener (to epoxy weight) was added to the epoxy–clay mixture and mixed until the solution turned to gelling stage. At this stage, the resin mixture was vacuum infused with fiber mat at 2 bar pressure. The experimental results

were analysed for the effects of fiber content, orientation and nanoclay concentration. The test results revealed that higher fiber content of 75 wt.% has less effect on wear rate and significant effect was noticed on the composites with low fiber loading of 25 and 50 wt.% and with nanoclay. Nanoclay improved the fiber matrix adhesion with low fiber content thereby improving the wear properties. However, 5 wt.% of nanoclay filled hybrid composite had shown fine wear particles indicating weak fiber-matrix adhesion due to agglomeration effect caused with higher addition of nanoclay thereby showing reduced wear properties by means of fiber pull-out and debonding mechanism.

Ahmed et al. [27] studied the mechanical properties of hybrid nanocomposite laminates prepared using GFRP reinforced with 10 wt.% of nanoclay in total content at three different steps. Nanoclay was added to epoxy in periodical steps and was mixed by sonication at amplitude of 70% with a mixing time of 20 min. In order to avoid the temperature rise during sonication, cooling was achieved by immersing the mixing beaker in a mixture of water and ice. Subsequently, the hardener was added to the mixture at a ratio of 1:2 by weight of epoxy composite system. The test results revealed that hardness increased to 53% with specimens having highest nanoclay percentage of 2 wt. % when compared to neat specimen. On the other hand, tensile strength, bearing strength and impact strength had insignificant effect with the addition of nanoclay reinforcement. The degradation in mechanical performance could be attributed due to the resistance to appropriate dispersion of nanoclay leading to agglomeration, weak filler-matrix interface bonding which reduces stress transfer capabilities, increase in resin viscosity and restricted processability. Ferreira et al. [28] analysed the impact strength of mat glass epoxy laminates reinforced with organo-montmorillonite nanoclay, Nanomer 1.30E (1 and 3 wt.%) and multiwalled nanotubes (0.5 and 1 wt.%) which was fabricated by using compression moulding. In this fabrication process both nanoclay and nanotubes were mixed with epoxy resin with direct mixing method which was mixed homogenously using high shear mixing method at 8000 rpm. Finally, the mixture of resin and nanoparticles was degassed under vacuum for 15 minutes and hardener was added to the mixture. The test results had shown that specific energy recovery tend to decrease with increase of nanoparticle percentage and peak load also decreased slightly with the addition of nanoparticles. This is due to poor distribution of nanoparticles at higher concentration which results in the formation of big clusters of clay that reduce

the plastic deformation of polymer matrix. The addition of nanoparticles had shown only slight improvement in impact property response.

In summary, nanoclay cannot be added directly to epoxy resin which forms globular structures. The dispersion of nanoclay in the epoxy matrix can be enhanced through appropriate dispersion techniques which in turn will reduce the agglomeration and the interfacial adhesion can be improved through surface treatment of nanoclay. Complete exfoliation and homogenous dispersion of the nanoclay is hard to achieve, which is a major limitation in synthesizing clay-reinforced nanocomposites. The homogenous distribution of the nanoclay in epoxy had been analysed by observing the microstructure of the composites using SEM analysis. The increase of nanoclay concentration above threshold limit leads to agglomeration which act as stress concentrators leading to the weak interfacial bonding strength and reduction in mechanical performance. The weak interfacial bonding also reduces the stress transfer capabilities due to the increase in resin viscosity and restricted processability.

2.4　Interfacial Bonding Characteristics of Glass Fiber Reinforced Polymer Composites

Glass fiber reinforced polymer composites are most widely used fiber reinforced composites due to their superior mechanical properties, high strength to weight ratio and low-cost performance ratio. Apart from the resin and fiber, the interfacial bonding between them play a key role in deciding the properties of the composites. With the intention of improving the binding property and interfacial compatibility between the glass fiber and resin matrix, the glass fibers are coated with an aqueous mixture of coupling agents, lubricants, emulsified polymers in the process of glass fiber production. The most commonly used coupling agents are silane coupling with amino, epoxy or vinyl etc. [29]. The second option is the addition of nanofillers which could lead to strengthened matrix as well as stronger fiber/matrix interphase.

Gu et al. [30] analysed the interfacial properties of glass fiber reinforced polymer composite through the vibration damping technique which provides a quantitative characterization of interfacial adhesion strength through the load transfer from the

matrix to reinforcement. Three samples were made with different surface treatment of glass fibers using various volume fractions. The experimental results had shown an inverse relationship between damping contributed by interface and the composite transverse shear strength. The samples with silane treatment exhibited the maximum fiber matrix interfacial adhesion and the samples with untreated fibers had shown the weakest interfacial adhesion between the fiber matrix interface. It was observed that as the fraction volume of the fiber increases, more fiber-interfacial area was created and more energy was dissipated by the fiber-matrix interface. Drescher et al. [31] observed the interfacial adhesion properties through the fiber surface modification and nanoparticle incorporation in matrix material which in turn will strengthen the linkage between fiber and matrix by increasing the surface area of the fiber and matrix. The results obtained from tensile fiber bundle test and single fiber pull out test indicated that considerable enhancement of the interphase and mechanical properties were obtained from composites with surface treated fibers whereas SEM analysis had shown homogenous dispersion of nanoparticles and glass fibers in the matrix system. The study concluded with the emphasis for future research to investigate further on the interfacial bonding mechanism and optimization on the mechanical properties of glass fiber reinforced polymer composites.

Bikramjit et al. [8] analysed the interfacial bonding strength of glass fiber reinforced polymer nanocomposite by reinforcing Cloisite 15A clay as nano-filler which was surface modified using two different silane agents 3-Aminopropyltriethoxy silane and 3-glycidyloxypropyltrimethoxy silane with varying proportions of 10, 50, 200 and 400 wt.% of nanoclay. The nanoclay was then dispersed in epoxy resin where the glass fiber reinforced epoxy laminates were prepared using vacuum bagging method. The glass fiber-reinforced polymer nanocomposites were characterised using XRD, TEM and differential scanning spectroscopy. It was observed that silane treatment of nanoclay aided the exfoliation of nanoparticles which improved the interfacial bonding between glass fiber and epoxy matrix resulting in improvement of mechanical strength. The optimized amount of silane coupling agents was 200 wt.% which exhibited an exfoliated morphology, improved tensile strength, flexural modulus and flexural strength. The improved interfacial bonding between silane modified nanoclay and epoxy matrix was also evident from significant increase in elongation at break. The functional groups in silane react with inorganic clay and epoxy resin thus forming a network between

nanoclay, silane and epoxy which enhances the interfacial adhesion between nanoclay and epoxy matrix. The second reason for the increase in properties are due to the increase in extent of curing leading to an increase in the crosslinking density of epoxy. Ram et al. [32] investigated the mechanical and tribological behaviour of GFRP composite reinforced with three different weight fractions (2, 3 and 4 wt.%) of organomodified nanoclay (15-20 nm) and 10 wt.% of calcium silicate particles (15-20 μm). Conventional hand lay-up technique was utilized for the preparation of nanocomposite and the laminate was pressed using compression moulding machine at 50°C for 5 minutes. Curing was carried out at ambient temperature for 24 hours followed by post-curing at 100, 140 and 150°C. The research work concluded that maximum mechanical properties such as tensile and flexural strength were achieved using 2 wt.% of nanoclay where there was degradation in mechanical properties with further addition of nanoclay. Wear analysis had shown that the numerous failures such as matrix wear, matrix/fiber debonding (adhesive failure) and fiber breakages (cohesive failure) occurred due to excessive reinforcement, uneven distribution and agglomeration effects. The loss of strength was mainly attributed due to the excessive reinforcement of nanoclay and the tendency for particle clumping. The bonding characteristics were expected to be poor in the matrix due to the weak interaction between the matrix and the particle aggregates. These lumps act as stress concentration point and potential site for crack nucleation.

Jeyakumar et al. [33] explored the morphological and mechanical behaviour of GFRP composites reinforced with and without Cloisite nanoclay at various weight fraction ranging from 0 to 7 wt.% with epoxy resin . The experimental results revealed that maximum tensile strength, flexural strength and hardness was attained with 5 wt.% of nanoclay. However, maximum compressive strength and impact strength was attained with 3 wt.% of nanoclay. The Vickers hardness value and interlaminar shear strength (ILSS) of the nanocomposites increased up to 3 wt.% of nanoclay concentration and with further addition of nanoclay the values reduced due to buckling failure. It was also noticed from SEM analysis that better adhesion between fiber-matrix was achieved with 5 wt.% filled nanoclay composites. The failure analysis was performed through SEM images where the main causes noticed were matrix-fiber debonding and fiber pull out. This was due to the fact that filler has filled the maximum voids in the matrix and thus saturation level was attained for the tensile properties. Furthermore, with higher nanoclay reinforcement there arises agglomeration which act like superior structures by

serving as crack initiation sites. Thiagarajan et al. [34] evaluated the effect of interfacial bonding on the impact strength of GFRP reinforced with organomodified nanoclay montmorillonite content varied at 0, 1, 3 and 5 wt.%. Experimental results from specimens prepared by hand lay-up method revealed that maximum load carrying capacity increased with 3 wt.% of nanoclay concentration and it was also noticed that impact strength reduced drastically with 5 wt.% concentration due to agglomeration resulting in weak interfacial bonding. It was evident that addition of nanoclay particles improved the impact strength through good interfacial bonding between fiber and nanoclay dispersed epoxy which was also confirmed through SEM analysis. The addition of nanoclay increased the interface surface of the constituents in the system and superficial area-volume ratio thus resulting in an improvement in the mechanical performance of the reinforced material.

Aktas et al. [35] studied the reinforcement effect of unmodified Cloisite clay with varying percentages ranging from 0 to 2 wt.% of waterborne epoxy resin and random oriented short glass fibers which was fabricated using compression moulding. The test results revealed that ILSS, flexural strength and flexural stiffness had shown maximum values at 0.5 wt.% of nanoclay loading. SEM analysis revealed that interfacial bonding between matrix and fiber increased with percentage of nanoclay loading which was identified through the increased amount of matrix residues on fiber after fracture. X-Ray Diffraction analysis indicated complete exfoliation of nanoparticles for 0.1, 0.2 and 0.5 wt.% loadings. The increased resin-clay residue on the fiber surfaces indicated that the addition of nanoclay improved the fiber-matrix adhesion at low level of clay concentration which contributed to the improved mechanical properties. The increase in properties at low nanoclay concentration was due to the exfoliation of platelets facilitated by the reduced interaction of nanoclay particles with each other. Singh et al. [36] observed the mechanical properties of E-Glass unidirectional fiber based polymer composites reinforced by natural Cloisite 30B nanoclay with different proportions (1,3 and 5 wt.%) manufactured by hand layup method. The nanoclay was dispersed in epoxy resin using mechanical stirring and ultrasonication to enhance uniform dispersion in the matrix system. The experimental test results revealed that tensile strength, flexural strength and hardness attained maximum performance with 3 wt.% of nanoclay concentration due to improvement in interfacial adhesion between fiber, matrix and nanoparticles but the mechanical properties tend to decrease with further addition of

nanoclay due to agglomeration effect caused by nanoparticles. The enhancement of mechanical properties was due to the intercalation of nanoclay occurred in the epoxy system with 1 and 3 wt.% of nanoclay concentration.

Hamed et al. [37] analysed the mechanical properties of basalt fiber/epoxy resin both theoretically and experimentally which was reinforced with silane modified nanoclay through varying range from 0 to 5 wt.% with respect to the epoxy matrix. Na-Mt nanoclays were surface modified using 3-GPTS which was confirmed using FTIR and XRD analysis. The test results revealed that there was increase of 11%, 28% and 43% increase in tensile strength, flexural strength and compressive strength respectively with 5 wt.% concentration of nanoclay in the matrix. The compressive modulus and strength of the specimens were also obtained theoretically using Euler-Bernoulli beam-based approach. Close correlation was observed between the theoretical and experimental results. SEM analysis confirmed that the enhancement in mechanical properties were due to the improvement in interfacial adhesion between the fiber and the matrix. The improvement in mechanical performance was due to the improved interfacial strength between basalt fiber and matrix with surface modified nanoclay. The surface modification of nanoclay particles had enhanced their interfacial interaction with the epoxy matrix. This had led to restricting mobility of polymer chains under loading, resulting in improved mechanical moduli. Helmy et al. [38] studied the tensile fatigue behaviour of nanoclay reinforced glass fiber nanocomposites fabricated with different stacking sequence. The main purpose of the experimental work was to study the effect of nanoclay addition to the epoxy resin. The test results revealed that the tensile strength and modulus of elasticity were enhanced by the addition of nanoclay in epoxy resin which increased the ultimate strength. In addition to that the nanoclay also supressed the fatigue damage growth in terms of damage index and crack growth rate over the whole fatigue life by increasing the interfacial surface area of polymer system with the incorporation of nanoclay to glass/epoxy system except during the early stage of loading. The nanoclay aids in the improvement of mechanical performance through the more filling of the cavity which in turn reduces the stress concentration at the fracture area. This improvement is more significant in low stress levels rather than the higher stress level.

From the literature review, it was evident that from the strengthened fiber/matrix interphase of fiber reinforced polymer materials, considerably improved mechanical properties were attained. By the addition of nanoscaled particles or by the use of suitably surface modified fibers such improvements were achieved. The enhancement of the mechanical and wear performance was due to the improvement in interfacial strength due to the surface treatment of glass fiber and addition of surface modified nanoparticles. The surface treatment had led to restricting mobility of polymer chain under loading resulting in improved mechanical moduli. The addition of nanoparticles benefits in the filling of the cavity through the increase of interfacial area of the constituents in the system which sequentially reduced the stress concentration. Critical literature review on the effect of nanoparticle reinforcement and their impact on the mechanical and wear properties of the nanocomposites are discussed in the next section of this chapter.

2.5 Addition of Nanomaterials in the Polymer System

Among different fiber reinforced composites, because of the cost adequacy, glass fiber strengthened epoxy composites are broadly used in applications, few of these applications include reinforcement in tanks, car bodies and boat hulls. In these applications, properties such as impact resistance, tensile strength, flexural strength and wear properties are crucial. Thus, there is a necessity to improve these properties of E-Glass-epoxy composites for those applications. Numerous attempts have been made to add different substances such as nanoclay, carbon nanofiber and carbon nanotubes to upgrade the mechanical and wear properties of the composites. Among all the nanofillers, amino-functionalized montmorillonite nanoclay has a better compatibility with both epoxy and E-Glass fiber. The amino functional groups introduced on the nanoclay (NC) surface reacts with the epoxy molecules resulting in a strong bond between NC and epoxy. In general, the upgrade in the mechanical properties of E-Glass-epoxy composites was attributed due to the addition of NC which promotes the crosslinking density (increased crosslinks within the matrix because of amino groups), giving rise to improved toughness of matrix and enhanced fiber–matrix interface toughness [39].

Sharma et. al [40] studied the mechanical and wear performance of the glass fiber reinforced polymer system with the addition of nanoclay ranging from 0 to 5 wt.% loading in the epoxy matrix system. The mechanical properties in terms of the tensile, impact and microhardness were evaluated. The test results revealed that the tensile strength and microhardness increased with increase of nanoclay concentration up to 3 wt.%. Moreover, the flexural strength increased significantly with increase in nanoclay loading and the highest value was observed with 5 wt.% of nanoclay. The nanocomposites have been characterised by XRD and SEM analysis. The XRD results revealed that the interlayer spacing between the clay platelets increased significantly which indicated that the polymer can intercalate between the nanoclay layers. Senthil et. al [41] studied the mechanical properties of glass fiber reinforced epoxy composites which was further reinforced with the addition of Cloisite 25A nanoclay from 2 to 10 wt.% in increments of 2 wt.% and fabricated using compression moulding. The test results concluded that 2 wt.% of nanoclay produced the best composites in terms of tensile strength and flexural strength. The SEM analysis had also shown appreciable morphological properties at 2 and 4 wt.% of nanoclay loadings. During the low clay content, the intercalated structure of nanoclay promoted better matrix and fiber mechanical interlocking resulted in better exposure of fiber surface to the clay filled matrix thereby enhancing the bonding strength between fibers and nanoclay modified epoxy resin. At higher nanoclay concentration non-homogenous mixture of clay/epoxy suspension resulted in weak interfacial adhesion at some portion which acted as stress concentrators leading to premature failure. Manjunath et. al [42] studied the mechanical properties of FRP-nanoclay hybrid nanocomposite with the addition of nanoclay at different loading levels from 0 to 10 wt.% of the epoxy system using hand lay-up method. The nanoclay was dispersed using mechanical stirrer for 2 hours at 2000 rpm and followed by sonication for 15-30 minutes at a frequency of 40-60 kHz. The tensile and flexural strength results revealed that both properties had significant improvement up to 5 wt.% of nanoclay concentration. The increase in nanoclay concentration beyond 5 wt.% had led to increase in void concentration, which could not withstand applied load and might have initiated cracks to propagate through the composite. These voids were created while mixing the nanoclay-resin mixture with hardener. Increase in the weight percentage of nanoclay into the resin beyond the optimum quantity led to viscous mixture. When the hardener is added into the sluggish mixture lead to void formation which promotes premature failure of the composite.

Sivasaravanan et. al [43] analysed the mechanical properties of the glass fiber reinforced epoxy polymer matrix nanocomposite. The nanocomposite was fabricated using hand layup technique with nanoclay loading ranging from 0 to 2 wt.% at a 0.5 wt.% increment. The test results revealed that the glass fiber reinforced epoxy composite with 0 wt.% nanoclay exhibited excellent tensile strength when compared to nanocomposites with nanoclay. The loss in tensile strength with nanoclay addition was justified by the increase in Youngs modulus. The Youngs modulus being an indication of the stiffness of the material, indicate an increase in stiffness of the composite material. The ductility of the material reduced with the addition of nanoclay due to the increase in stiffness and 27% loss in impact strength was observed with addition of nanoclay. Sakthivel et. al [44] studied the mechanical behaviour of polymer nanocomposites containing epoxy resin as matrix and carbon fiber, glass fiber and nanoclay as reinforcements prepared by using the melt stirring method. The tensile modulus and breaking load values were higher for nanocomposite with carbon fiber, glass fiber and nanoclay which was mainly due to the exfoliation within the epoxy matrix. The composite containing nanoclay with fibers had attained high hardness when compared to the neat composites (without nanoclay addition). The SEM analysis had shown better dispersion of nanoclay particles in carbon-glass fiber reinforced epoxy matrix nanocomposite. The enhancement of mechanical properties of the nanocomposite was mainly due to the addition of 0.5 wt.% of nanoclay within the epoxy matrix. The enhancement of properties was due to the exfoliated type of nanoclay structures formed due to the shearing action of impeller blades in melt stirring process and uniform dispersion of nanoclay particles.

Andrea et. al [45] studied the effect of various kinds of organo-modified nanoclay addition on the fiber/matrix adhesion in epoxy matrix nanocomposite with respect to mechanical and thermal properties. The formation of intercalated microstructures had led to substantial improvement in thermal glass transition temperature and fracture toughness of the nanocomposite by 5% with the addition of Cloisite 10A nanoclay. The interfacial shear strength increased to about 30% due to stronger fiber-matrix interface which was evaluated through single-fiber microdebonding method. The evaluation of fiber/matrix contact angle also had shown an improved wettability through the addition of organo-modified nanoclay. The evaluation from the single fiber fragmentation test indicated that the addition of nanoparticles induced substantial increase in fiber-matrix

load transfer ability of the epoxy matrix. The positive contribution of the clay presence on the adhesion mechanism had contributed to the enhancement of interlaminar crack propagation resistance. Ratna et. al [46] analysed the mechanical behaviour of vinyl ester/glass fiber composites reinforced with three different nanoclay loading of Cloisite-15A, Cloisite-93A and Cloisite-Na ranging from 0-5 wt.% using ultrasonication and twin-screw extrusion. It was observed from the mechanical test results that the tensile, flexural and microhardness were highest for 4 wt.% concentration of Cloisite-15A. It was also noted that addition of Cloisite-15A nanoclay increased the stress intensity factor and the glass transition temperature. The improvement in mechanical properties were highest for Cloisite-15A based specimens followed by those with Cloisite-Na and Cloisite-93A, which was further confirmed through SEM analysis. The increase in microhardness was mainly due to the addition of nanoclay that contributed to the formation of network like structure of intercalated/exfoliated platelets with vinyl ester molecules effectively restricting the indentation. Furthermore, the fracture toughness was explained using Faber and Evans model, that when a growing crack meets nanoclay, the crack gets deflected out of plane and when the crack encounters further nanoclay particles it gets twisted and tilted. This increases the fracture surface area leading to increase in fracture toughness.

Ahmad et. al [47] studied the effect of nanoclay concentration on the glass fiber reinforced epoxy composites made using hand layup method followed by hot pressing process ranging from 0-5 wt.%. The flexural strength had achieved an improvement of 11% for 1.5 wt.% of nanoclay concentration. The SEM images had also shown better adhesion properties with 1.5 wt.% of nanoclay concentration. However, with the higher loading of nanoclay, agglomeration and presence of micro-voids had led to reduction in flexural strength and more hydrophilic of the composites. As such, the exposure to moisture had resulted in degradation of flexural properties to around 36% for 80ºC and 8% at room temperature. The improvement of the flexural strength up to 1.5 wt.% nanoclay concentration was due to the formation of exfoliated nanocomposite structure. The presence of nanoclay attributed to the improvement in the adhesion of the nanocomposite matrix resulting in better interfacial bonding of the final laminate. Good interfacial adhesion provides better stress transfer and inherent properties of clay. The relatively negative effect of the addition of clay beyond 1.5 wt.% can be attributed to agglomeration of nanoclay which acted as stress raisers. This effect was noticed at higher

clay loadings because of the increase in viscosity of the matrix making processing and degassing more difficult leading to air gaps or micro-voids thereby reducing the mechanical performance of the nanocomposite. Ngo et. al [48] studied the effect of nanoclay concentration (ranging from 0-5 wt.%) on the mechanical and thermal properties of epoxy/glass fiber composites prepared using vacuum infusion method. The cone calorimeter test in horizontal configuration was used as bench scale test to determine the heat and smoke production for samples with nanoclay. The fire test result also demonstrated that the samples with less than 3 wt.% of nanoclay concentration had a scattered dispersion and it was insufficient for char formation. The SEM analysis of the samples with organophilic clay before and after the cone tests were presented to analyse the distribution of nanoclay particles in the nanocomposites. The mechanical properties of the nanocomposites were evaluated through the tensile test and it was noticed that the presence of nanoclay had enhanced the mechanical properties up to 3 wt.% of nanoclay. It was concluded that with further addition of nanoclay, negative effects arose due to high viscosity and infusion time. The phenomenon was explained though the distribution of nanoclay platelets in the matrix and surface interaction between the organic resin and nanoclay particles. Additional nanoclay into the resin contributes positive effects on the fire performance as well as mechanical strength of the nanocomposite. This could also be explained by increasing the nanoclay percentage that enhances the thermomechanical properties coupled with higher viscosity of the resin which in turn could affect the distribution of nanoclay particles as well as infusion time. Therefore, threshold limit for clay content was obtained to achieve optimum fire performance and as well as mechanical performance.

Shanti et. al [39] observed the effect of nanoclay concentration and glass fiber volume/orientation on the tensile properties of epoxy glass composite prepared by hand lay-up technique using the Taguchi method. From the experimental analysis and optimization, it was observed that the main significant factor for the tensile strength was the fiber orientation. On the other hand, nanoclay addition and volume of glass fiber insignificantly influenced on the strength properties. This was attributed due to agglomeration and void content in the composite which acted as stress concentration locations resulting in decrease of tensile strength. Thus, it was recommended to utilize high speed mechanical stirrer or ultrasonication with appropriate degassing for improvement of mechanical performance. The mode of failure for FRP composites

occurred at the interface which indicated that the bonding between the glass fiber and matrix was very weak. The failure occurred due to the debonding between the fiber and the matrix followed by fiber breakage. For epoxy-glass clay nanocomposite (EGCN), the fracture mechanisms were altered because of the presence of clay and the mode of fracture implied that the interface in EGCN was stronger than the FRP. Thiagarajan et. al [49] studied the nanoclay influence on the mechanical properties of epoxy glass fiber (woven ring and chopped strand mat) composites prepared using hand lay-up technique ranging from 0-5 wt.% of nanoclay concentration. From the mechanical test results, it was observed that 1 wt.% of nanoclay concentration enhanced the tensile strength of the composites by 14.8%, flexural strength by 9% and interlaminar shear strength by 25%. The SEM analysis of the fractured surface of the test specimen indicated that the mode of failure for neat glass fiber/epoxy composite was fiber pull-out and fiber breakage. On the other hand, for 1 wt.% and 3 wt.% of nanocomposites, the SEM images revealed that there was good interfacial bonding between glass fiber and matrix with the addition of nanoclay. The X-ray diffraction analysis (XRD) was used to characterize the structure of the dispersed nanoclay particles into matrix material. XRD test results revealed that the dispersion of nanoclay particles was fully intercalated or orderly exfoliated structure which confirmed that the nanoclay particles were uniformly dispersed within the epoxy resin. This dispersion of nanoclay structure had acted as an interface material between fiber and the matrix which led to the improvement in mechanical performance of the nanocomposite.

Ansal et. al [50] studied the effect of nanoclay concentration on the tensile and hardness properties of epoxy glass fiber composite prepared using hand lay-up method. The nanoclay concentration was varied from 0-3 wt.% in increments of 1wt.%. The test results shown that the tensile strength was higher with 1 wt.% concentration and decreased with further increase in nanoclay percentage. The hardness also increased with increase of nanoclay concentration and the maximum hardness was recorded with 3 wt.% of nanoclay concentration. The SEM analyses also indicated uniform distribution of the nanomaterials enhancing the interfacial bonding and tensile strength, whereas increase in nanoclay concentration results in assemblage and it negatively affects the homogeneity of the dispersion. From the mechanical test results and ANSYS analysis it was evident that the composite with 1 wt.% of nanoclay concentration had shown higher tensile properties with optimum hardness suitable for wind turbine blade applications.

Omer et. al [51] analysed the axial and lateral buckling characteristics of the epoxy/S-Glass composites with the addition of nanoclay particles of 0, 1, 1.5, 2 and 3 wt.% in epoxy system using hand lay-up method. The effect of glass fiber orientation angles on critical buckling loads for both axial and lateral buckling were investigated. The test results indicated that maximum axial and lateral buckling loads were attained with fiber orientation angle of [0º/90º] and [15º/-75º] respectively. The tensile and flexural properties were analysed for 1 wt.% nanoclay concentration and it was concluded from the test results that the axial bucking load increased by 8.6%. It was also observed that with further increase of nanoclay concentration, resulted in reduction of properties due to the poor interfacial bonding between nanoclay and epoxy resin. The addition of nanoclay with low content (1 wt.%) contributed for improved mechanical performance through enhancement of epoxy characteristics by good interfacial bonding of epoxy with clay particles. At higher concentrations of nanoclay, the reduction of properties was attributed due to agglomeration thereby resulting in decrease of load transfer between nanoparticles and epoxy resin.

Cong et. al [52] investigated the effect of nanoclay addition on the mechanical properties of epoxy/3D orthogonal glass fiber woven composite prepared using resin infusion under flexible tooling process by varying the nanoclay concentration from 0-4 wt.% in epoxy matrix. SEM images have been analysed for the fracture and failure modes of the test specimens which revealed that delamination and debonding has been decreased due to the increase in bonding strength between fiber and the matrix with 3 wt.% nanoclay concentration. The tensile strength and modulus have gained efficiency of 23.32% and 16.42% with 3 wt.% of nanoclay addition. The contact angle also demonstrated that the dispersion and wettability was better with 3 wt.% of nanoclay addition. The nanoparticles modified the composite by improving the wettability of glass fiber and the polymer matrix which further act as a bridge between the glass fiber and epoxy thereby enhancing the interfacial adhesion between the epoxy resin and glass fiber. In conclusion, the composite prepared with 3 wt.% of nanoclay concentration had shown significant improvement in mechanical properties due to the enhancement of interfacial bonding between the clay particles and the polymer matrix which limits the fluidity of polymer chain. Ahmad et. al [53] analysed the effect of nanoclay concentration on the impact properties of glass fiber reinforced epoxy (GFRE) composites prepared using hand lay-up method and hot pressing. The nanoclay was

added in three different loadings at 0, 1.5 and 3 wt.%. The composites were subjected to low-velocity impact with energies ranging between 10J and 50J. The composite prepared with 1.5 wt.% of nanoclay had shown 23% improvement in peak load and 11% increase in stiffness when compared to the neat composite. The reduction in impact properties with 3 wt.% of nanoparticle addition was mainly due to clay agglomeration and micro void formation which in turn reduced the adhesion between the resin and the glass fibers and acted as stress concentrators. This clay agglomeration or poor dispersion resulted mainly due to the increase in matrix viscosity.

From the above literature review, it can be concluded that low clay content led to intercalated structure, better fiber and matrix mechanical interlocking which in turn enhanced the interfacial bonding strength. Nanofillers such as nanoclay and carbon nanotubes (CNT) which possess higher aspect ratios when compared with particulate fillers can improve the mechanical and wear behaviour of polymer composites. The strength of the composite depends on the bonding between the matrix and fiber, the stronger the bond the stronger the composite. However, as the clay content increases in the matrix, the tendency for the formation of agglomerates becomes more pronounced, which not only causes decrement in the stress transfer, but also those sites of agglomerations act as stress concentration resulting in the premature breaking, which usually results in clay content above 3 wt.%. In addition, the tensile and flexural strength of the composites varied with the void content. The voids may have originated during the mixing and integration of two or more different material parts [39]. Generally, the improvement in mechanical properties of glass fiber reinforced epoxy composites was due to enhancement in the crosslink density that led to improved properties of matrix, because of the nanoclay addition.

2.6 Effect of Curing Temperature and Time of Polymer Nanocomposites

The mechanical performance of the fiber reinforced polymer composite depends on the interfacial bonding strength and properties of the structural epoxy adhesives. Nevertheless, the mechanical performance is significantly influenced by the curing process where curing temperature and curing time are the important factors. The strength, modulus, fiber volume fraction, bond stiffness and maximum pull out force

also exhibit significant dependence on the curing temperature and time. The curing temperature could accelerate both the curing process and evolution of bond performance through improved wetting of the fibers by resin as a result lowered viscosity and enhanced mechanical interlocking of the fiber and the resin are attained. According to the phenomenon of fibers splitting and pulled-off, the composites fabricated at higher temperature had shown better interfacial properties with higher bonding strength. Curing is an irreversible process for thermosetting polymers where chemical covalent cross-links are formed which are thermally and mechanically stable. During cross-linking the state of matrix changes from liquid to gel and then transforms to solid. Post curing is done to improve the modulus and mechanical strength of the composite and thereby reducing the residual stress.

Rao et. al [54] studied the effect of curing temperature, glass fiber percentage and epoxy to hardener ratio on the tensile strength of the glass fiber reinforced polymer composite prepared using hand lay-up method. The glass fibers were used at 20 wt.%, 50 wt.% and 80 wt.% of the matrix and the curing temperature were maintained at 20°C, 60°C and 100°C. It was observed from the ANOVA analysis that the fiber content was the main contribution factor for the tensile strength followed by the curing temperature and epoxy to hardener ratio. It was well known that fiber was the main constituent for the composite material for increase in tensile strength as the fiber takes the applied load on it. Furthermore, the curing temperature of the composite also plays a vital role by curing the overall composite without any residue of uncured resin. This was the main reason for obtaining the high temperature as the better response for tensile strength. It was concluded from the test results that appropriate curing temperature needed to be maintained to achieve the curing process to be complete. Liu et. al [55] analysed the influence of curing temperature on the mechanical behaviour of Kevlar epoxy composite. The tensile properties were measured at four different curing temperatures and tested with ±45° off-axis tensile loading on a universal test machine coupled with digital image correlation (DIC). The tested results had shown that the tensile mechanical behaviours were sensitive to the curing temperature and the relationship was non-monotonic. Also, as the temperature increases, the thicknesses of the specimens were significantly enlarged. By analysing the SEM micrographs of the matrix grooves in the damage zone and DIC strain contours, it was concluded that the non-monotonic relationship was dominated by the properties of the Kevlar/epoxy interfaces and

deformation of the distorted fibers. The occurrence of fibers pulled-off and fibers splitting had indicated that the composites at higher curing temperature possess better interfacial properties with higher bonding strength since the deformation of the distorted fibers contribute to the energy absorption. At lower curing temperature the fibers possesses insufficient reinforcing effect thereby reducing the strength and stiffness of the composite.

Kumar et. al [56] analysed the effect of post curing temperature effect on the thermal and mechanical behaviour of glass fiber reinforced epoxy composites fabricated using hand lay-up method followed by curing in a hydraulic press at 60°C and 1MPa for 20 minutes. The dried specimens were post cured in an oven at 80°C, 110°C and 140°C for 2h, 4h, 6h, 8h and 12h at heating rate of 2°C/min. It was observed from the mechanical test results that at 80°C there was no significant improvement in interlaminar shear strength (ILSS) as the energy available at these post curing temperature could not be sufficient for enhancing the wettability of the fiber/matrix interphase. But with higher curing temperature of 140°C a tremendous increase in ILSS was obtained with a duration of 6 hours whereas further increase of curing time did not show any improvement in ILSS which indicated the saturation point for curing time. The post curing of the composite makes the polymer matrix sufficiently strong through the formation of cross-linked polymer network thereby improving the interfacial bonding strength.

Charlotte et. al [57] studied the effect of post curing temperature on the fibers, resin or interface of the flax fiber reinforced epoxy composite. The composites were prepared using vacuum infusion method in controlled atmosphere which were later cured at 80°C for 24 hours. Post curing was done at three different temperatures of 100°C, 120°C and 150°C for 2 hours. The maximum tensile strength does not have significant effect at 100°C and 120°C but decreased by 20% with post curing temperature of 150°C. The composite glass transition temperature and the cross-linking rate increases when post curing was carried out. It was observed that higher the post-curing temperature, higher the cross-linking rate where the interaction between the fiber and epoxy resin allowed the stress transfer from the resin to reinforcement. Ammar et. al [58] analysed the post curing temperature effect on the fatigue life, modulus and interlaminar shear strength of the glass fiber reinforced polymer composites. Three samples were prepared with weight ratio of 65 parts fiber and 35 parts epoxy using hand

lay-up method. The samples were post cured with three different temperature where the first sample was cured at room temperature for 12 hours followed by post curing at 70°C for 6 hours and 140°C for 6 hours. The second sample was post cured at 70°C for 6 hours followed by 140°C for 6 hours. The third sample was directly post cured at 140°C for 6 hours. The fatigue test results revealed that the composites with faster curing rates had shown lower fatigue life due to greater volume content of soft epoxy phase and non-homogenous network leading to variable crosslink density. However, if sufficient time was given for curing to gel state, samples had shown similar microstructures and improved fatigue life of the composite. The storage modulus and interlaminar shear strength remains unaffected by the change in the resin microstructure.

Andrea et. al [59] studied the influence of temperature on the curing process of the structural epoxy and its effect on the bond behaviour of near surface mounted carbon fiber reinforced polymer (NSM-CFRP) strengthening applications. The test was carried out at three different temperatures 20, 30 and 40°C where the elastic modulus was evaluated through the Elasticity Modulus Monitoring through Ambient Response Method (EMM-ARM). Direct pull-out tests with concrete specimens strengthened with NSM CFRP strips were carried out at the same three distinct temperatures to compare the evolution of bond performance with the E-modulus of epoxy since early ages. The results showed that increasing the curing temperature significantly accelerated both the curing process of the epoxy adhesive and the evolution of bond performance. The method was also able to assess the increase of the epoxy stiffness with the increase of the curing and testing temperatures. The failure mode was cohesive due to the lower mechanical properties at the beginning of curing, but with further curing the failure mode changed from cohesive failure to debonding at fiber-epoxy surface due to the enhancement in interfacial adhesive strength.

Laoubi et. al [60] analysed the chemical, physical and mechanical behaviour of E-Glass fiber unsaturated polyester composites under moderate and high temperatures. Thermogravimetry analysis (TGA) revealed that the thermal degradation of the composites occurred in two steps. The first step occurred between 130 to 200°C and the second step between 250 to 440°C. The characterization of the specimen after heating revealed that at moderate temperatures less than 100°C there were improvement in mechanical properties of the composite. For exposure to higher temperature but less than

the degradation temperature (Td) the mechanical strength does not seem to be affected significantly but noticeable fractures of the fiber-matrix interface were observed through SEM analysis. On the other hand, when the temperature had reached the degradation temperature (Td) a drastic fall in mechanical properties were noticed for both resin and the composite. The main reason for the increase in properties for curing temperature around 100°C is the evolution of the state of linkage of the resin because in thermosetting resins, post-cure or further cross linking occurs at elevated temperatures around 100-150°C. However, with further increase of curing temperature there arises degradation of properties with severe damages to the glass fibers and resin.

In order to enhance both the efficiency of hot-pressing process and maintain lower deformation of the composite laminates, the curing temperature and curing time are two key factors. The experimental results had shown that elevated curing temperature could accelerate both the curing process of the epoxy adhesive and the evolution of bond performance due to improved wetting of the fibers by resin as a result of lower viscosity and improved mechanical interlocking of fiber and resin. The cross-linking rate between the fiber and the matrix also increases thereby increasing the load transfer capability of the composite. Nevertheless, with higher curing temperature around 250 to 440°C which is close to the degradation temperature, severe damage to glass fiber and resin occurs, resulting in drastic degradation of the mechanical performance.

2.7 Wear Performance of Polymer Nanocomposites

In previous sections, critical literature review related to surface treatment of glass fibers and nanoclay, dispersion mechanism for the addition of nanoclay in the matrix system, interfacial bonding characteristics between glass fiber and epoxy, effect of curing temperature and curing time on the interfacial bonding mechanism has been discussed in detail. Friction behaviour and wear were one of the most characteristic features of polymer-metal components transferring load under sliding motion. The wear rate is affected by various operating parameters such as load, sliding distance, sliding velocity, temperature etc. and material parameters such as fiber volume fraction, fiber treatment, fiber orientation and filler content. In this section, review was done on the wear performance of polymer nanocomposites. Polymer based nanocomposites are

commonly reinforced by nanofillers such as silica and oxides, carbides of different materials. Recent studies have shown that small amount of ceramic nanoclay in polymer composite improves mechanical and tribological properties. Montmorillonite based clays (MMT) offer high interest from an industrial point of view since the use of small amounts of them is enough to improve the overall properties of a polymer matrix at a relatively low cost. But the degree of the dispersion of nanoclay in epoxy resin has been reported to have significant effect on the mechanical properties of the nanocomposites.

Vinayagamoorthy [61] reviewed the effect of various parameters such as the sliding velocity, sliding distance, applied pressure and temperature on the friction and wear performance of glass fiber reinforced polymer nanocomposites. In addition, the author also addressed the significance of the fiber geometry, fiber matrix composition, orientation of the glass fibers. It was noted from the literature review that the friction and wear were mainly affected by the process parameters followed by the material factors. It was also noticed that the addition of nanoparticles had shown a positive effect on the tribological behavior of the nanocomposites. The key factor influencing the tribological failure was the debonding between the fiber and the matrix. Mehmet et. al [62] studied the effect of nanoclay on the erosion rate of glass fiber reinforced epoxy nanocomposites prepared using hand lay-up method followed by vacuum infusion method. Further, the curing of the nanocomposite was done at 100ºC for one hour followed by 200ºC for two hours. The nanoclay was added in two different ratios of 1 wt.% and 3 wt.% of the epoxy/glass fiber composite. The erosion rate was observed at three different impingement angles of 30º, 60º and 90º with two different velocities 23 m/s and 34 m/s. It was observed from the test results that the mechanical properties were the highest with 1 wt.% of nanoclay and the properties reduced with further addition of nanoclay. On the other hand, the erosion rate increased with the addition of nanoclay and the lowest erosion rate was observed with neat epoxy and glass fiber composite for all impingement angles and velocities. The study also concluded that the addition of nanoclay caused negative effect on the materials tribological properties such as decreased erosion wear resistance of the nanocomposites.

Shanti et. al [63] studied the optimization of microhardness and erosion resistance of the epoxy-glass fiber-Cloisite 15A nanoclay composites prepared using the hand lay-up method. The key parameters considered were nanoclay concentration, volume of the

glass fiber and the orientation of the glass fiber. It was observed from the test results that microhardness was significantly influenced by the nanoclay concentration, glass fiber reinforcement but the fiber orientation had the least effect on the microhardness result. The highest hardness of 27.23 HV was attained with 2.5 wt.% nanoclay, 31.5 vol% of glass fiber and with 0°/90° orientation of the glass fiber. It was noticed from the SEM images that the surface roughness of the eroded surface reduced with increase in nanoclay content which indicates that the nanoclay had good compatibility with the epoxy resin and glass fibers forming a strong bond thereby reducing the erosion rate. Smaranika et. al [64] analysed the mechanical and tribological behavior of the glass fiber reinforced polymer nanocomposites reinforced with 0-7 wt.% of nanoclay prepared using hand lay-up method. Post curing was carried out at 140°C for six hours before testing. It was observed from the test results that nanocomposites with 5 wt.% of nanoclay had shown optimum amount for all the properties like impact strength, flexural strength, hardness and specific wear rate, whereas with further addition of nanoclay concentration had shown reduction in the above-mentioned properties.

Jeyakumar et. al [65] reviewed the mechanical and wear performance conducted on the various glass fiber reinforced epoxy composites which was further reinforced with nanoclay concentration. Wear test was conducted using pin-on-disc apparatus under various applied load, sliding distance and sliding speed to understand the wear performance and the specific wear rate. The dispersion of the nanoclay in the matrix of the composites was examined by XRD analysis and affirmed that nanostructure in both the nanocomposites and fiber reinforced composite were derived from the same matrix. SEM analysis was done to investigate the damages in fiber and the matrix, debonding of fiber-matrix interface and fracture behaviour of broken fibers. It was observed from the mechanical test results that tensile strength, impact strength, flexural strength and hardness increased with nanoclay concentration to certain extent and with further addition of nanoclay the properties tend to decrease. Sathish et. al [66] studied the optimization of wear properties for the glass fiber/carbon reinforced epoxy composites prepared using hand lay-up process with clamp loading. The wear test was carried out using pin-on-disc method using design of experiments based on the response surface methodology with variation in speed, applied load and sliding distance. The speed was varied between 200 to 600 rpm, applied load between 20 to 40N and sliding distance between 300-900m. It was concluded from the experimental test results that lower

weight loss and lower coefficient of friction was obtained with epoxy/glass fiber/carbon at the speed of 600rpm, 20N applied load and sliding distance of 600m.

Isiaka et. al [67] studied the wear resistance of the pawpaw-glass fiber hybrid reinforced epoxy composites prepared using open mold casting hand lay-up technique followed by post curing at an ambient temperature of 24ºC. The wear test was performed using Taber abrasion testing machine and it was observed that the wear resistance of the developed composites was increased for 3 wt.% of the linear fiber and for 15 wt.% of the network pawpaw fibers. It was also observed that the network structured pawpaw fiber obtained better thermal conductivity and improved the curing rate when compared to the linear structured fiber thereby promoting the development of epoxy composites. Pranjal et. al [68] analysed the wear behaviour of the glass fiber/jute reinforced hybrid epoxy composites which was further reinforced with saw dust, fish scale powder and SiC fillers prepared using the hand lay-up method. Post curing was carried out at room temperature for a duration of 48 hours. The fiber weight was kept constant at 50% glass fiber and 50% jute fiber. The dry sliding tests were performed using pin-on-disc method with varying sliding velocities from 2-5 m/s and applied loads from 20-35N with a constant sliding distance of 1800m and track radius of 50mm. It was observed from the wear tests results that the composite with the sawdust filling had shown the minimum wear loss at all applied loads and at higher velocities when compared to fish scale and SiC filled composites.

Diptikanta et al. [69] studied the mechanical and abrasion behavior of glass fiber reinforced epoxy polymer composites prepared using the hand lay-up method with fiber to epoxy ratio of 60:40. The post curing was carried out at 140ºC for 6 hours. The mechanical properties such as the tensile, impact and hardness were evaluated experimentally and it was compared with the previous experimental results presented in the literature review. It was observed from the hardness test results that the 49.84 Barcol was lesser than the experimental test results from the literature though the fiber content of 60 wt.% was the same, which might be because of the difference in matrix properties. Biswajyoti et. al [70] studied the erosion wear behaviour of the glass fiber reinforced epoxy composite which was further reinforced with iron-mud with varying weight percentages from 0-20 wt. %. The composite was prepared using hand lay-up method with a light compression mould followed by post curing for 2 hours in hot air oven at

100°C. It was observed from the experimental test results that the wear resistance of the fabricated composites enhanced with the fillers addition. Based on the design of experiments and ANOVA test carried out it was concluded that the optimum parametric combination was 20 wt.% of iron-mud with 70 m/s erodent velocity with 90° impingement angle and 12 gm/min erodent discharge rate.

Ali et. al [71] studied the mechanical and wear performance on the effect of Na+-montmorillonite nanoclay concentration in the E-Glass chopped strand mat epoxy nanocomposites. Nanoclay was added in increments of 2 wt.% from 1-7 wt.% of the epoxy matrix. The experimental results had shown that the best mechanical strength was obtained in the specimen using 5 wt.% of amino-silanized Na+-montmorillonite loading with 18%, 38% and 53% improvement in tensile, flexural and compressive strengths when compared to neat chopped strand mat/epoxy composite. The result of the pin-on-disc wear test exhibited approximately 81% and 58% decrease in the wear rate and coefficient of friction due to the addition of 5 wt.% of nanoclay into the chopped strand mat/epoxy nanocomposite. The qualitative analysis from the microscopic examination of the fractured and worn surfaces were evaluated and the results were in line with the mechanical and wear performance results obtained. The successful grafting of the organosilane compound on the Mt surface was also confirmed through X-ray diffraction, thermal analysis and Fourier-transform infrared spectroscopy. The decreased wear rate was due to the nanoclay addition that contributed to improvement in fiber-matrix interfacial strength followed by the reduction of stress concentration on the fibers and enhancement of mechanical performance. However nanofiller loading above 1 wt.% led to non-continuous matrix which in turn gave rise to stress concentration regions thereby increasing the wear rate and coefficient of friction. Dipak et. al [72] analysed the mechanical and wear properties of glass/carbon fiber reinforced polymer composite fabricated using hand-layup method. Three different samples were prepared with glass fiber, carbon fiber and glass/carbon fiber with a stacking sequence of glass and carbon fiber. The mechanical test result indicated that the flexural strength and tensile strain was improved in hybridization sample. The wear properties of the hybrid composite were evaluated by DUCOM TR-50 three body abrasion tester with different operating conditions such as applied load and sliding distance. The predicted value using response surface methodology for minimum specific wear rate of 16.8511 x 10^{-3} mm^3/Nm with an applied load of 33 N and sliding distance of 1221 m for hybrid composite was in line

with the experimental values obtained. Thus based on hybridization and optimization of operating conditions, improvement of mechanical and wear performance was attained.

Hiral et. al [73] studied the effect of temperature on the wear behaviour of glass fiber reinforced epoxy composite which was fabricated using pultrusion manufacturing technique. The study was carried out with different operating parameters such as corresponding load (1, 2, 3 and 4 kg), speed (500, 750, 1000 and 1250 rpm), sliding distance (1000, 1500, 2000 and 2500 m) and temperature (30°, 60°, 90° and 120°C). The wear behaviour of epoxy glass fiber composite was examined on a pin on disc equipment as per ASTM G99 standard. The wear test results concluded that the load was the most influenced parameter followed by the temperature, while the speed and sliding distance had a minor effect on the wear behaviour. The worn surfaces were observed using SEM analysis for 60°C, 90°C and 120°C temperature samples. It has been observed from the microscopic analysis that increase in the temperature led to the wear debris and further microcracks in the specimen that led to the high wear of the composites. It was noticed that at lower load the material had lesser wear rate as the amount of frictional heat generated was lesser between two matching surfaces. As the applied load increased, the wear rate also increased due to the fact that increase in interface temperature led to increased material loss. However, with higher loads the material had shown good wear resistance due to the formation of material protective layer on the disc which reduces direct asperity contact. Similarly, the wear initially increased with increase in sliding distance and after a certain distance it was reduced due to the formation of protective layer. Ozsoy et. al [74] studied the tribological behaviour of the glass fiber reinforced epoxy composites fabricated by using hand lay-up technique and optimization was done by Taguchi design of experiment method. The samples were prepared with glass fiber orientation of 0º, 90º and 0º/90º. The wear test was carried out using pin-on-disc device with a constant distance of 1000m and design of experiments under different sliding and loading conditions. It was observed from the experimental results that applied load had the highest influence (82.60%) on the wear rate of E-Glass fiber reinforced epoxy composites. According to the analysis of variance for coefficient of friction, sliding speed was the most significant factor (50.45%).

Pujan et. al [75] studied the tribological behaviour of woven glass fiber reinforced epoxy composite prepared using hand lay-up technique followed by compression

moulding process with 60 wt.% of woven glass fiber reinforcement. The wear test was carried out using pin-on-disc type wear and friction monitor in dry condition at applied normal loads of 5, 10, 20, 30, 40 and 50 N with sliding velocities of 0.5, 1, 2 and 3 m/s. The orientation of the glass fiber was kept perpendicular to the sliding direction. It was observed that the coefficient of friction decreased with the increase of the normal load and increased with increase of the sliding velocities. On the other hand, the wear loss increased with increase of the normal loads and sliding velocities for all the conditions. The coefficient of friction decreased with increase of normal load for all sliding velocities which could be due to the formation of thin lubricating film at the counter surface occurred because of the plastic deformation of the epoxy matrix. However, the coefficient of friction increased with increase of sliding velocities for all normal load which could be due to more adhesion of sliding disc with the composite. Ragunath et. al [76] analysed the tribological behaviour of nanoclay particles reinforced with sisal, jute, glass fiber in epoxy polymer system prepared using hot compression technique. In this investigation specific wear rate and coefficient of friction were studied using pin on disc apparatus under dry sliding conditions. The experiment was carried out using Box-Behnken design based on design of experimental techniques with influence on wear properties such as applied load, filler content, sliding distance and the responses were analysed using response surface methodology. The test results indicated that filler content played a significant effect on both wear rate and coefficient of friction than the other factors. The wear rate of composite increased with increasing applied load, sliding distance and velocity which could be due to the thin film formed around worn surface of the specimen during the test because the fibers are pulling out from the reinforcement and at higher speed.

Thirumalai et. al [77] investigated the mechanical properties of epoxy-based hybrid composite reinforced with basalt and jute fiber using hand lay-up method. Each specimen consists of eight layers of fibers oriented accordingly to achieve high strength. The tensile test, flexural test, compressive strength and wear test were conducted to investigate the wear behaviour and the mechanical properties of the composite material. Tensile test, flexural test and compressive tests were performed using the universal testing machine and the wear test was carried out using the pin-on-disc wear testing machine. It was observed from the experimental analysis, that the key factor influencing the wear rate was applied load followed by type of the specimen and density of the

material. It was also shown that the tensile modulus increased with the increased layers of basalt fiber and the compressive modulus and compressive strength increased rapidly with the increase of basalt fiber layers. It was concluded that specific wear rate increased gradually with applied load and decreased rapidly with the density of the composite material. Mahesha et. al [78] analysed the wear and mechanical properties of basalt fiber-based epoxy composite which was further reinforced with nano titanium dioxide and nanoclay prepared using Vacuum-Assisted Resin Infusion technique (VARI). The wear performance was measured by varying the loads from 10 to 30 N and sliding distances from 2000 to 8000 m. Slight increase in coefficient of friction for nano Clay-BE composite, reduction of coefficient of friction was noticed for the nano TiO_2 and TiO_2/Clay filled composites. The rate of wear decreased with addition of fillers and increased with increase of sliding distance. Failure mechanisms of the worn surfaces of the filled and unfilled composites were examined with SEM and it was noticed that under greater sliding distance and higher load, most of the matrix material was taken out and loosening of basalt fibers resulted in the exposure of the fibrous region to sliding contact. It was observed from the mechanical test results that the tensile strength and dimensional stability increased with increasing fillers. The nanoparticles play a vital role in the interfacial bonding strength of the composite through the ability to transfer stress and elastic deformation of the matrix material at all applied loads.

Abdel et. al [79] studied the effect of fiber orientation on the abrasive wear behaviour of glass-fiber reinforced polymer composite prepared using hand lay-up technique. The composite was further reinforced with silicon carbide (SiC) of 0 wt.%, 5 wt.% and 10 wt. % of the epoxy matrix. The glass fiber was reinforced with angle-ply of different orientations 0º, 45º and 90º. The influence of operative parameters such as filler wt. %, normal load, abrasive size and abrading distance on the wear rate were discussed. It was noticed from the test results that the hardness of the specimen increased with increase in filler percentage. The experimental results had shown that the wear behaviour was superior with $\pm$ 45º fiber orientation when compared with 0º and 90º. From the experimental results, the recommended wear parameters were 10 wt.% filler, 30 N normal load and 1,260 m sliding distance. The specific wear rate reduced with increased applied load since the apparent contact area was significantly increased at higher loads due to the increase in contact area caused by the deposits of small particles of wear debris between the counterface of the abrasive asperities that chipped off from

the softer materials. During the sliding action the hard asperities on the counterface disentangled the contacting materials on the surface as wear debris. This accumulation of wear debris covered the cutting edges which was speeded up by the applied load thereby decreased the wear rate. Ismail et. al [80] studied the effect of fiber orientation on the tribological behaviour of carbon fiber-reinforced composite material. The wear test was carried out using pin-on-ring tribometer. The tests were conducted using three different parameters such as load (92 N and 150 N), sliding velocity (1 m/s and 2 m/s) and the direction of reinforcement (parallel, antiparallel and normal direction). The frictional force was measured for every 500 m of sliding distance and the mass of the sample were measured before and after each experiment beforehand calculating the specific wear rate. It was concluded from the experimental test results that the parallel oriented fiber in the sliding direction had better tribological behaviour than normal and antiparallel fiber orientation. The sample surfaces were also examined using SEM which was compared with the wear test results attained based on the abrasive wear mechanism. The friction and wear behaviour of polymer composites against the metal countersurfaces were affected by the existence of the transfer film. The formation of transfer film reduced the plowing effect of metal residues over the polymer surface, thereby reducing the friction and adhesion by providing a cushioning effect.

Megahed et. al [81] studied the abrasive wear performance of the glass fiber reinforced epoxy composite which was further reinforced with SiC/Carbon black hybrid nanofillers prepared using the hand lay-up technique. The nanoparticles were added in two different weight proportions i.e. 0.5 and 1 wt.% of the composite system. It was observed from the mechanical test results that at all applied loads, the incorporation of silica and carbon black nanoparticles either single or combined significantly improved the wear resistance of the neat glass fiber reinforced epoxy composite. From the Analysis of Variance (ANOVA) results it was concluded that the most influencing factor for the wear performance was the time followed by the nanoparticle concentration. The SEM images of the neat as well as 0.5 wt.% of the nanoparticles had shown fiber-matrix debonding and matrix cracking which arises due to the weak interfacial bonding between the matrix and the glass fiber. On the other hand, with 1 wt.% of the nanoparticles addition had shown improvement in the fiber matrix interfacial adhesion through better fiber matrix bonding, as represented in the Figure 2.1.
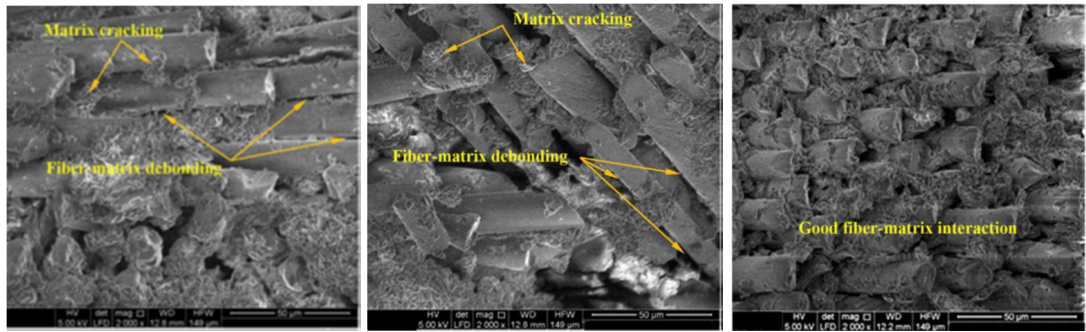
Figure 2.1: SEM Images of neat, 0.5 and 1 wt.% nanofillers [81]

In summary, there is evidence that the tribological properties of FRPs can be enhanced through the incorporation of reinforcing nanofillers such as SiC, SiO_2, TiO_2, Al_2O_3, graphene, nanoclay and carbon nanotubes (CNTs) which in turn improves the interfacial bonding strength between matrix and fiber. Additionally, few systematic works have been carried out regarding the effect of nanoclay on the tribological properties of FRPs. Wear had been found to be influenced by the properties of the material, operating conditions and stacking sequence of laminating layers for hybrid composites. Thus, optimization of operating conditions such as sliding distance and applied load can result in the improvement of wear properties. The major load is supported by the fillers resulting in increased wear resistance and nanofillers improved the adhesion of transfer film to the counter surface thereby reducing the wear process. Addition of nanoparticles also reduced the coefficient of friction and have polishing effect on the hard steel, thus reducing the abrasive effect of the nanocomposite [68].

Table 2.1: Summary of Critical Literature Review

Author	Year	Process	Research Gap
Vinayagamoorthy	2020	The epoxy-glass fiber-nanoclay based composites were analysed for friction and wear performance with variation in sliding velocity, sliding distance, applied pressure and temperature.	Debonding between fiber and the matrix.
Mehmet et al.	2020	The epoxy-glass fiber-nanoclay based composites were analysed for mechanical and erosion rate with the variation in impingement angles and velocities.	Agglomeration, weak bonding strength between epoxy, glass fibers and nanoclay.
Shanti et al.	2019	The epoxy-glass fiber-nanoclay based composites were analysed for the microhardness and erosion rate with variation in nanoclay concentration, volume and orientation of the glass fiber.	Interfacial bonding between fiber and the matrix.
Smaranika et. al	2019	The epoxy-glass fiber-nanoclay based composites were analysed for impact strength, flexural strength, hardness and specific wear rate.	Agglomeration of nanoparticles.
Jeyakumar et. al	2020	The epoxy-glass fiber composites further reinforced with nanoclay was observed for tensile, flexural, impact, hardness and specific wear rate.	De-bonding of fiber-matrix interface.
Sathish et. al	2019	Optimization of wear properties of the glass fiber/carbon reinforced epoxy composites.	Delamination of fillers and voids between fibers and the matrix.
Isiaka et. al	2020	Wear resistance of the pawpaw-glass fiber hybrid reinforced epoxy composites prepared using open mold casting.	Fiber/matrix interfacial adhesion.
Pranjal et. al	2020	Wear behaviour of the glass fiber/jute reinforced hybrid epoxy composites which was further reinforced with saw dust, fish scale powder and SiC fillers.	Bonding between matrix and the reinforcement.
Diptikanta et. al	2019	Mechanical and abrasion behavior of glass fiber reinforced epoxy composite.	Matrix cracking along with interfacial debonding.
Biswajyoti et. al	2018	Wear behavior of Iron-mud/Glass fiber reinforced epoxy composite prepared using hand lay-up method.	De-bonding of the filler matrix interface.

Ali et. al	2019	The mechanical and wear performance on the effect of Na+-montmorillonite nanoclay concentration in the E-Glass epoxy nanocomposites.	Weak Interfacial fiber matrix bonding.
Dipak et. al	2018	Analysed the mechanical and wear properties of glass/carbon fiber reinforced polymer composite.	Brittleness of carbon fiber reinforcement influencing wear rate.
Hiral et. al	2016	The effect of temperature on the wear behaviour of glass fiber reinforced epoxy composite which was fabricated using pultrusion manufacturing technique.	Interfacial bonding strength between glass fiber and epoxy matrix.
Ozsoy et. al	2015	The tribological behaviour of the glass fiber reinforced epoxy composites and optimization done by Taguchi design of experiment method.	Interfacial bonding strength between matrix & glass fiber in terms of wear rate.
Pujan et. al	2017	Studied the tribological behaviour of woven glass fiber reinforced epoxy composite prepared using hand lay-up technique with 60 wt.% of woven glass fiber reinforcement.	Tribological Performance in terms of wear rate and coefficient of friction.
Ragunath et. al	2017	Analysed the tribological behaviour of nanoclay particles reinforced with sisal, jute, glass fiber in epoxy system prepared using hot compression technique.	Interfacial adhesion between matrix/filler and nanoclay.
Thirumalai et. al	2019	Investigated the mechanical properties of epoxy-based hybrid composite reinforced with basalt and jute fiber prepared using hand lay-up method.	Interfacial bonding strength between basalt/jute fiber and epoxy matrix.
Mahesha et. al	2017	Wear and mechanical properties of basalt fiber-based epoxy composite which was further reinforced with nano titanium dioxide and nanoclay.	Interfacial bonding between epoxy matrix/filler and nanoclay.
Abdel et. al	2018	Effect of fiber orientation on the abrasive wear behaviour of glass-fiber reinforced polymer composite.	Interfacial adhesion between glass fiber and epoxy matrix.
Ismail et. al	2018	The effect of fiber orientation on the tribological behaviour of carbon fiber-reinforced composite.	Interfacial bonding strength in terms of specific wear rate.
Megahed et. al	2017	The wear performance of glass fiber reinforced epoxy composite which was further reinforced with SiC/Carbon black hybrid nanofillers.	Weak fiber matrix interface.

2.8 Overall Summary of Literature Review:

This chapter presented detailed literature review on various aspects influencing the interfacial bonding strength such as surface treatment of the fillers, dispersion mechanism of nanoparticles, interfacial bonding characteristics, effect of nanoclay concentration, curing temperature and curing time of the glass fiber reinforced polymer nanocomposites. The major findings from the analysis were insufficient bonding, fragmentation, agglomeration, fiber pull out, excess resin and delamination of glass fibers which could have caused degradation in the interfacial bonding strength of the nanocomposites. In this literature review, the effects of fiber/filler reinforcement on the tribological behaviour of polymer nanocomposites were also addressed to enhance the interfacial bonding strength. The addition of nanoparticles as a filler material between glass fiber and epoxy matrix were one of the solutions to enhance the bonding i.e. provide improvement in mechanical and tribological properties of the composite. However, the diffusion of nanoparticles in the matrix hamper the formation of the well performed composite mainly due to agglomeration of nanoparticles which was addressed through different dispersion mechanism. Quantitative characterization of interfacial adhesion strength was done in evaluating the mechanical behaviour and capabilities of composite materials. The interfacial bonding quality ultimately dictates the mechanical and wear performance of the glass fiber reinforced polymer composites.

CHAPTER 3

RESEARCH METHODOLOGY

3.1   Overall Research Methodology

The primary focus of this research work is to improve the wear performance through enhancing the interfacial bonding characteristics of the glass fiber reinforced polymer composite via addition of nanoclay. The overall methodology of this research work is described in Figure 3.1.

Firstly, the effect of surface treatment on wear properties was analysed in terms of hardness through a series of experiments conducted using untreated, silane treated and acid treated glass fibers. On the other hand, nanoclay was used as untreated and surface modified with 25 wt.% trimethyl stearyl ammonium condition [10,14]. The surface morphology of the specimen was analysed by using Scanning Electron Microscope (SEM). Secondly, the nanoclay concentration was varied from 0-6 wt.% of the epoxy matrix with increments of 1 wt.% based on the effective surface treated samples (based on the hardness test results) of glass fibers and nanoparticles [40-53]. The hardness testing was carried out again to characterise the wear performance for all nanoclay reinforced samples. Other mechanical tests namely the tensile, impact and flexural tests were also conducted. The surface morphology of the specimen, elemental characterisation and bonding mechanism were evaluated using SEM and Energy-Dispersive X-ray spectroscopy (EDX). Thirdly, nanoclay dispersion effect was analysed by using two different dispersion mechanism i.e. mechanical stirring by varying the speed in rpm and ultrasonication process by varying the amplitude in percentage. The wear performance was evaluated through hardness test and supported by other mechanical testing followed by characterization through SEM analysis. Furthermore, the effect of thermal behaviour on the hardness properties were analysed by varying the curing temperature and curing time of the specimen. Similarly, other mechanical properties were evaluated, and characterisation were carried out using SEM analysis.

Finally, validation of the hardness performance was conducted by pin-on-disc wear test based on the hardness of best, least and control sample (0% nanoclay as reference) and analysed using X-Ray Diffraction (XRD) for bonding analysis followed by SEM, EDX and Fourier Transform Infrared (FTIR) Spectroscopy. After the validation test and analysis, all five objectives were satisfied, and conclusion for research work was made based on the results and analysis.

Figure 3.1: Overall Research Methodology
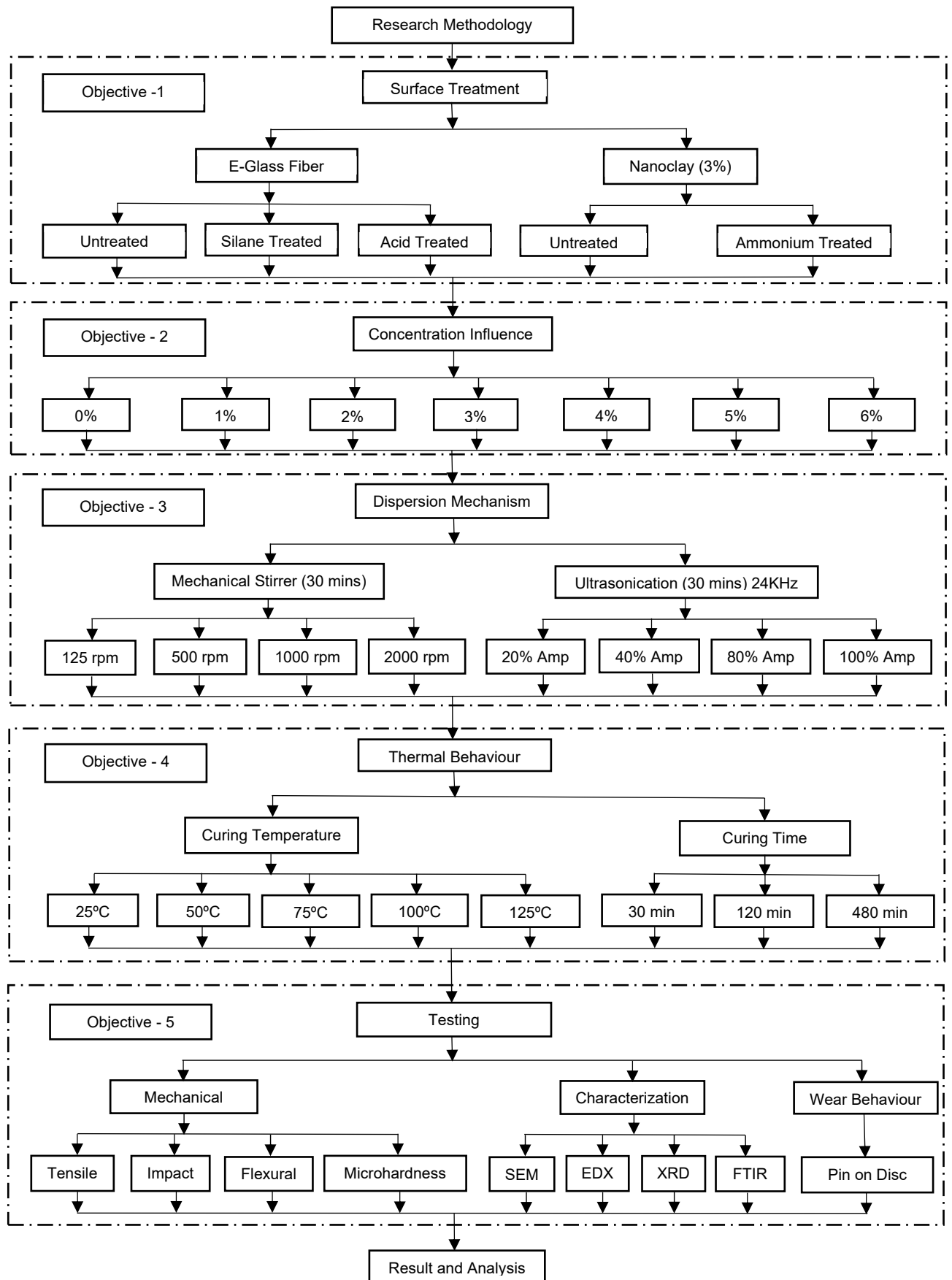
3.2   Experimental Details

3.2.1   Research Materials

In this research work epoxy resin, Araldite LY 556 with hardener, Aradur HY 951 were used as the matrix system both supplied by Huntsman Advanced Materials, India. Woven bidirectional E-Glass fibers with a density of 360 gsm purchased from Javanthee Enterprises was used as glass fiber reinforcement. Nanoclay, Montmorillonite Clay (MMT) with a trade name of Nanomer clay and Nanoclay, Montmorillonite clay (MMT) with a trade name of Nanomer 1.28 clay which has been surface modified with 25 wt.% trimethyl stearyl ammonium both purchased from Sigma Aldrich was used as nanofiller. Among different nanoparticles, nanoclay (NC) has gained special interest mainly because of its two particular characteristics: one is the ability to disperse into individual layers because of the weak Van der waals bonding between layers; the other is the ability to engineer its surface chemistry through ion exchange reactions.

3.2.2   Fabrication of the Composites

Glass fibers were cut to size of 270 x 270 mm to fit the standard size of the mold as specified in ASTM D638 standard for sample preparation. The laminates are prepared using compression molding machine. At first the mold was cleaned and wax was applied as the mold releasing agent. The epoxy resin was mixed with hardener at the ratio of 100:10 by weight which was stirred thoroughly to attain homogenous mixing. A thin layer of epoxy was applied on the lower mold. Then the glass fibers were stacked layer by layer and the resin was applied in between each layer till final layer was placed in the mold for attaining 40 wt.% weight of epoxy system. Then the upper mold half was closed and the excess resin if any was squeezed out from the mold. Both the upper and lower mold halves were maintained at a temperature of $100^{\circ}C$ which has been verified through the thermocouple connected and maintained at pressure of 1500 psi for a duration of 30 minutes. Finally, de-molding was done using an ejector pin to remove the composite prepared. The composites were allowed to cool down at room temperature for 24 hours.

For composites with nanoparticles addition, the first step was to heat up the epoxy to $70^{\circ}C$. The next step was to disperse the nanoparticles (natural or surface modified)

in solvent acetone. Epoxy resin was added to the acetone/nanoclay mixture which was further mixed uniformly using ultrasonication process with a frequency of 20,000 hertz for a period of 30 minutes to eliminate the agglomeration. Then it was placed in a heated mandrel at 80°C for 5 minutes to evaporate the acetone. Once acetone has been completely evaporated then it was cooled down to room temperature. Then the above process of adding hardener and preparation of nanocomposite was done in a similar procedure as explained in the above paragraph [41]. The detailed flow chart for the fabrication of the composites is shown in the Figure 3.2.
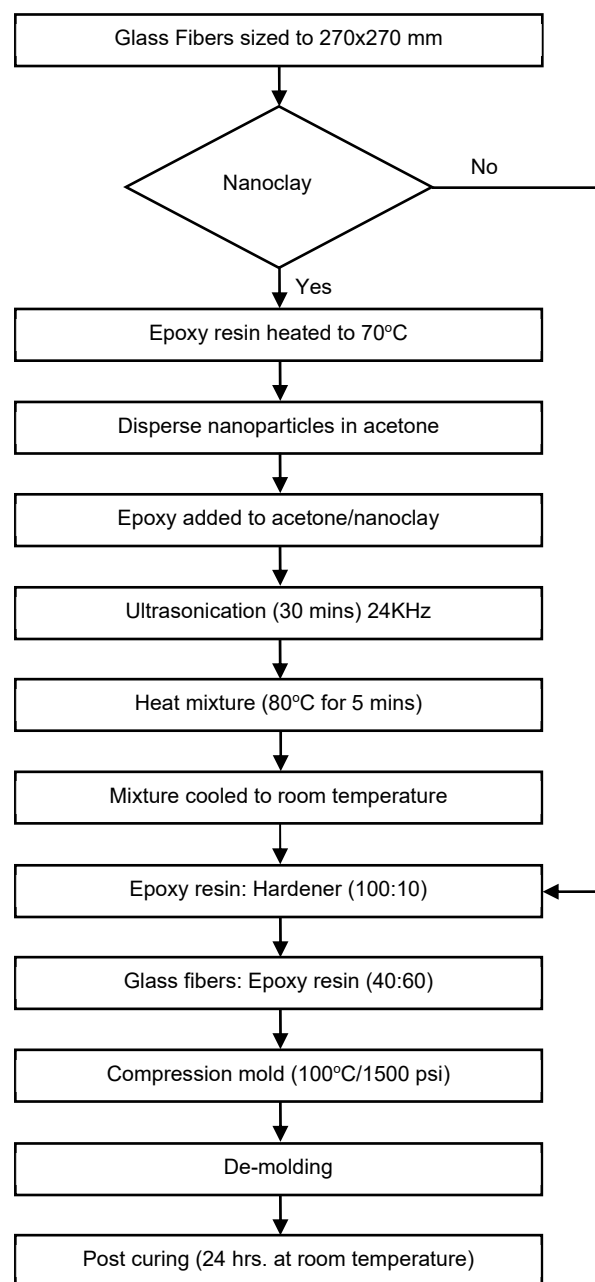
Figure 3.2: Fabrication of the Composites

3.2.3 Surface Treatment of the Glass Fiber and Nanoclay

The E-Glass bidirectional fibers were sized into 270 x 270 mm and two different surface treatments, silane treatment and acid treatment were done. For silane treatment, the glass fibers were dried at 200°C for 24 hours to remove moisture and impurities from the surface of the fibers. The surface treatment solution was prepared using a mixture of silane, ethanol and acetic acid mixed in a mass ratio of 5:4:1. The treatment solution was added to the glass fibers in a 100:1 mass ratio. Finally, the treated glass fibers were further dried at temperature of 140°C for 4 hours before putting into use.

For acid treatment, the glass fibers were treated by soaking in two solutions 1N sodium hydroxide and 1N sulfuric acid separately for 24 hours at room temperature. After that the fibers were thoroughly washed with distilled water to remove any sodium hydroxide and sulphuric acid and then dried at room temperature. Finally, the treated glass fibers were used with further drying at temperature of 140°C for 4 hours.

Ten different samples (S1-S10) were prepared with different possible combinations to compare the effect of surface treatment for glass fibers (untreated, silane treated and acid treated) and nanoclay (untreated and trimethyl stearyl ammonium modified) as per the sample designation mentioned in the Table 3.1 which was prepared by compression molding. For the samples (S5-S10) with nanoclay addition the weight of nanoclay concentration was fixed at 3 wt.% of the matrix system, where UGF stands for untreated glass fiber, AGF stands for acid treated glass fiber, SGF stands for silane treated glass fiber, UNC stands for untreated nanoclay and MNC stands for surface modified nanoclay.

Table 3.1: Sample Designation for Surface Treatment Effect

Samples	Description
S1	Epoxy
S2	Epoxy+UGF
S3	Epoxy+AGF
S4	Epoxy+SGF
S5	Epoxy+UGF+3% UNC
S6	Epoxy+UGF+3% MNC
S7	Epoxy+AGF+3% UNC
S8	Epoxy+AGF+3% MNC
S9	Epoxy+SGF+3% UNC
S10	Epoxy+SGF+3% MNC

3.2.4 Nanoclay Concentration Effect on Hardness

Seven different samples (N1-N7) were made with variation in nanoclay concentration to compare the effect of nanoclay influence on mechanical and wear properties. The experimental set-up and process conditions were explained clearly in the fabrication of the composite. In this process, the only variable was the weight of surface modified nanoclay percentage which is added to the matrix system. The nanoclay percentage was varied gradually from 0 to 6 wt.% in increments of 1 wt.% of the epoxy matrix system. The sample designations for nanoclay concentration effect are listed in the Table 3.2.

Table 3.2: Sample Designation for Nanoclay Concentration Effect

Samples	Description
N1	Epoxy+SGF+0% MNC
N2	Epoxy+SGF+1% MNC
N3	Epoxy+SGF+2% MNC
N4	Epoxy+SGF+3% MNC
N5	Epoxy+SGF+4% MNC
N6	Epoxy+SGF+5% MNC
N7	Epoxy+SGF+6% MNC

3.2.5 Dispersion Mechanism Effect on Hardness

Eight different samples (D1-D8) were prepared with variation in dispersion mechanism of nanoclay addition to analyse the effect of dispersion with respect to wear and morphological properties. Mechanical stirrer and ultrasonication were used for dispersing the nanoclay into the epoxy system. Figure 3.3 represents the ultrasonication process and Figure 3.4 represents the mechanical stirrer. The time period for both the dispersion process was kept constant at 30 mins. For all the samples the nanoclay concentration was fixed at 1 wt.% of nanoclay. The literature review also mentioned that the amount of nanoclay addition and effective dispersion of the nanoparticles plays a vital role in the final property of the composite [23, 24]. Based on critical literature review the speed for mechanical stirring was fixed at 125 rpm, 500 rpm, 1000 rpm and 2000 rpm and for ultrasonication process the amplitude was varied from 20%, 40%, 80% and 100% where all the parameters were increased in linear progression according to the literature review. The main aim was to establish the best dispersion process and speed or amplitude for effective dispersion of nanoparticles. In this experimental set-up the only variable was the process involved in dispersing the nanoclay into the epoxy matrix and the other experimental set-up and process conditions remains the same as explained earlier. The sample designations for dispersion mechanism effect are listed in Table 3.3.

Table 3.3: Sample Designation for Dispersion Mechanism Effect

Samples	Description	Dispersion Mechanism	Time (mins)	Speed/Amplitude
D1	Epoxy+SGF+1% MNC	Mechanical Stirrer	30	125 rpm
D2	Epoxy+SGF+1% MNC	Mechanical Stirrer	30	500 rpm
D3	Epoxy+SGF+1% MNC	Mechanical Stirrer	30	1000 rpm
D4	Epoxy+SGF+1% MNC	Mechanical Stirrer	30	2000 rpm
D5	Epoxy+SGF+1% MNC	Ultrasonication	30	20%
D6	Epoxy+SGF+1% MNC	Ultrasonication	30	40%
D7	Epoxy+SGF+1% MNC	Ultrasonication	30	80%
D8	Epoxy+SGF+1% MNC	Ultrasonication	30	100%

Figure 3.3: Ultrasonication Process   **Figure 3.4: Mechanical Stirrer**

3.2.6   Curing Temperature and Curing Time Effect on Hardness

Five different samples (T1-T5) were prepared to analyse the effect of curing temperature and three different samples (C1-C3) were prepared to analyse the curing time effect of the specimen on the wear and morphological properties of glass fiber reinforced epoxy nanocomposites using nanoclay, Nanomer 1.28E by compression molding. The effect of curing temperature and time has been analysed by increasing the temperature from 25ºC to 125ºC in increments of 25ºC, then by increasing the curing time from 30 mins, 120 mins and 480 mins in eight different combinations of the experimental work. The sample designations for curing temperature and curing time effect are listed in the Table 3.4.

Table 3.4: Sample Designation for Curing Temperature and Curing Time Effect

Samples	Description	Temperature (ºC)	Time (mins)
T1	Epoxy+SGF+1% MNC	25	30
T2	Epoxy+SGF+1% MNC	50	30
T3	Epoxy+SGF+1% MNC	75	30
T4	Epoxy+SGF+1% MNC	100	30
T5	Epoxy+SGF+1% MNC	125	30
C1	Epoxy+SGF+1% MNC	100	30
C2	Epoxy+SGF+1% MNC	100	120
C3	Epoxy+SGF+1% MNC	100	480

3.3 Mechanical Testing

Figure 3.5 represents the samples prepared for each mechanical testing as per the ASTM standards. The reference standards used for testing are ASTM D638 for tensile testing, ASTM D790 for flexural testing, ASTM D256 for impact testing, ASTM E384 for microhardness and ASTM G99 for wear testing with pin on disc apparatus. As mentioned in the ASTM standards, five samples were prepared for each composite type for all mechanical tests including tensile, flexural and impact test and one 10 mm x 10 mm sample for micro hardness test. The test specimens of required sizes were cut from the composite samples using water jet machining.
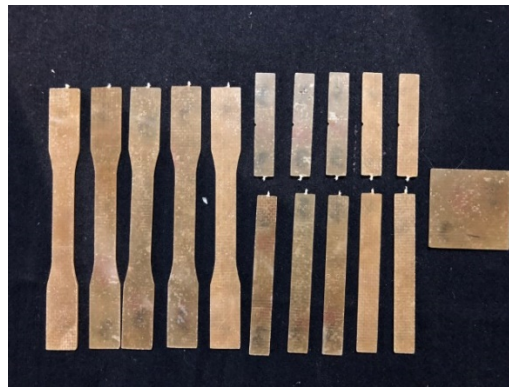
Figure 3.5: Mechanical Testing Samples

3.3.1   Microhardness

In Vickers microhardness testing, a highly polished, pointed, square-based pyramidal diamond is used as the indenter. Microhardness is preferred to be used in fiber reinforced polymer (FRP) since the material may not respond accurately to measurements conducted with standard hardness instruments. The indentations are so tiny that microscopic measurement is required to obtain precise readings. The micro hardness samples were cut to size of 10 mm x 10 mm. All tests were carried out at room temperature and five indentations were made at different points of each sample using Micro Vickers Hardness Tester, Model 402MVD at a load of 100 kgf with a dwell period of 10 seconds. The average of the five readings were taken as a representative sample for the hardness.

3.3.2   Tensile Testing

Tensile testing was carried out as per the ASTM Standard D638 using the Universal Testing machine model F100 with a cross head speed of 10 mm/min. The specimens were cut into strips of 165 mm length, 19 mm width and 3.2 mm thickness. Five identical test samples were prepared for each composite type and the testing was carried out at room temperature. Average of the five specimen readings have been taken for comparison of test results.

3.3.3   Flexural Testing

Flexural testing was carried out as per the ASTM Standard D790 using the Auto Instruments GT 500, Universal testing machine with a fixture for conducting the three-point flex test. The specimens were cut into strips of 100 mm length, 12.7 mm width and 3.2 mm thickness with a notch of 45º and 2.5 mm depth in the centre as specified in the ASTM Standard. Five identical samples were prepared for each composite type and the testing was carried out at room temperature. The flexural strength (σ_{bh}), which is the maximum stress at the break is calculated by using the formula given in equation 1:

$$\sigma_{bh} = 3FL/2bh^2 \ldots\ldots\ldots\ldots\ldots(1)$$

where F is the breaking force in Newton (N),

L is the span/distance between the load bearing supports in mm,

b is the width of the specimen in mm and

h is the thickness of the specimen in mm.

3.3.4   Impact Testing

Impact testing was carried out as per the ASTM Standard D790 using the Krystal equipment impact tester. The specimens were cut into strips of 65.5 mm length, 12.7 mm width and 3.2 mm thickness. Five samples were prepared for each composite type and the test was carried out at room temperature. Average of the five readings have been taken for comparison of test results.

3.3.5   Pin-on-disc wear test

The wear behaviour is mostly studied by experimental techniques using, for example, a Pin-on-Disc Configuration (PoDC). In a PoDC the weight reduction of the pin is measured to represent the volume of the material loss and to calculate the specific wear rate, which is a widely used parameter of the wear behaviour for different sliding pairs under given conditions. Figure 3.6 represents the experimental set-up of the wear analysis equipment.
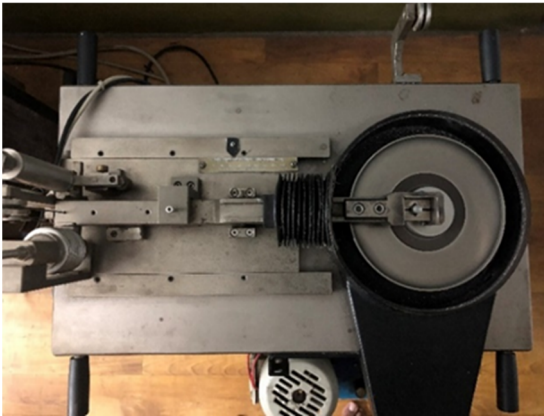
Figure 3.6: Wear Analysis Equipment   **Figure 3.7: Wear Test Samples**

The dry sliding wear test was performed with three parameters: applied load, sliding speed and sliding distance. A pin on disc wear testing equipment was used to investigate the dry sliding wear characteristics of composites according to ASTM G99 standard. The test specimens for conducting the wear performance were also prepared as per ASTM G99 standard. The length of the specimen was 32mm and diameter of 8mm as shown in the Figure 3.7. The test surfaces of the pins and disc were first cleaned with acetone and then with compressed air before and after the wear test. The initial weight of the specimen was measured using an electronic balance machine with an accuracy of 0.0001 g. During the test the pin was pressed against the counterpart rotating against EN31 hardened ground steel disc with hardness of 60 HRC by applying three different loads of 30N, 60N and 90N with a constant sliding speed of 1m/s. The experimental work was conducted at room temperature with a relative humidity of 35%. After running through a fixed sliding distance of 500 m, the specimens were removed, cleaned with acetone, dried and weighed to determine the weight loss of the specimen due to wear. The difference in the weight measured before and after test gave the sliding

wear of the composite specimen. The density of the specimen was measured and then the specific wear rate (W) of the composite in mm^3/Nm was calculated according to the equation 2.

Specific wear rate (W) and coefficient of friction (μ) are determined by using the below formula:

Specific wear rate (W) = $(\Delta m)/(\rho \times d \times N)$……………(2)

where Δm is the weight loss (g),

ρ is the density (g/mm^3),

d is the sliding distance (m) and

N is the applied load in Newton (N).

Coefficient of friction (μ) = frictional force/applied force.

3.4   Characterization

3.4.1   Scanned Electron Microscope (SEM) / Energy-Dispersive X-Ray Spectroscopy (EDX) In this research work, the morphological characterization was done using Hitachi S-3400N scanning electron microscope which has a magnification range of 5x to 300,000x. The samples were cut into size of 10 mm x 10 mm which is then sputtered with gold to a thickness of 150 A$^\circ$ to make the composite electrically conductive using ion sputter coater with gold target. The coated samples were mounted on a specimen stub using electrically conductive double-sided adhesive tape. The images were captured in five different magnification ranges of 100x, 1000x, 2000x, 5000x and 10,000x. The images were analysed for effect of surface modification on glass fibers and nanoclay after surface treatment, bonding characteristics between glass fiber, epoxy and nanoclay, type of failure that occurred during the tensile testing and surface texture characterization on wear specimen.

An Energy-Dispersive X-ray spectroscopy (EDX) detector was used to separate the characteristic x-rays of different elements into an energy spectrum and EDX system software was used to analyse the energy spectrum in order to determine the presence of

specific elements as well as the concentration of each element. The data obtained from the EDX analysis was used to analyse the effect on hardness due to the presence of elements such as sodium, potassium, chlorine etc.

3.4.2 Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information. In this research work FTIR analysis was carried out using Agilent, Cary 630 FTIR spectrometer with a spectral range of 500 to 5000 cm^{-1} for seven samples (N1 to N7). When the samples were analysed a spectrum of characteristic bands was produced that can be used as a fingerprint to identify and characterize the sample. The spectra were recorded in solid state and the range of frequency was recorded as wave numbers over the range of 4000 to 500 cm^{-1}.

3.4.3 X-Ray Diffraction Analysis (XRD)

The X-Ray Diffraction analysis is a non-destructive rapid analytical technique primarily used for phase identification of a crystalline material in the prepared composite. In this research work, XRD analysis was performed using Rigaku Smartlab high-resolution X-Ray diffractometer equipped with Smartlab Studio II Software at 2θ angle ranging from 5-100°. The scanning speed of the sample is 10.0619 deg/min with step width of 0.100 deg with continuous scanning mode. Based on the samples prepared as per the research methodology and the hardness readings attained, three samples (N1(0% Nanoclay), N2(1% Nanoclay) and N7(6% Nanoclay)) were analysed using XRD spectrometer to study the crystalline structure behavior of the samples and to identify the compound which influences the hardness behavior of the composite.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General Introduction

This chapter analyses and discusses the test results of the experiments conducted based on the research methodology in previous chapter. The effective surface treatment for glass fibers and nanoclay was found by varying the surface treatment for glass fibers through untreated, silane treatment and acid treatment whereas the nanoclay was used as untreated and ammonium surface modified condition. Then the effective nanoclay addition was determined by varying the concentration between 0 to 6 wt. % of the epoxy matrix. Furthermore, the effective dispersion mechanism was observed by varying the speed of mechanical stirrer between 125 rpm to 2000rpm and ultrasonication process by varying the amplitude from 20% to 100%. Finally, the thermal behaviour was analysed through the variation of curing temperature from 25ºC to 125ºC and curing time from 30 minutes to 480 minutes. The mechanical properties were evaluated through tensile, flexural, impact and hardness tests. The morphological behaviour was analysed through the SEM and EDX analysis. The characterization was done using FTIR spectroscopy and XRD analysis. Finally, the validation of the hardness results was performed using pin-on-disc wear test. The mechanical strength for the glass fiber reinforced polymer being currently used in the industry and literature review are listed in Table 4.1.

Table 4.1: Mechanical Test Results for Glass Fiber Reinforced Polymer

S. No	Tensile Strength	Microhardness	Reference
1	70-230 MPa	18-21 HV	Manufacturer 1
2	230 MPa	21 HV	Manufacturer 2
3	270 MPa	16 HV	Kumar et. al [25]
4	319.86 MPa	47 HV	Research Finding

4.2 Surface Treatment Effect

In this section results were analysed to understand the effect of surface treatment for glass fibers and nanoclay on the interfacial bonding in terms of surface hardness and also to identify the effective surface treatment. The glass fibers were used as untreated, acid treated and silane treated while the nanoclay was used in untreated and surface modified condition with a fixed 3 wt. % concentration of the epoxy matrix where the experimental set-up and process conditions were followed according to section 3.2.3 in Chapter-3. The mechanical test results attained from the experimental work are presented in Table 4.2.

4.2.1 Surface Morphology Analysis

Figure 4.1a and 4.1b represent the SEM images of sample S1 prepared with epoxy resin and hardener with different magnifications. It was observed from the micrographs that there are several surface imperfections and damages on the specimen. In addition there was no filler reinforcement to the epoxy matrix. Due to these defects observed and lack of reinforcement there might be significant impact on the mechanical properties of the specimen. But the bonding between the matrix looks well bonded from the surface of the specimen. This sample was considered as a reference to compare the mechanical properties of the polymer composites prepared using epoxy, glass fiber and with the polymer nanocomposites prepared using epoxy, glass fiber and nanoclay.
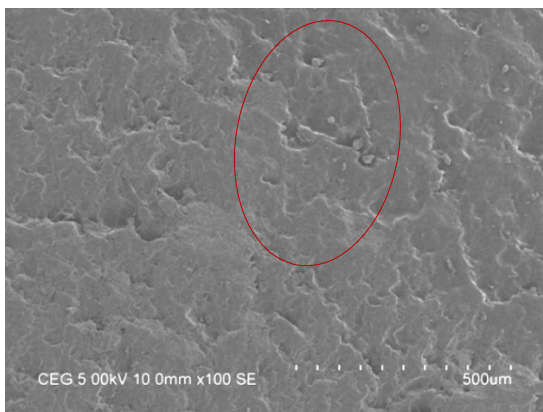

Figure 4.1a – Sample S1 (100x)   **Figure 4.1b– Sample S1 (1000x)**
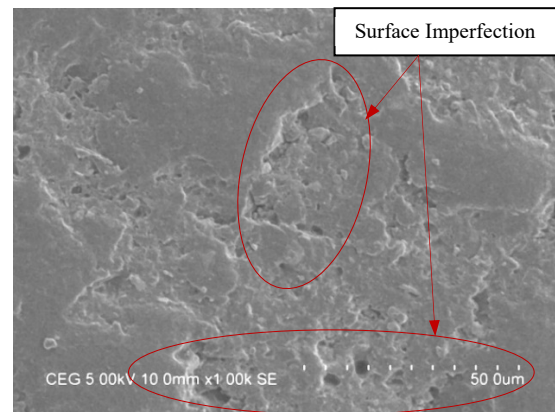
Figure 4.1c and 4.1d represent the SEM images of sample S2 prepared with epoxy resin and untreated glass fibers. It can be observed from the microscopic images that noticeable surface damage was found on the glass fibers. It was also evident from the images that there was lack of filling of epoxy matrix between the glass fibers. It can also be observed from the micrographs that unbonded matrix material found in the nanocomposite which could be due to the increase in the viscosity of the epoxy matrix. Similar viscosity behaviour of the matrix was also reported by Pujan et. al [75]. There were incomplete fusion of resin noticed in the composite which could be due to lack of filling of epoxy resin between the glass fibers.
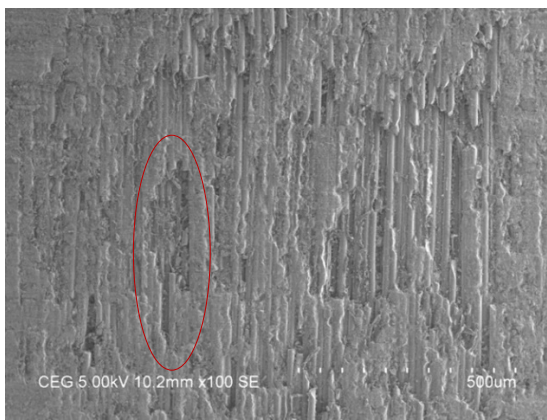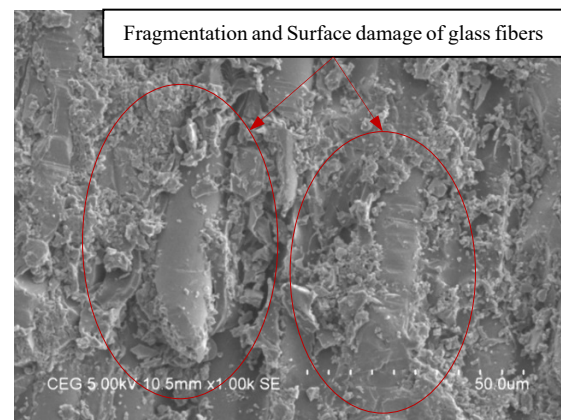

Figure 4.1c – Sample S2 (100x)   **Figure 4.1d– Sample S2 (1000x)**
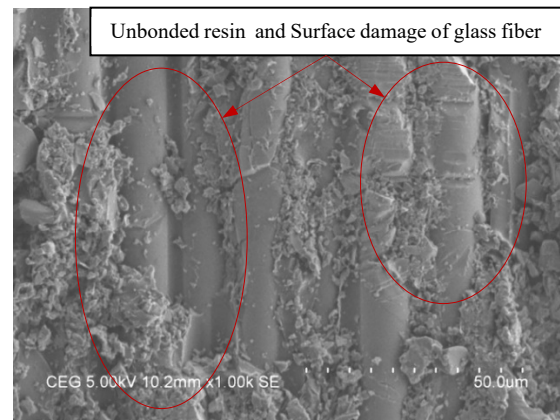
Figure 4.1e and 4.1f represent the SEM images of sample S3 prepared with epoxy resin and acid treated glass fibers. It can be observed from the micrographs that there were severe surface damages to the glass fibers which may be due to the etching action occurred during the acid treatment. It can also be noticed fragmentation of glass fibers which could be due to the brittle behaviour after the acid treatment which was similarly reported by Kutlay et al. [12]. It was also evident that incomplete penetration of matrix in the composite which could also create lack of adhesion between glass fiber and epoxy matrix. Due to these defects there might be significant effect on the interfacial bonding characteristics which in turn will lead to drastic reduction in mechanical properties of the composite.
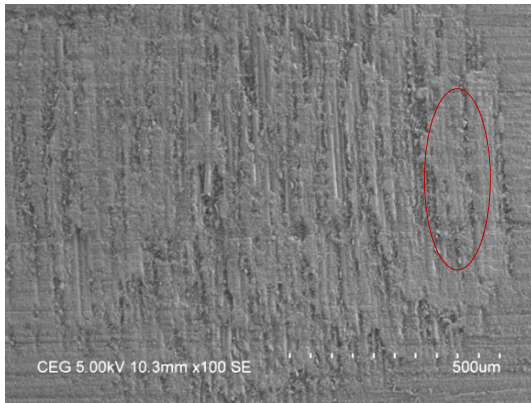
Figure 4.1e – Sample S3 (100x)
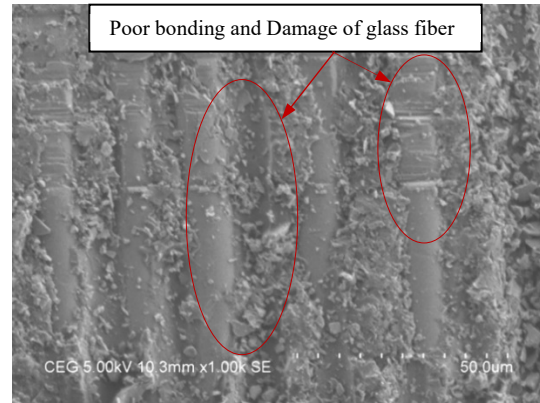
Figure 4.1f– Sample S3 (1000x)

Figure 4.1g and 4.1h represent the SEM images of sample S4 prepared with epoxy resin and silane treated glass fibers. The SEM images indicates that there was a smooth adhesion between silane treated glass fibers and epoxy resin. These will lead to effective load transfer between the glass fiber and epoxy resin which in turn will improve the interfacial bonding characteristics thereby improving the mechanical properties of the composites. There were few signs of glass fiber damage noticed and similarly there were insignificant cluster of epoxy matrix found in the composite. It can be observed from the microscopic images that some minor surface damages were found on the glass fibers.
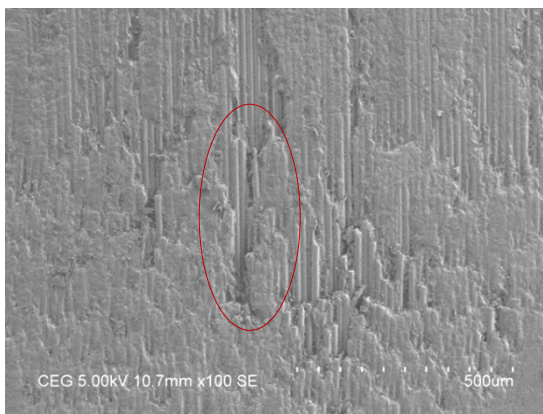

Figure 4.1g – Sample S4 (100x)
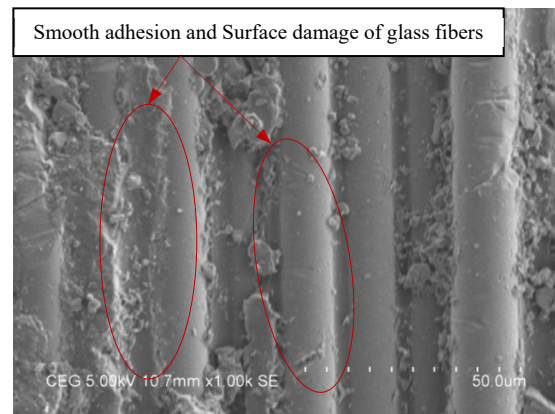
Figure 4.1h – Sample S4 (1000x)

Figure 4.1i and 4.1j represent the SEM images of the sample S5 prepared with epoxy resin, untreated glass fiber and unmodified nanoclay. From the micrographs it was noticed that there were severe fragmentation of glass fibers, which could have occurred due to brittle nature of the untreated glass fiber along with heat and pressure applied during the composite fabrication. It was evident from the images that there exists

poor matrix fiber interfacial bonding as the delamination of glass fibers with the matrix were smooth and prominent. There were incomplete fusion found in the nanocomposite which could be due to lack of filling of epoxy resin within the glass fibers. Thus fiber-matrix debonding and matrix cracking were dominant mechanism for untreated glass fiber composites.
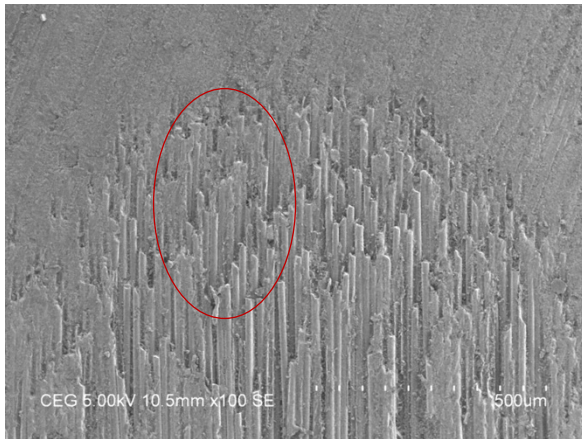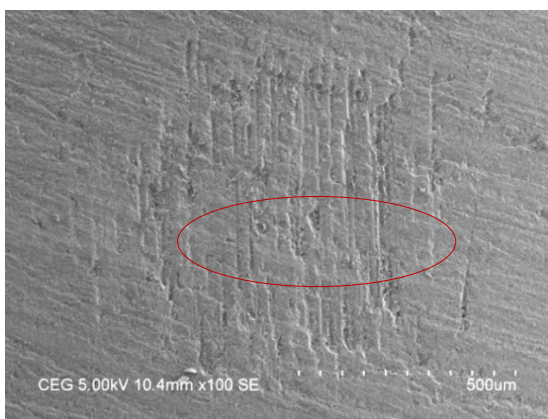

Figure 4.1i – Sample S5 (100x)
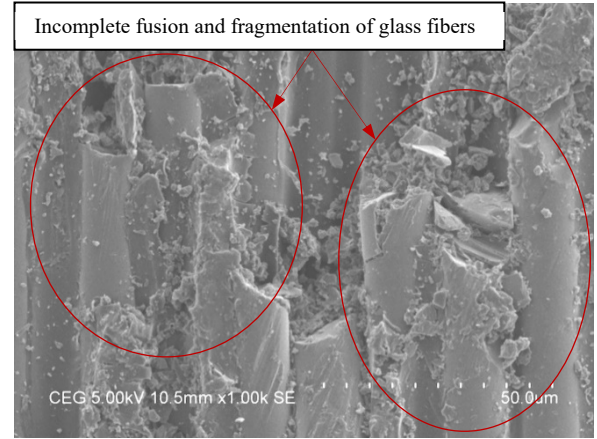
Figure 4.1j – Sample S5 (1000x)

Figure 4.1k and 4.1l represent the SEM images of the sample S6 prepared with epoxy resin, untreated glass fibers and surface modified nanoclay. It can be noticed from the SEM images that enormous glass fibers were broken and damaged on the surface. It was also noticed from the broken fibers that the failure mode was brittle in nature. There were lot of microvoids noticed in the nanocomposite which could be due to lack of filling of epoxy resin within the glass fibers. Based on the defects observed there could be significant impact on the mechanical performance of the nanocomposite.
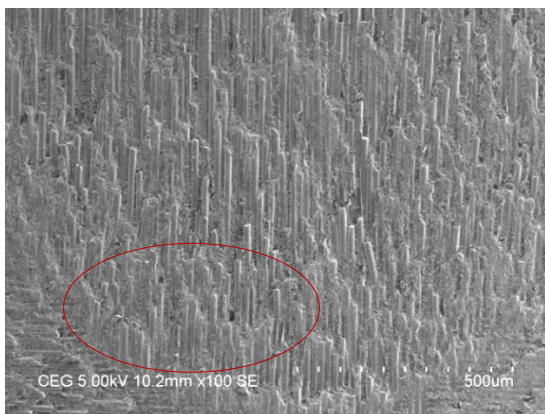

Figure 4.1k – Sample S6 (100x)
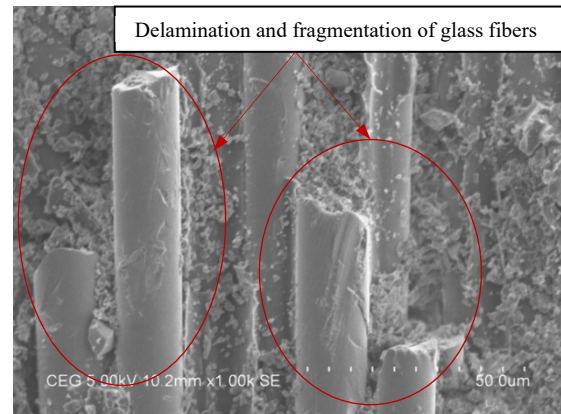
Figure 4.1l – Sample S6 (1000x)

Figure 4.1m and 4.1n represent the SEM images of sample S7 prepared with epoxy resin, acid treated glass fibers and untreated nanoclay. From the micrographs it can be noticed that there were significant surface damages to the glass fibers which may be due to the etching action during the acid treatment. It can also be observed that there were fragmentation of glass fibers which indicates that the glass fibers became more brittle after the acid treatment and it can be clearly seen that there was noticeable delamination between glass fibers and epoxy matrix. Due to these defects there might be significant impact on the interfacial bonding strength which in turn will lead to drastic reduction in mechanical properties.
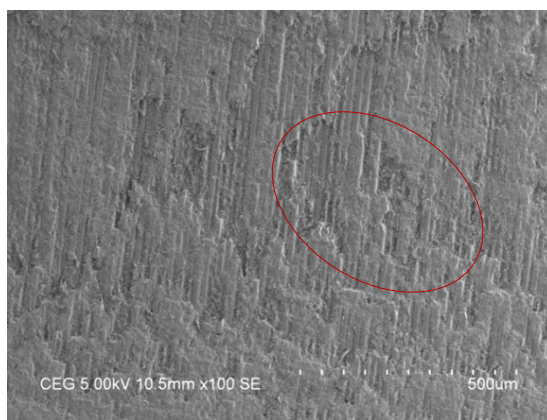
Figure 4.1m – Sample S7 (100x)   **Figure 4.1n – Sample S7 (1000x)**

Figure 4.1o and 4.1p represent the SEM images of sample S8 prepared with epoxy resin, acid treated glass fibers and surface modified nanoclay. It can be observed from the micrographs that there were severe surface damages to the glass fibers which may be due to the etching action occurred during the acid treatment. It can also be observed that there were fragmentation of glass fibers noticed which could be due to the brittle behaviour after the acid treatment had been carried out. It was also evident that delamination was prominently noticed between glass fibers and epoxy matrix. Lack of adhesion between glass fiber and epoxy matrix were observed. Due to these defects there might be significant effect on the interfacial bonding characteristics between the glass fibers and epoxy matrix which in turn could lead to drastic reduction in mechanical performance of the nanocomposite.
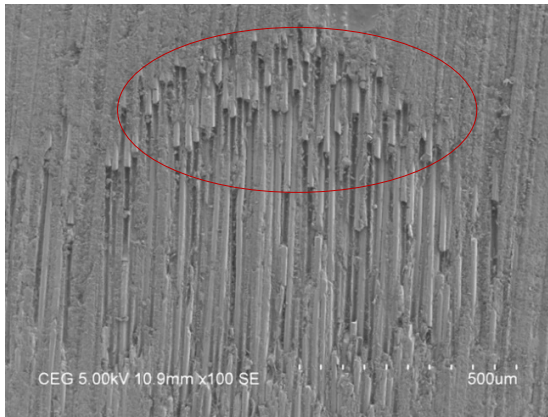
Figure 4.1o – Sample S8 (100x)
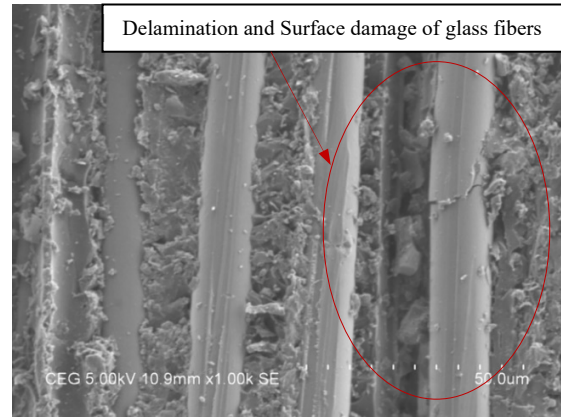
Figure 4.1p– Sample S8 (1000x)

Figure 4.1q and 4.1r represent the SEM images of the sample S9 prepared with epoxy resin, silane treated glass fibers and untreated nanoclay. From the micrograph it can be noticed that the glass fibers were smoothly blended with epoxy matrix and no delamination was observed. In additon, there were no signs of damages to the glass fibers which clearly indicates that the silane treatment of glass fibers had done surface modification which in turn had improved the brittle nature of glass fibers. In addtion, the silane treatment has enhanced the interfacial bonding of the glass fiber, epoxy resin and nanoclay. It was also evident there were no significant agglomeration and microvoids present in the nanocomposite. There were flakes of resin with nanoclay noticed on the surface of the nanocomposite which could be due to the excess resin occured in the fabrication process because of the increase in viscosity of the matrix.

Figure 4.1q – Sample S9 (100x)
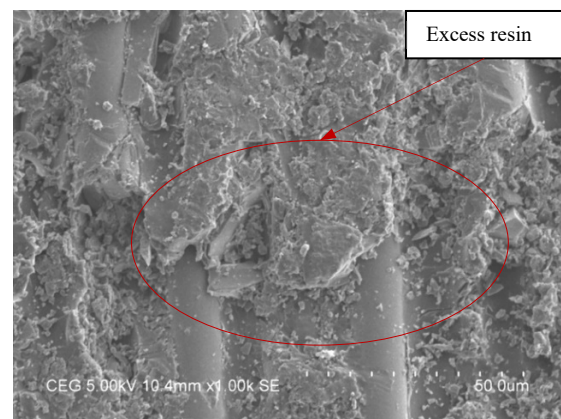
Figure 4.1r – Sample S9 (1000x)

Figure 4.1s and 4.1t represent the SEM images of sample S10 prepared with epoxy resin, silane treated glass fibers and surface modified nanoclay. The SEM images

indicate that there was smooth adhesion between glass fibers, epoxy resin and surface modified nanoclay. It can also be compared with the previous samples made with untreated glass fibers that there were no sign of glass fiber damage and similarly there were no clusters of epoxy matrix found in the composite. These will lead to effective load transfer between the glass fiber, nanoclay and epoxy resin which in turn will improve the interfacial bonding characteristics thereby improving the mechanical performance of the nanocomposites.
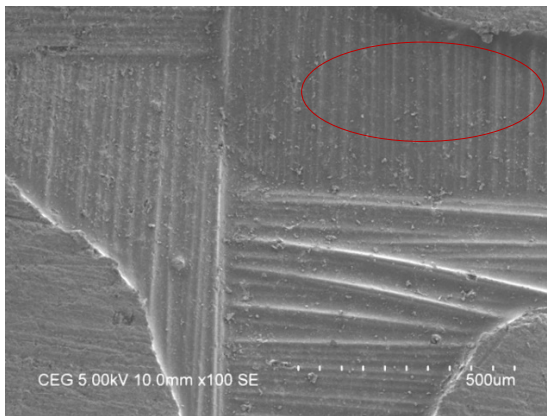
Figure 4.1s – Sample S10 (100x)   **Figure 4.1t – Sample S10 (1000x)**
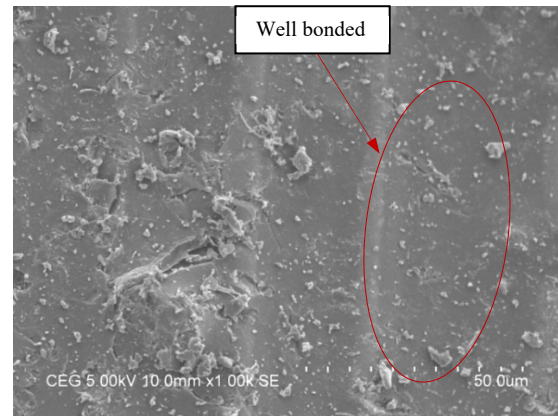
Figures 4.2a to 4.2j represent the scanned electron microscope images for samples S1 to S10 at 1000x magnification. It can be summarized that the microscopic images of the samples prepared using untreated glass fibers and acid treated glass fibers were found fragmented which could be due to the brittle nature of glass fibers along with the heat and pressure applied when the composites were prepared using compression molding. It was also noticed from the samples prepared using acid treated glass fibers that the glass fibers were damaged on the surface during the acid treatment which might have occurred due to etching action. It can also be observed from the microscopic images of samples prepared using acid treated glass fibers that the glass fibers have been delaminated from the epoxy matrix and the nanoclay distribution was not uniform in the matrix system.

On the other hand, the images from the samples which were prepared using silane treated glass fibers revealed that the surface of the glass fibers were continuous and smooth blend occurred between the matrix and nanoclay. The microscopic images of samples prepared using silane treated glass fibers also revealed that the interfacial

bonding between the silane treated glass fibers, epoxy and nanoclay were enhanced and the nanoclay was distributed uniformly throughout the matrix system, furthermore no agglomeration was noticed. It was established from the experimental results in the next section, that the hardness readings were higher for the samples prepared using silane treated glass fibers when compared to untreated and acid treated which clearly justify that the interfacial bonding between the epoxy resin, glass fibers and nanoclay had been improved due to the silane treatment of glass fibers.
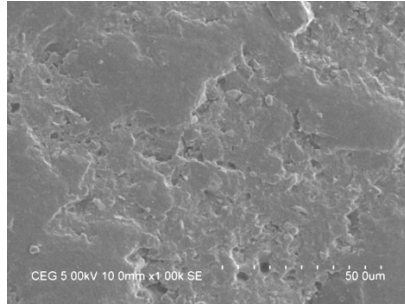
Figure 4.2a - Sample of Pure Epoxy (S1)
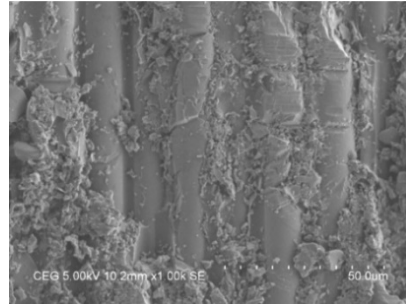
Figure 4.2b – Sample of Epoxy+UGF (S2)
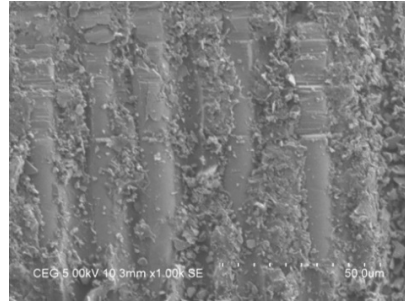
Figure 4.2c – Sample of Epoxy+AGF (S3)
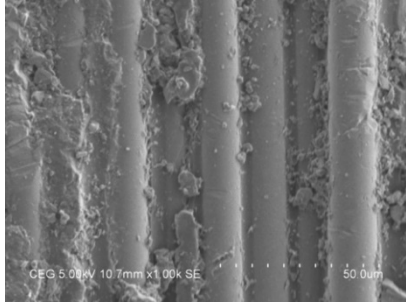
Figure 4.2d – Sample of Epoxy+SGF (S4)
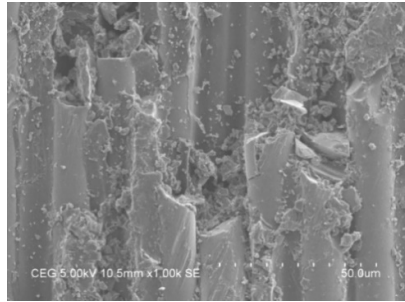
Figure 4.2e - Sample of Epoxy+UGF+UNC (S5)
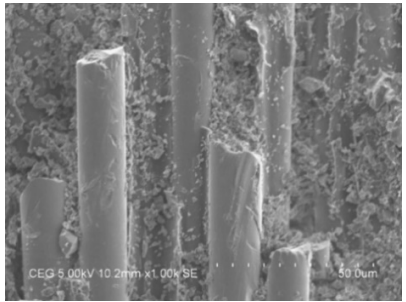
Figure 4.2f - Sample of Epoxy+UGF+MNC (S6)
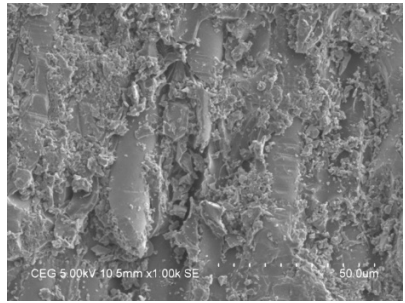
Figure 4.2g – Sample of Epoxy+AGF+UNC (S7)
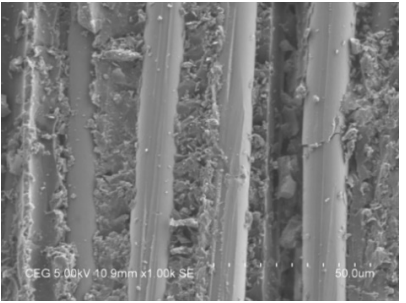
Figure 4.2h – Sample of Epoxy+AGF+MNC (S8)
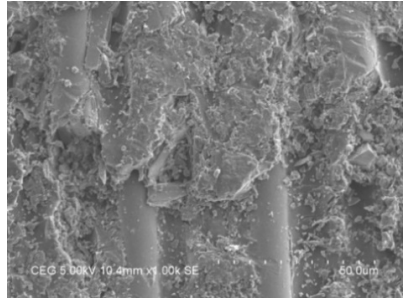
Figure 4.2i – Sample of Epoxy+SGF+UNC (S9)
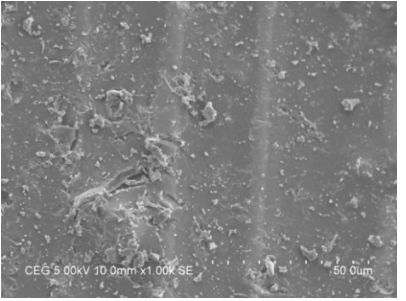
Figure 4.2j - Sample of Epoxy+SGF+MNC (S10)

Figure 4.2a-4.2j – SEM images of Samples S1 to S10 (1000x)

4.2.2 Mechanical Testing for Surface Treatment Effect

4.2.2.1 Microhardness with the Surface Treatment Effect

The microhardness test results for samples S1 to S10 were represented in Figure 4.3 for variation in surface treatment effect of glass fibers and nanoclay. The test results indicated that the sample S10 prepared with epoxy, silane treated glass fiber and surface modified nanoclay had achieved the highest hardness of 47 HV whereas the sample S8 prepared with epoxy, acid treated glass fiber and surface modified nanoclay had achieved the lowest surface hardness of 24.47 HV. From these two hardness readings it can be concluded that the type of surface treatment of glass fibers play a vital role in improving the interfacial bonding strength in terms of surface hardness. In this case, the silane treatment for S10 was much superior compared to acid treatment for S8. The above comparison was also supported by the SEM images, Figures 4.1s and 4.1t where sample S10 indicates better bonding, smooth adhesion between epoxy, glass fiber and nanoclay which have contributed to improved interfacial adhesion leading to increased hardness. Conversely, from the SEM images, Figures 4.1o and 4.1p of sample S8 insufficient bonding, delamination and surface damage of the glass fibers were noticed which have attributed to the poor interfacial bonding strength leading to lowest hardness among all the samples. Sample S1 made of epoxy was done to have a basic reference on the mechanical properties.

From the test results, it can also be noticed that the samples S4 (32.30 HV) and S9 (34.30 HV) prepared with silane treated glass fibers exhibit higher hardness than those of the samples made with untreated and acid treated glass fibers. From the above trend, it can be observed that the silane through the surface modification reacts with inorganic clay and epoxy resin forming a network between nanoclay, silane and epoxy thereby enhancing the interfacial interaction between epoxy matrix and nanoclay through restriction of the mobility of polymer chains. Furthermore, the addition of nanoclay also acts as an interface material thereby providing a bridge by improving the wettability of glass fiber and enhancing the interfacial adhesion between the glass fiber and epoxy resin. In addition, the nanoclay particles also acts as rigid connectors which results in improved stress transfer in the composite system. The increase in microhardness of the nanocomposite was mainly due to the formation of network like structure of intercalated

platelets with epoxy resin molecules effectively resisting the indentation. Similar behaviour of nanoparticle effect and surface treated glass fibers on mechanical performance were reported by Cong et al. [52] and Hamed et al. [37].
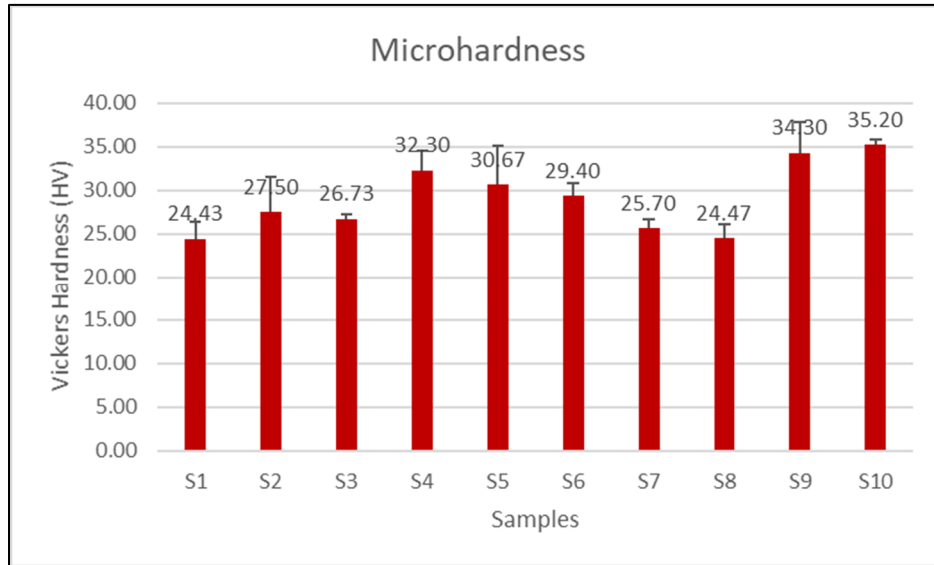

Figure 4.3: Microhardness Results for Surface Treatment Effect

4.2.2.2 Tensile Testing with the Surface Treatment Effect

The tensile test results for samples S1 to S10 were represented in Figure 4.4 for analysing the variation in surface treatment effect of glass fibers and nanoclay. The test results indicated that the sample S10 prepared with epoxy, silane treated glass fiber and surface modified nanoclay had recorded the highest tensile strength of 318.97 MPa whereas the sample S5 prepared with epoxy, untreated glass fiber and untreated nanoclay had recorded the lowest value of 137.00 MPa. The 132.8% increase in tensile strength results indicate that the surface modification of glass fibers as well as nanoclay using silane treatment has major impact on the interfacial bonding strength. The micrographs, Figures 4.1i and 4.1j of sample S5 clearly indicated fragmentation of glass fibers, insufficient bonding between glass fiber/epoxy and delamination of glass fibers whereas the SEM images, Figures 4.1s and 4.1t of sample S10 indicated better bonding and smooth adhesion between the glass fibers and epoxy matrix which was harmonised with the tensile strength results attained. It was also noticed from the test results that sample S2 prepared with epoxy and untreated glass fiber had achieved tensile strength of 300.81 MPa. The increase in tensile strength of 6% between sample S10 and sample

S2 could be due to the silane treatment of glass fibers and addition of surface modified nanoclay. On the other hand, the micrographs of sample S2 had shown insufficient bonding and surface damage of glass fibers which could have diminished the tensile strength.

From the above discussion, it was evident that the increased tensile strength of the silane treated samples were mainly due to the interaction that occurred between the silane and the surface of the glass fiber. The silane treatment creates greater flexible interphase which contributes to the improvement of interphase bonding performance between glass fiber and matrix. Furthermore, when the epoxy resin was polymerized with the catalyst, the reaction occurs at the surface with the silane affiliation. Similarly, the surface treatment of nanoclay attribute to the better clay dispersion, smaller particle size attained during treatment and no significant agglomeration leading to the improved tensile strength. The silane treatment act as a bridge thereby providing mechanical interlocking as well as chemical bonding between the glass fiber and matrix which in turn tailored the mechanical performance of the composite material. As a result, the interfacial adhesion between the epoxy resin, glass fiber and nanoclay was significantly improved thereby enhancing the tensile strength of the nanocomposite which was confirmed through the SEM analysis and also similarly reported by Hyeong et al. [9] and Mengyuan et al. [11].
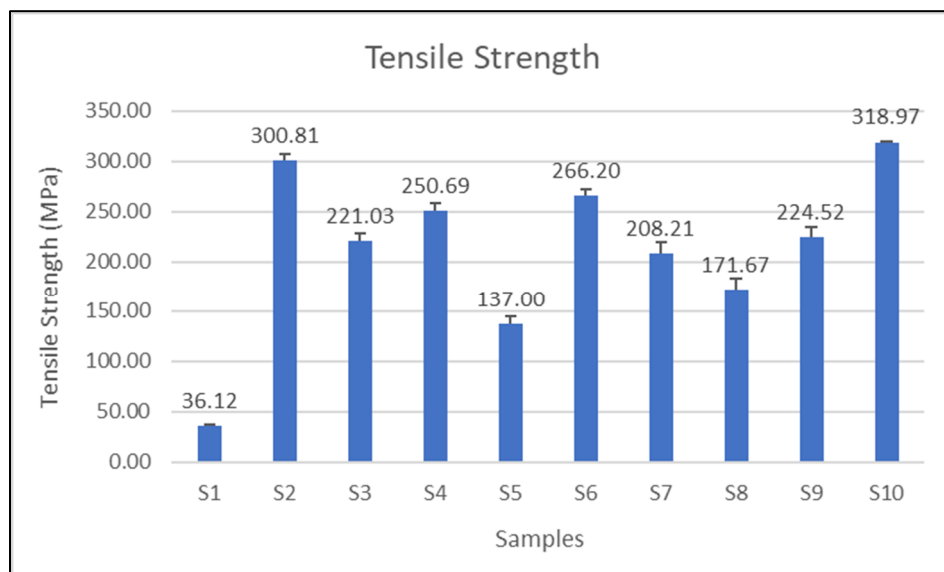
Figure 4.4: Tensile Strength Results for Surface Treatment Effect

4.2.2.3 Flexural Testing with the Surface Treatment Effect

The flexural test results for samples S1 to S10 were represented in Figure 4.5 for variation in surface treatment effect of glass fibers and nanoclay. The test results indicated that the sample S4 prepared with epoxy and silane treated glass fiber had recorded the highest value of 176.58 MPa whereas the sample S8 prepared with epoxy, acid treated glass fiber and surface modified nanoclay had achieved lowest value of 64.95 MPa. The flexural strength of sample S2 prepared with epoxy and untreated glass fiber is 156.59 MPa. The 171.9% increase in flexural strength between samples S4 and S8 and 12.7% increase in flexural strength between sample S4 and S2 could be due to the silane treatment effect of glass fibers which had reduced the brittle behaviour of glass fiber and improved the flexural behaviour of the composite. The SEM micrograph, Figures 4.1g and 4.1h of the sample S4 had shown better bonding between glass fiber and epoxy than the sample S8 which was also evident from the SEM images, Figures 4.1o and 4.1p of sample S8 showing insufficient bonding and surface damage of glass fibers which could have reduced the flexural properties of the composite. On the other hand the SEM images, Figures 4.1c and 4.1d of sample S2 with untreated glass fiber had shown some surface damage of glass fibers and unbonded excess resin in the composite which could have contributed to the reduction of flexural strength.

The trend shown above indicate that silane treatment for the glass fibers had improved the interfacial mobility between the glass fibers and epoxy resin through the enhancement of interfacial adhesion between the fiber and matrix adhesion which had contributed through the enhancement of flexural strength results which was also similarly reported by Kutlay et al. [12]. It can also be concluded from the flexural strength results of samples S4 (176.58 MPa), S9 (142.09 MPa) and S10 (140.98 MPa) that the addition of nanoclay reduced the flexural properties of the nanocomposite which can be attributed by the lack of capability of nanoparticles to sustain high flexural load. The relative negative effect on the addition of nanoclay above 1 wt.% can attribute to agglomeration effect due to the increase in viscosity of the epoxy matrix making degassing and processing more difficult during fabrication which led to formation of voids and porosity contributing to reduction in the flexural performance of the nanocomposite and as similarly reported by Ahmad et. al [47].
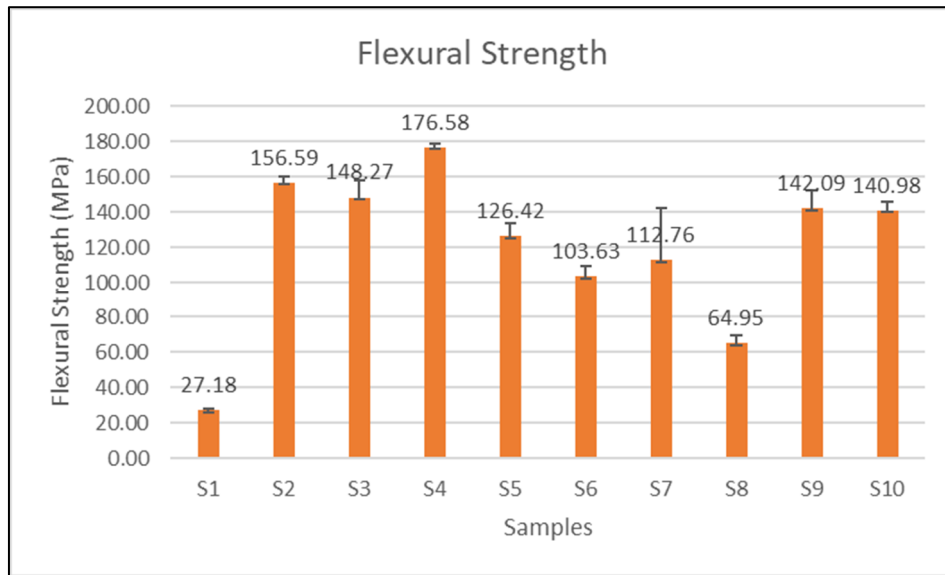
Figure 4.5: Flexural Strength Results for Surface Treatment Effect

4.2.2.4 Impact Testing with the Surface Treatment Effect

The impact test results for samples S1 to S10 were represented in Figure 4.6 for variation in surface treatment effect of glass fibers and nanoclay. The test results indicated that the sample S7 made with epoxy, acid treated glass fiber and untreated nanoclay had achieved the highest impact strength of 244.51 KJ/m^2 whereas the sample S8 prepared with epoxy, acid treated glass fiber and surface modified nanoclay had achieved the lowest impact strength of 97.56 KJ/m^2. The increase of 150.6% in impact strength was observed mainly due to the difference in untreated and surface modified nanoclay concentration. This also indicates that untreated nanoclay addition improves the toughness properties of the nanocomposites. From the SEM images, Figures 4.1m and 4.1n of the sample S7 it can be noticed that fragmentation and surface damage of the glass fibers exists. For the SEM images, Figures 4.1o and 4.1p of sample S8 it can be observed that insufficient bonding, delamination and surface damage of the glass fibers were dominant. In spite of defects noticed in sample S7, the gap between the epoxy, glass fiber and nanoclay were observed to be filled with nanoclay, thereby contributed to the radical increase in impact strength. Furthermore, the impact strength of samples S2 as well as sample S10 also were noticed close to sample S7. It can be observed from the SEM images, Figures 4.1s and 4.1t of sample S10 that sufficient

bonding and smooth adhesion between epoxy, glass fiber and surface modified nanoclay were observed which was also harmonised with impact test result achieved.

From the experimental results it was observed that silane treatment and the addition of nanoclay improves the absorbed energy when compared to controlled samples. The addition of nanoparticles improved the impact strength through enhanced interfacial bonding between the fiber and epoxy, thereby increasing the interface surface of the constituents in the system and increased superficial area-volume ratio. From the Faber and Evan model, it was explained that when a growing crack meets nanoclay the crack gets deflected out of plane and when the crack propagates further and reaches further nanoclay, it gets twisted and tilted thereby increasing the fracture surface area leading to increased fracture toughness which was similarly reported by Ratna et. al [46]. Furthermore, it was also not possible to establish an unequivocal relationship between surface treatment and impact energy absorbed which was similarly reported by Ferreira et al. [10].
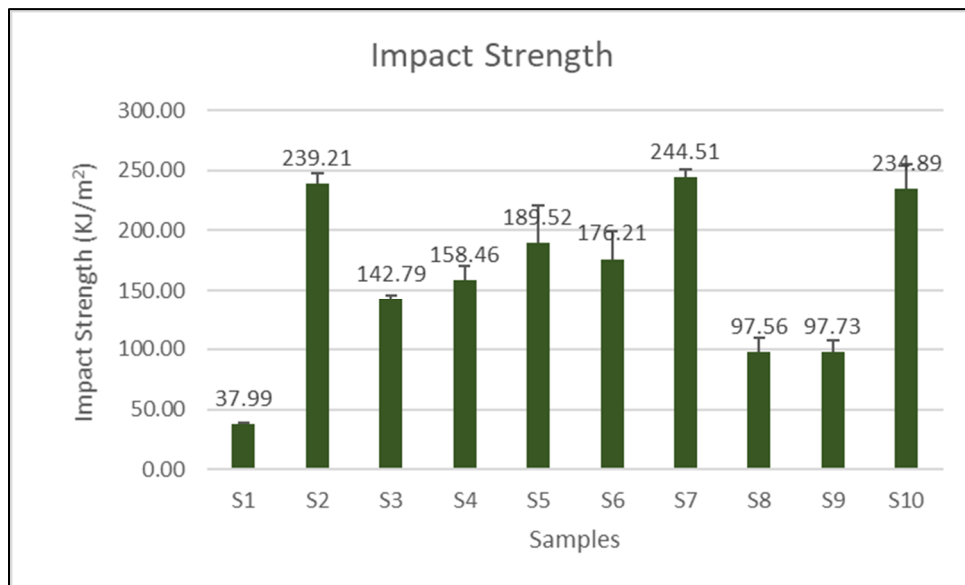
Figure 4.6: Impact Strength Results for Surface Treatment Effect

Table 4.2: Mechanical Test Results for Surface Treatment Effect

Sample	Description	Micro hardness (HV)	Tensile Strength (MPa)	Flexural Strength (MPa)	Impact Strength (KJ/m²)
S1	Epoxy	24.33	36.12	37.99	27.18
S2	Epoxy + UGF	27.50	300.81	156.59	239.21
S3	Epoxy + AGF	26.73	221.03	148.27	142.79
S4	Epoxy + SGF	32.30	250.69	176.58	158.46
S5	Epoxy + UGF + UNC	30.67	137.00	126.42	189.52
S6	Epoxy + UGF + MNC	29.40	266.20	103.63	176.21
S7	Epoxy + AGF + UNC	25.70	208.21	112.76	244.51
S8	Epoxy + AGF + MNC	24.47	171.67	64.95	97.56
S9	Epoxy + SGF + UNC	34.30	224.52	142.09	97.73
S10	Epoxy + SGF + MNC	35.20	318.97	140.98	234.89

4.2.3 Summary of Surface Treatment

This section presented an experimental analysis related to the effect of surface treatment on the glass fibers and nanoclay towards the interfacial bonding in terms of surface hardness. The key finding from those analysis was to identify the effective surface treatment that address the interfacial bonding characteristics through improved surface characteristics i.e. surface hardness with complementing other mechanical characteristics, demonstrated through the tensile, flexural and impact tests. In general, samples prepared using silane treated glass fibers exhibit better tensile strength and hardness properties without compromising flexural and impact properties. Nevertheless, it was revealed based on the micrography and surface hardness analysis, silane treated glass fiber with surface modified nanoclay sample (S10) had shown the most effective interfacial bonding performance in terms of surface hardness.

The tendency shown indicate that silane treatment for the glass fibers as well as the surface treatment of the nanoclay act as a bridge thereby providing mechanical interlocking between the glass fiber, epoxy and nanoparticles which in turn enhanced the interfacial bonding strength. This in turn have improved the interfacial mobility between the glass fibers and epoxy resin through which enhancement of mechanical performance had been achieved. Therefore, silane treated glass fiber with trimethyl stearyl ammonium modified nanoclay was considered as the effective surface treatment which have been concluded in this section.

4.3 Nanoclay Concentration Effect on Hardness

In this section results were analysed to understand the behaviour of nanoclay concentration influence on the interfacial bonding in terms of surface hardness and also to identify the effective nanoclay concentration. The nanoclay concentration is varied between 0 to 6 wt. % with the epoxy matrix system where the experimental set-up and process conditions were followed according to section 3.2.4 in Chapter-3. The experimental test results attained through the variation of nanoclay concentration are presented in Table 4.4.

4.3.1 Surface Morphology Analysis

The SEM analysis of the nanocomposites with different nanoclay loading shows homogeneity of dispersion of nanoclay in the epoxy matrix. The examination was carried out on the surface of the nanocomposites in a raster pattern with magnification ranging from 100x to 10000x.

Figure 4.7a and 4.7b represent the SEM images of sample N1 prepared with silane treated glass fibers and epoxy resin. The SEM images indicate that there was smooth adhesion between the silane treated glass fibers and epoxy resin. These will lead to effective load transfer between the silane treated glass fibers and epoxy resin which in turn will improve the interfacial bonding characteristics thereby improving the mechanical properties of the nanocomposites. There were few signs of glass fiber damage and similarly there were minor cluster of epoxy matrix found in the composite. It can also be observed from the microscopic images that some minor surface damages were noticed on the glass fibers.

Resin cluster and surface damage of glass fibers
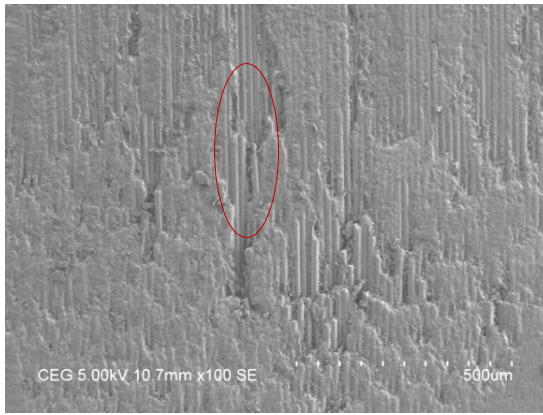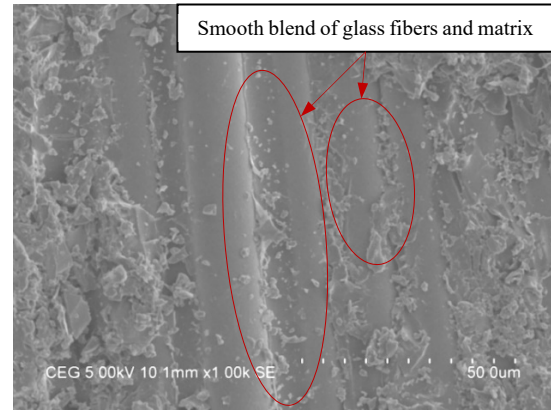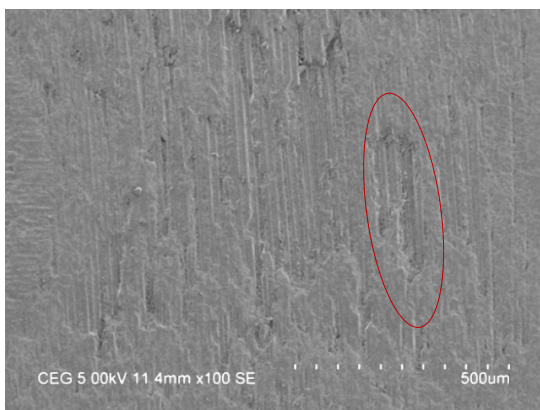
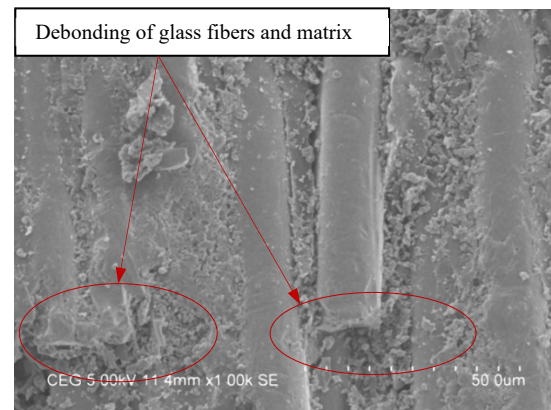**Figure 4.7a- Sample N1 (100x)**　　　　**Figure 4.7b- Sample N1 (1000x)**
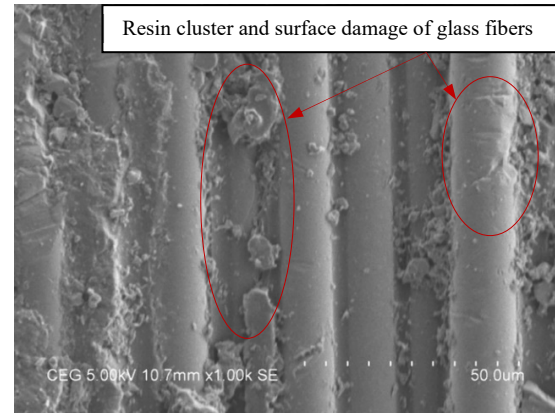
Figure 4.7c and 4.7d represent the SEM images of sample N2 prepared with silane treated glass fibers, epoxy resin and with 1 wt.% of surface modified nanoclay. From the micrographs as highlighted, it is evident that there exists better bonding between glass fibers and nanoclay. It can also be noticed from the images that there was smooth blend of the glass fibers with the epoxy resin and the surface of the glass fibers were uniformly covered with epoxy resin and nanoclay. The glass fibers were not fragmented even though there were minor surface damages noticed which might have occurred during the surface treatment process. It was also noticed that the nanoclay has been uniformly dispersed in the epoxy matrix and no signs of agglomeration has been noticed. The micrographs also revealed that there exists strong bonding between the fiber and matrix since traces of matrix were left on the glass fiber. The nanoclay clusters with nanosized diameters were found on the surface and the distance between the clusters are relatively large which was an evidence of good dispersion and exfoliation. The addition of nanoclay had contributed to significant increase in mechanical properties of tensile strength, impact strength and microhardness which was also due to the uniform dispersion and had revealed an efficiently load transferring between epoxy, glass fiber and nanoparticles.
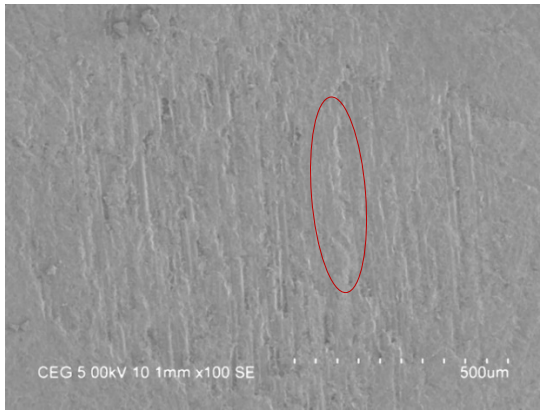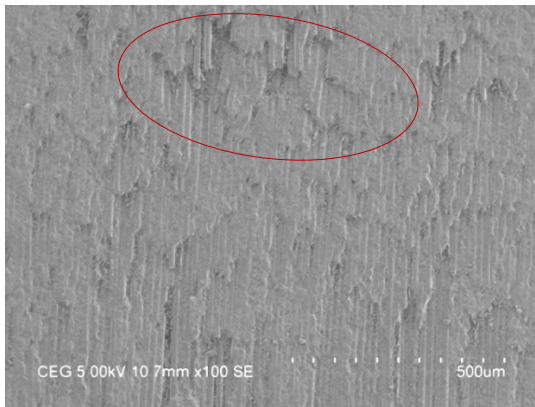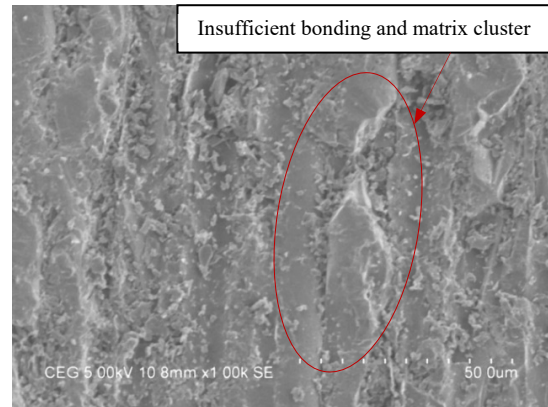
Figure 4.7c- Sample N2 (100x)

Figure 4.7d - Sample N2 (1000x)

Figure 4.7e and 4.7f represent the SEM images of sample N3 prepared with silane treated glass fibers, epoxy resin and 2 wt. % of surface modified nanoclay. From the micrographs, it was noticed that there exists uniform blend of glass fiber with nanoclay and epoxy resin. Unfortunately, fiber failure and fragmentation of glass fibers were noticed from the micrographs which could be due to the surface treatment process of glass fibers or thermal impact that occurred during the compression molding process. It was also noticed from the images that both matrix damage and fiber damage were present. Flakes of epoxy resin with nanoclay presence were also seen isolated on the micrographs.
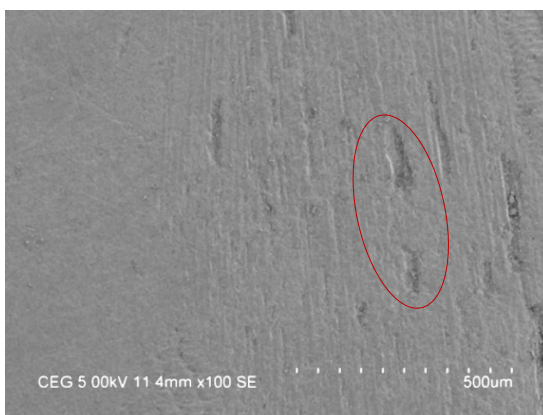

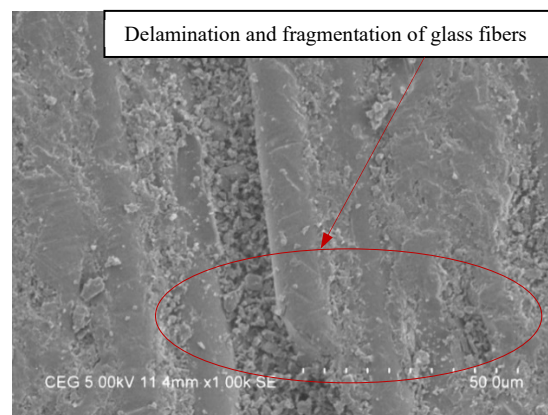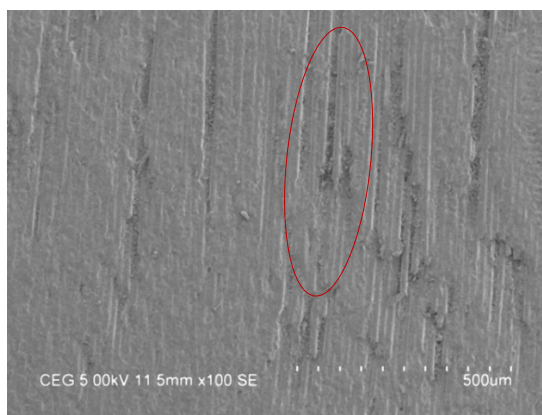**Figure 4.7e - Sample N3 (100x)**

Figure 4.7f - Sample N3 (1000x)

Figure 4.7g and 4.7h represent the SEM images of sample N4 prepared with silane treated glass fibers, epoxy resin and 3 wt. % of surface modified nanoclay. The SEM images indicate that there exists smooth adhesion between glass fibers, epoxy resin and surface modified nanoclay. It can also be noticed that there were some signs of glass

fiber damage and similarly there were clusters of epoxy matrix found in the composite. These will lead to reduction in load transfer capability between the glass fibers, nanoclay and epoxy resin which in turn will reduce the interfacial bonding characteristics thereby reducing the mechanical performance of the nanocomposites.

Figure 4.7g – Sample N4 (100x)

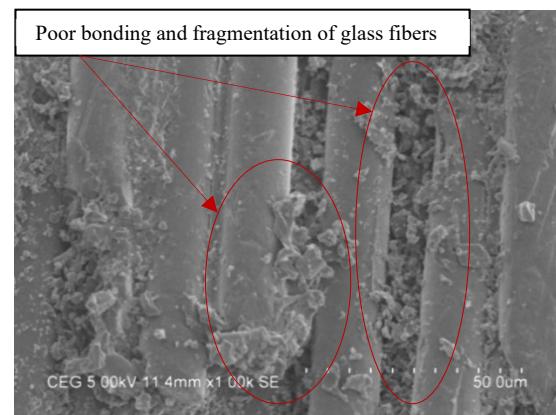Insufficient bonding and matrix cluster

Figure 4.7h – Sample N4 (1000x)

Figure 4.7i and 4.7j represent the SEM images of sample N5 prepared with silane treated glass fibers, epoxy resin and 4 wt. % of surface modified nanoclay. It was noticed from the micrographs that there is uniform blend of epoxy resin with nanoclay and glass fibers. It has been noticed that serious fragmentation of glass fibers were present in the nanocomposite which might have occurred during the surface treatment of glass fibers and during composite fabrication. The images also represent that the nanoclay were uniformly distributed in the epoxy matrix and no signs of agglomeration were noted in the nanocomposite.

Figure 4.7i - Sample N5 (100x)

Delamination and fragmentation of glass fibers

Figure 4.7j - Sample N5 (1000x)

Figure 4.7k and 4.7l represent the SEM images of sample N6 prepared with silane treated glass fibers, epoxy resin and 5 wt. % of surface modified nanoclay. The microscopic images represent that there were further fragmented glass fibers noticed. The clusters of epoxy matrix with nanoclay were prominently noticed and spread over a large area in the nanocomposites, which resulted mainly due to the increase in matrix viscosity. These clay clusters were expected to negatively affect the hybrid nanocomposite mechanical properties, including microhardness. Debonding of filler material with the matrix were also noticed in addition to the lack of filler matrix between the glass fibers.

Figure 4.7k - Sample N6 (100x)   **Figure 4.7l - Sample N6 (1000x)**

Figure 4.7m and 4.7n represent the SEM images of sample N7 prepared with silane treated glass fibers, epoxy resin and 6 wt. % of surface modified nanoclay. The microscopic images represent that there occurs better adhesion between glass fibers, epoxy resin and surface modified nanoclay since nanoclay act as rigid fillers in matrix and as well as rigid connectors between matrix and the filler material. However, there were collections of epoxy matrix with nanoclay seen obviously in the micrographs which could be due to the increase in the viscosity of the epoxy matrix.
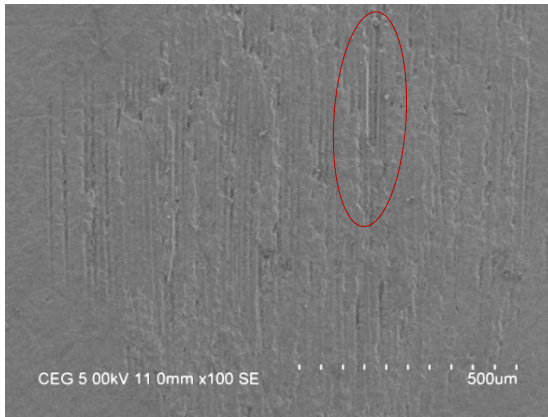
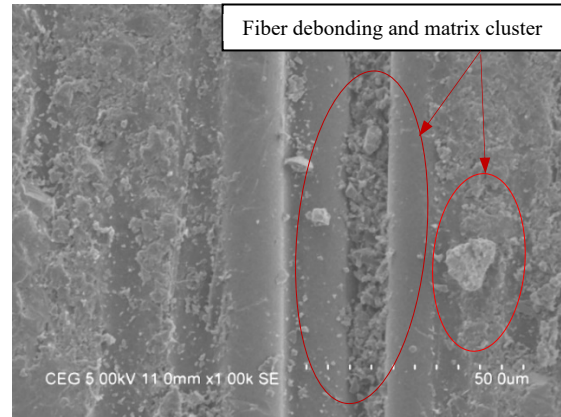**Figure 4.7m - Sample N7 (100x)**

Figure 4.7n - Sample N7 (1000x)

Figure 4.7o and 4.7p represent the SEM images of samples N2 (1% Nanoclay) and N7 (6% Nanoclay) at 10000x magnification. The microscopic images of sample N1 indicates the nanoclay distribution was uniform within the epoxy matrix and very little signs of agglomeration or matrix clusters were observed. On the other hand, in sample N7 clusters of nanoclay were noticed prominently which could be due to the agglomeration effect caused by insufficient dispersion of nanoclay. This could be attributed due to the high concentration of nanoclay that had exceeded the saturation limit in the epoxy resin. This in turn had resulted in agglomeration effect which acts as the source of stress concentration resulting in poor mechanical performance. It is worth mentioning that the nanoclay works as a bridge by providing a mechanical interlock between the fiber and the matrix which enhances the interfacial bonding strength. In contrast, in the case of excessive nanoclay concentration, nanoclay may act as a barrier due to the high concentration of nanoparticles at the interface which deteriorates the mechanical performance.
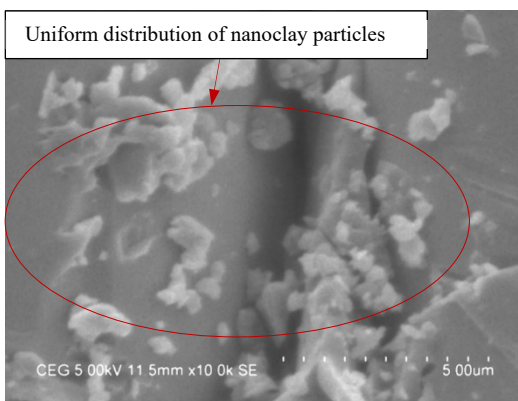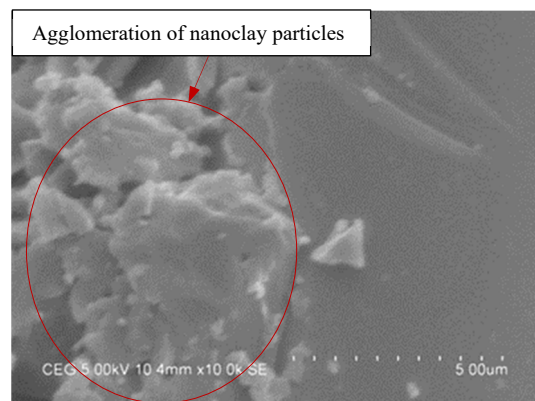

Figure 4.7o - Sample N2 (10000x)

Figure 4.7p - Sample N7 (10000x)

From the figures 4.8a to 4.8g it was observed from the microscopic images of the samples that in general the nanoclay distribution in the epoxy matrix were uniform and there was no significant agglomeration noticed in the composites. It was also observed from the microscopic images that there was smooth adhesion between glass fiber and epoxy matrix in the composites. It can be concluded from SEM analysis that epoxy resin penetrates between clay layers, some nanoclay were stripped and the orientation and structure of clay layers were changed. It is possible to conclude that nanoclay acted as a bridge between the matrix and the reinforcing body and enhanced the interfacial bonding ability. It was clear that samples exhibit the highest hardness and wear properties with 1 wt. % of nanoclay concentration, revealing efficient load transfer between nanoparticle and matrix which was significantly affected by interaction and adhesion of the nanoclay particles with epoxy and glass fibers.
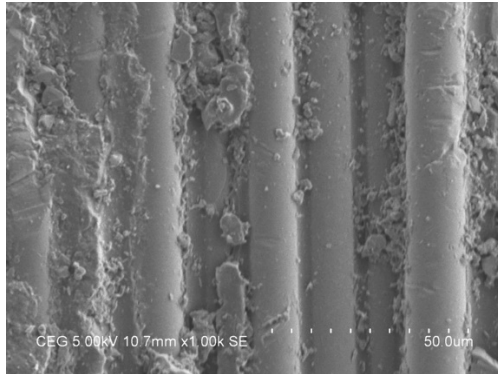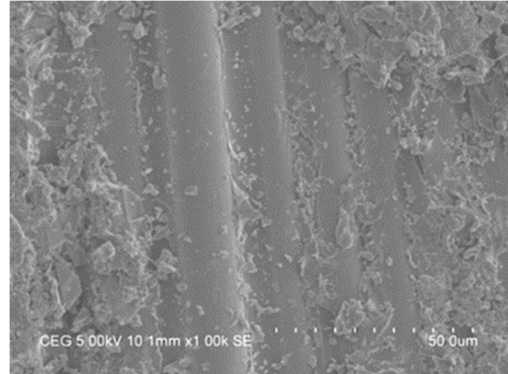
Figure 4.8a – Sample of 0% nanoclay (N1)

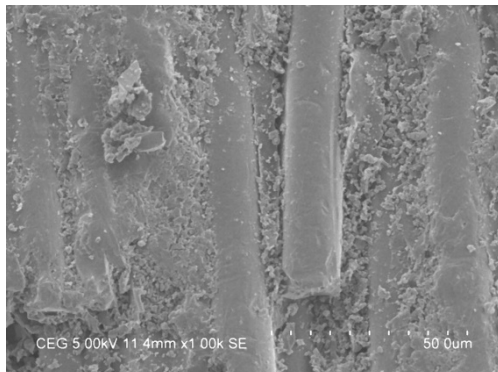
Figure 4.8b – Sample of 1% nanoclay (N2)

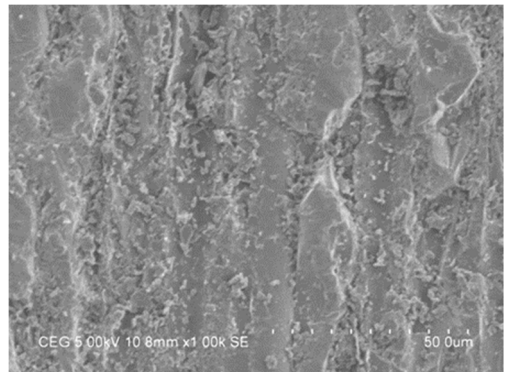**Figure 4.8c – Sample of 2% nanoclay (N3)**

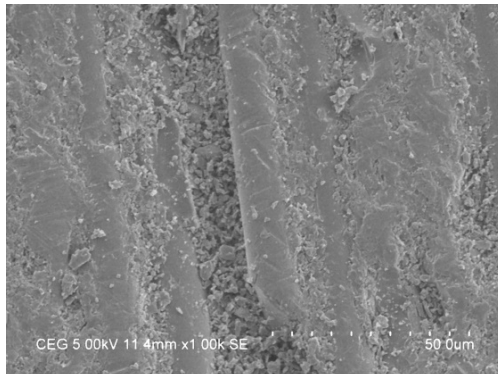**Figure 4.8d – Sample of 3% nanoclay (N4)**
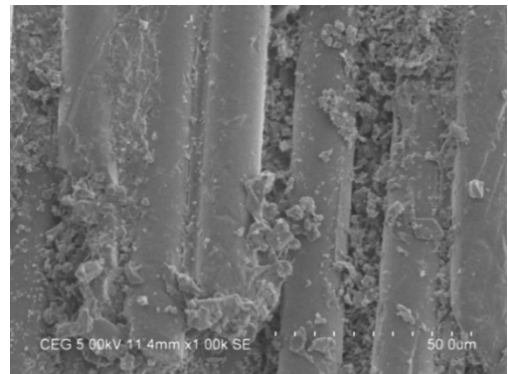

Figure 4.8e – Sample of 4% nanoclay (N5)
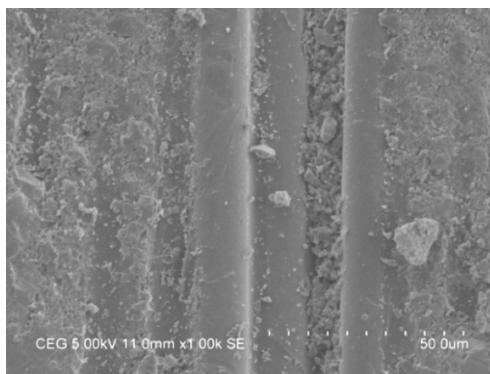

Figure 4.8f – Sample of 5% nanoclay (N6)

Figure 4.8g – Sample of 6% nanoclay (N7)

Figure 4.8a-4.8g – SEM images of Samples N1 to N7 (1000x)

4.3.2 EDX Analysis

Energy-Dispersive X-ray spectroscopy (EDX) analysis was conducted to analyse the elemental composition of the nanocomposite and their role related to hardness of the nanocomposite. Overall, the weight percentage provided by EDX indicates that silicon is the highest element followed by oxygen which is mainly due to the presence of silane treated glass fibers and surface modified nanoclay in the composite. The third most available element is aluminium and rest are: carbon, sodium, magnesium, calcium, chlorine and potassium. There were also observed minor traces of titanium and iron.

Figure 4.9a shows EDX results of sample N1 (0% Nanoclay) prepared using the silane treated glass fibers and epoxy resin. From the EDX analysis report it can be observed that oxygen is the highest element followed by silicon. The third highest element is the calcium followed by the presence of carbon and the rest are aluminium, sodium, magnesium, chlorine and potassium where sodium is 1.06%. There were also minor traces of titanium and iron identified.
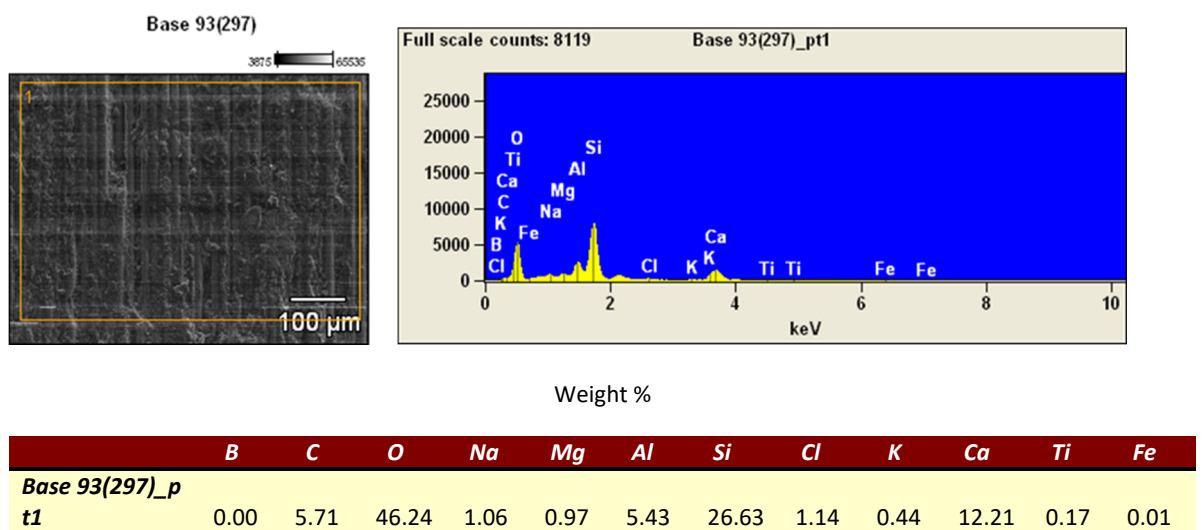

Weight %

	B	C	O	Na	Mg	Al	Si	Cl	K	Ca	Ti	Fe
Base 93(297)_pt1	0.00	5.71	46.24	1.06	0.97	5.43	26.63	1.14	0.44	12.21	0.17	0.01

Figure 4.9a - Sample N1 (0% Nanoclay) EDX Analysis

Figure 4.9b illustrates the EDX results of sample N2 (1% Nanoclay) prepared using the silane treated glass fibers, epoxy resin and with 1 wt.% of surface modified nanoclay. From the EDX analysis report it can be observed that oxygen is the highest element followed by silicon. The third highest element is the calcium followed by the

presence of aluminium and the rest are carbon, magnesium, sodium, chlorine and potassium where sodium is 0.22%.
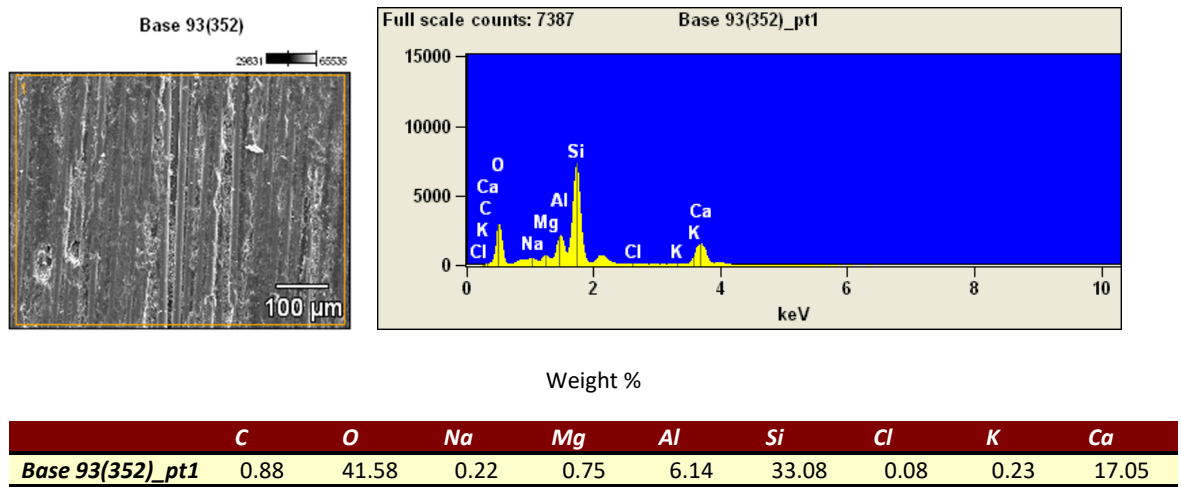

	C	O	Na	Mg	Al	Si	Cl	K	Ca
Base 93(352)_pt1	0.88	41.58	0.22	0.75	6.14	33.08	0.08	0.23	17.05

Figure 4.9b - Sample N2 (1% Nanoclay) EDX Analysis

Figure 4.9c displays the EDX results of sample N3 (2% Nanoclay) prepared using the silane treated glass fibers, epoxy resin and with 2 wt.% of surface modified nanoclay. From the EDX analysis report it can be observed that oxygen is the highest element followed by silicon. The third highest element is the calcium followed by the presence of aluminium and the rest are carbon, magnesium, sodium, chlorine and potassium where sodium is 0.26%.
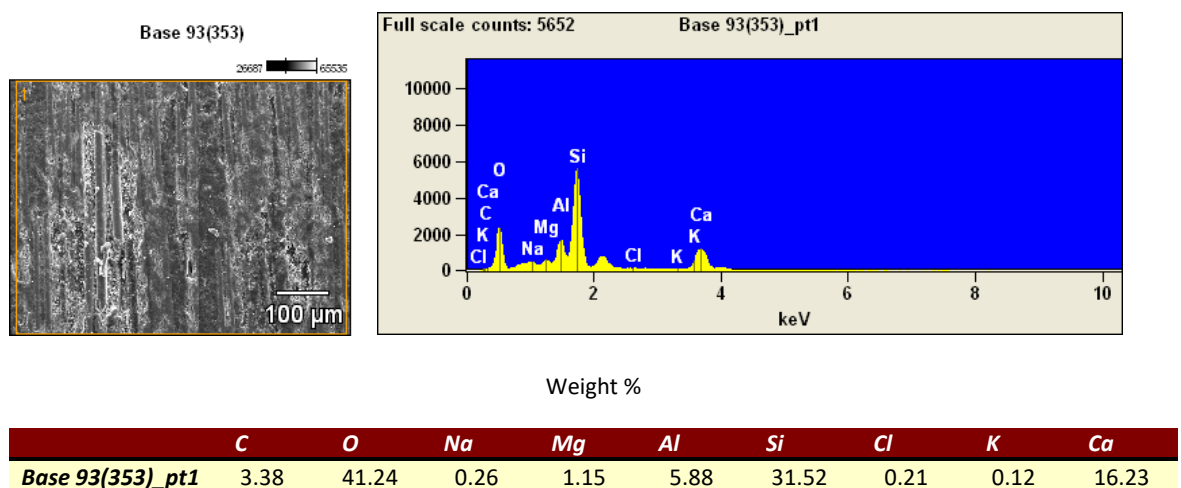

	C	O	Na	Mg	Al	Si	Cl	K	Ca
Base 93(353)_pt1	3.38	41.24	0.26	1.15	5.88	31.52	0.21	0.12	16.23

Figure 4.9c - Sample N3 (2% Nanoclay) EDX Analysis

Figure 4.9d indicates the EDX results of sample N4 (3% Nanoclay) prepared using the silane treated glass fibers, epoxy resin and with 3 wt.% of surface modified nanoclay. From the EDX analysis report it can be observed that oxygen is the highest element followed by silicon. The third highest element is the calcium followed by the presence of aluminium and the rest are carbon, magnesium, sodium, chlorine and potassium where sodium is 0.31%. There were also minor traces of titanium identified.
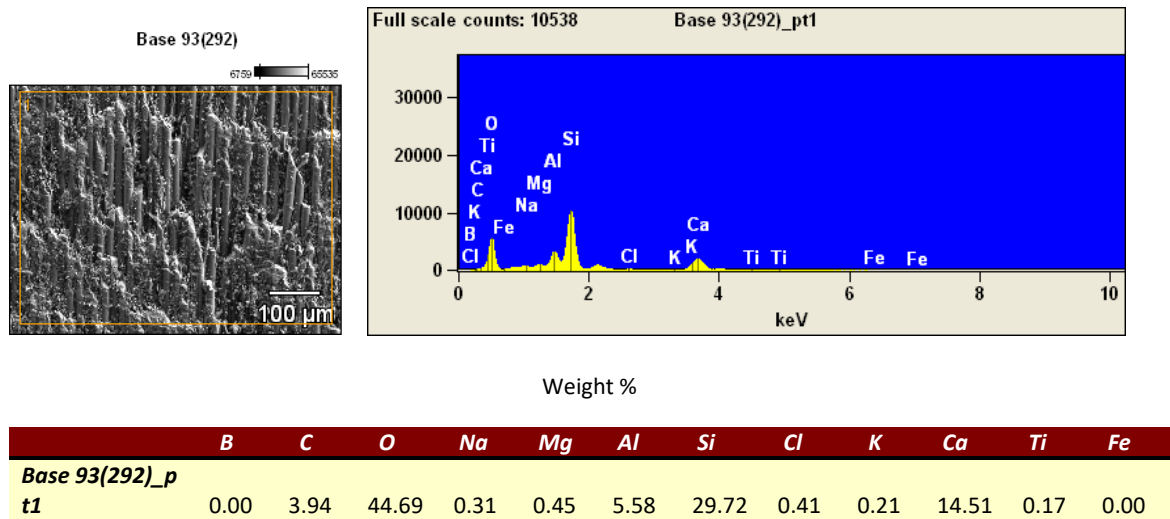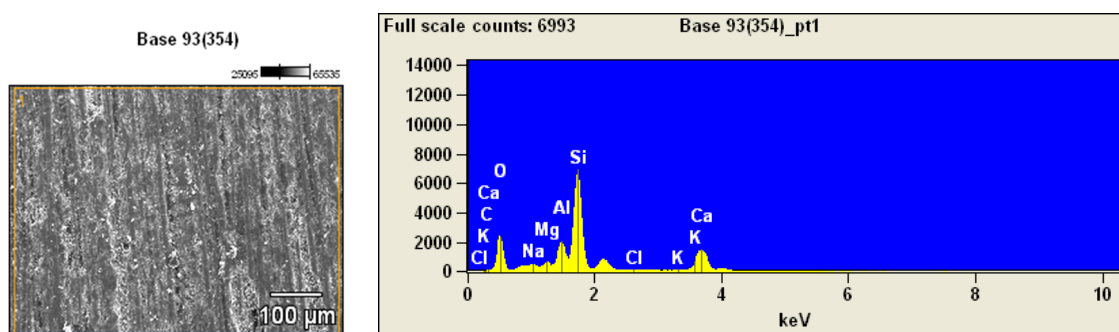

Weight %

	B	C	O	Na	Mg	Al	Si	Cl	K	Ca	Ti	Fe
Base 93(292)_pt1	0.00	3.94	44.69	0.31	0.45	5.58	29.72	0.41	0.21	14.51	0.17	0.00

Figure 4.9d - Sample N4 (3% Nanoclay) EDX Analysis

Figure 4.9e shows the EDX results of sample N5 (4% Nanoclay) prepared using the silane treated glass fibers, epoxy resin and with 4 wt.% of surface modified nanoclay. From the EDX analysis report it can be observed that oxygen is the highest element followed by silicon. The third highest element is the calcium followed by the presence of aluminium and the rest are carbon, magnesium, sodium, chlorine and potassium where sodium is 0.39%.
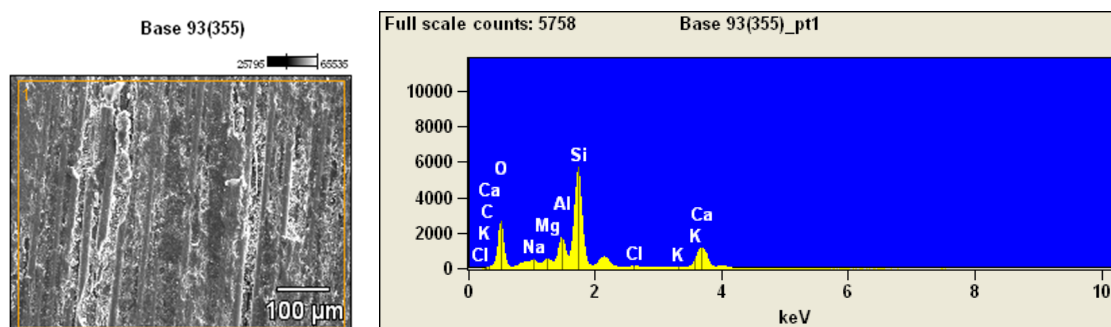
	C	O	Na	Mg	Al	Si	Cl	K	Ca
Base 93(354)_pt1	1.53	38.49	0.39	1.25	6.59	33.56	0.46	0.25	17.49

Figure 4.9e - Sample N5 (4% Nanoclay) EDX Analysis

Figure 4.9f represents the EDX results of sample N6 (5% Nanoclay) prepared using the silane treated glass fibers, epoxy resin and with 5 wt.% of surface modified nanoclay. From the EDX analysis report it can be observed that oxygen is the highest element followed by silicon. The third highest element is the calcium followed by the presence of aluminium and the rest are carbon, magnesium, sodium, chlorine and potassium where sodium is 0.49%.

Weight %

	C	O	Na	Mg	Al	Si	Cl	K	Ca
Base 93(355)_pt1	3.32	42.15	0.49	1.18	6.12	30.46	0.58	0.29	15.40

Figure 4.9f - Sample N6 (5% Nanoclay) EDX Analysis

Figure 4.9g indicates the EDX results of sample N7 (6% Nanoclay) prepared using the silane treated glass fibers, epoxy resin and with 6 wt.% of surface modified nanoclay. From the EDX analysis report it can be observed that oxygen is the highest element followed by silicon. The third highest element is the calcium followed by the presence of aluminium and the rest are carbon, magnesium, sodium, chlorine and potassium where sodium is 0.32%.
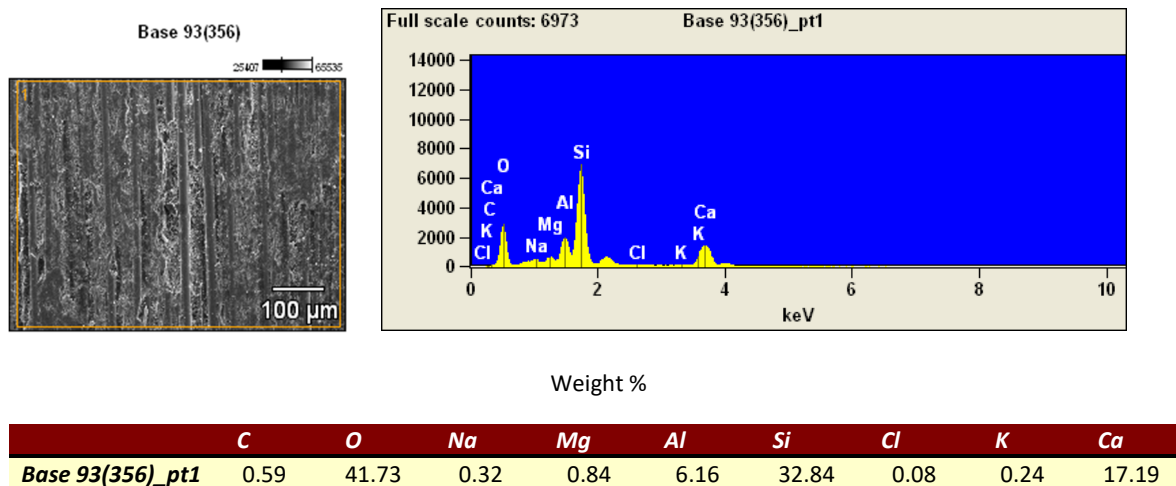
	C	O	Na	Mg	Al	Si	Cl	K	Ca
Base 93(356)_pt1	0.59	41.73	0.32	0.84	6.16	32.84	0.08	0.24	17.19

Figure 4.9g- Sample N7 (6% Nanoclay) EDX Analysis

From the EDX analysis summarised in the Table 4.3, it is interesting to observe there is an existence of trend between sodium and nanoclay which is increasing trend of sodium presence along the increase of nanoclay concentration except the threshold concentration of 1 wt.% nanoclay.

Table 4.3 Summary of Elemental Composition from EDX Analysis

Sample	Description	Elemental Composition (wt. %)								
		C	O	Na	Mg	Al	Si	Cl	K	Ca
N1	Epoxy+SGF+0% MNC	5.71	46.24	1.06	0.97	5.43	26.63	1.14	0.44	12.21
N2	Epoxy+SGF+1% MNC	0.88	41.58	0.22	0.75	6.14	33.08	0.08	0.23	17.05
N3	Epoxy+SGF+2% MNC	3.38	41.24	0.26	1.15	5.88	31.52	0.21	0.12	16.23
N4	Epoxy+SGF+3% MNC	3.94	44.69	0.31	0.45	5.58	29.72	0.41	0.21	14.51
N5	Epoxy+SGF+4% MNC	1.53	38.49	0.39	1.25	6.59	33.56	0.46	0.25	17.49
N6	Epoxy+SGF+5% MNC	3.32	42.15	0.49	1.18	6.12	30.46	0.58	0.29	15.40
N7	Epoxy+SGF+6% MNC	0.59	41.73	0.32	0.84	6.16	32.84	0.08	0.24	17.19

4.3.3 Mechanical Testing for Nanoclay Concentration EffectMicrohardness with the Nanoclay Concentration Effect

The microhardness test results for samples N1 to N7 were represented in Figure 4.10 for variation in nanoclay concentration effect. It had been observed from the test results that sample N2 prepared with epoxy, silane treated glass fiber and 1 wt.% of surface modified nanoclay had achieved the highest hardness of 47 HV whereas the sample N7 prepared with epoxy, silane treated glass fiber and 6 wt.% of surface modified nanoclay had attained the lowest surface hardness of 26.33 HV. The hardness value for the control sample N1 without nanoclay is 32.30 HV. There is an increase of 45.5% in hardness when comparing samples N1 and N2. It can be observed from these two readings that nanoclay concentration plays a vital role in improving the interfacial bonding strength in terms of surface hardness. From the SEM images, Figures 4.7c and 4.7d of sample N2 it can be observed that sufficient bonding, smooth adhesion between epoxy, glass fiber and nanoclay were noticed which have attributed to improved interfacial adhesion leading to increased hardness. Conversely from the SEM images, Figures 4.7m and 4.7n of sample N7 it was observed that insufficient bonding, delamination and matrix cluster were noticed which could have attributed to the poor interfacial bonding strength leading to lowest hardness among all the samples. It has also been observed from the hardness values that as the nanoclay concentration increased the hardness decreased gradually, which also indicated that 1 wt. % nanoclay concentration was sufficient to increase the surface hardness and with further addition deteriorated the hardness properties.

From the above discussion, it was observed that at lower nanoclay concentration, the intercalated structures of nanoclay were formed which promoted the improved fiber and matrix mechanical interlocking. This behaviour resulted in better exposure of the fiber surface to the clay filled matrix thereby enhancing the interfacial bonding strength between the fibers and nanoclay modified epoxy resin. The increase in microhardness of the nanocomposite was due to the enhancement of cross link density due to the formation of network like structure of intercalated platelets with epoxy resin molecules through the limitation of the fluidity of the polymer chain thereby effectively resisting the indentation. Similar behaviour of nanoclay addition and influence on wear performance were reported by Sharma et. al [40] and Ratna et. al [46]. At higher

concentration of nanoclay, the increase in the viscosity of the matrix makes processing and degassing more difficult leading to the formation of voids or airgaps. This non-homogenous mixture of clay/epoxy suspension resulted in the weak interfacial adhesion which acted as stress concentrators leading to the reduction in mechanical performance. Therefore, the threshold limit of the addition of nanoclay concentration was 1 wt. % to obtain the maximum hardness performance of the nanocomposite.
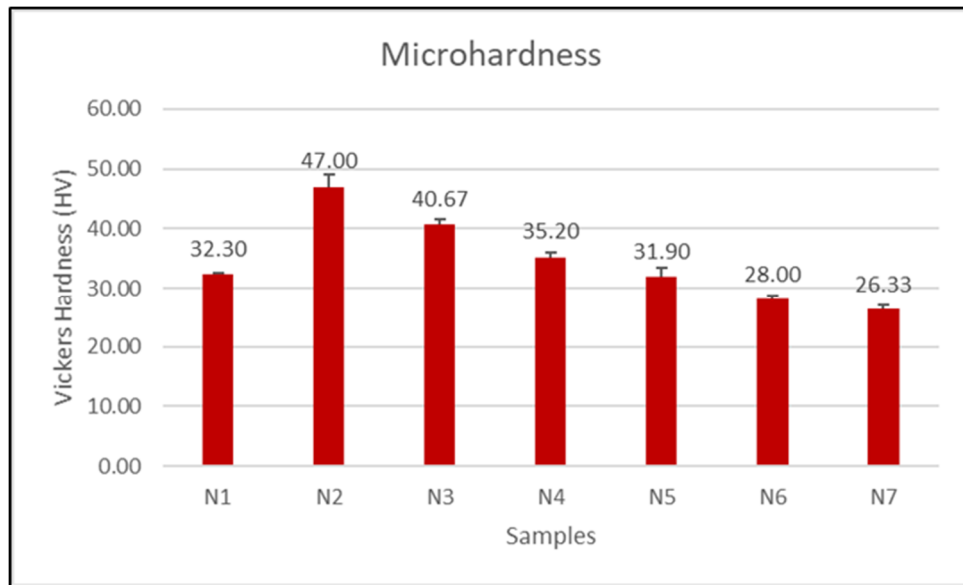

Figure 4.10: Microhardness Results for Nanoclay Concentration Effect

4.3.3.2 Tensile Testing with the Nanoclay Concentration Effect

The tensile test results for samples N1 to N7 were represented in Figure 4.11 for variation in nanoclay concentration effect. It had been observed from the test results that sample N6 prepared with epoxy, silane treated glass fiber and 5 wt.% of surface modified nanoclay had recorded the highest tensile strength of 340.08 MPa whereas the sample N1 prepared using epoxy and silane treated glass fiber had attained the lowest tensile strength of 250.69 MPa. There is an increase of 35.7% in tensile strength when comparing samples N1 and N6. From the SEM images, Figures 4.7k and 4.7l of sample N6 it can be observed that fragmentation and insufficient bonding between epoxy, glass fiber and nanoclay were noticed in some areas, however it had attained the maximum tensile strength. From the SEM images, Figures 4.7a and 4.7b of sample N1 it was observed that insufficient bonding, matrix cluster and surface damage of glass fiber were

noticed which could have attributed to the poor interfacial bonding strength leading to lowest tensile strength among all the samples. It can also be noticed from the tensile test results that addition of nanoclay have major impact on the increase of tensile strength, but the variation of nanoclay concentration does not have significant variation in tensile strength of the nanocomposite.

The trend shown below in Figure 4.11 indicate that the addition of nanoclay with certain concentration till 5 wt.% contributed for improved tensile strength. The increase in the tensile strength was due to the influence of nanoclay in modifying the composite through improvement of wettability between glass fiber and epoxy matrix thereby enhancing the interfacial adhesion between them. The addition of the nanoclay fills up the cavity thereby increasing the interfacial area of the constituents in the system which sequentially reduces the stress concentration. At higher concentration of nanoclay, the reduction of properties was attributed due to agglomeration thereby resulting in decrease of load transfer between nanoparticles and epoxy resin. The reduction in tensile strength was coupled with higher viscosity of the resin which in turn could affect the distribution of nanoclay particles as well as the infusion time. Therefore, threshold limit of 1 wt.% for nanoclay content was obtained to achieve optimum tensile strength.
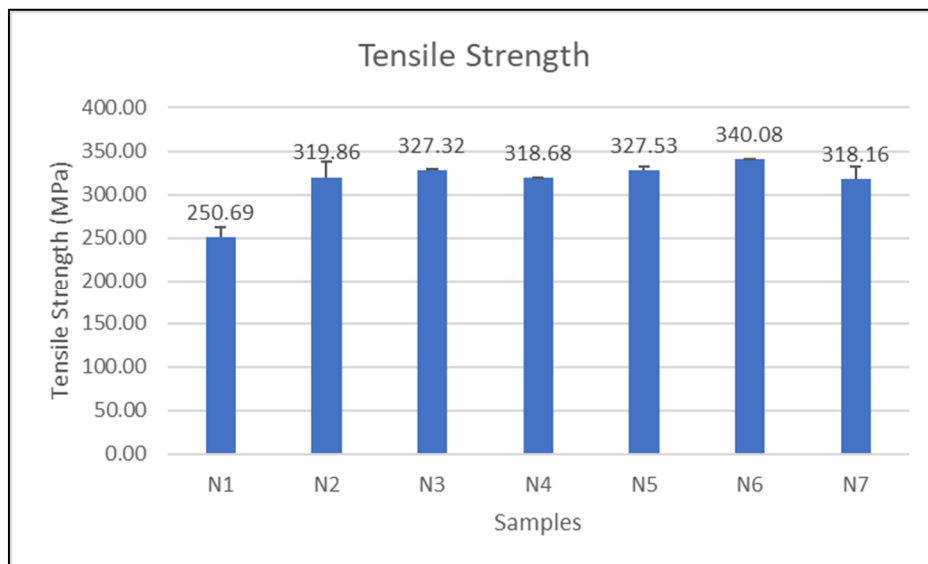

Figure 4.11: Tensile Strength Results for Nanoclay Concentration Effect

4.3.3.3 Flexural Testing with the Nanoclay Concentration Effect

The flexural test results for samples N1 to N7 were represented in Figure 4.12 for variation in nanoclay concentration effect. It had been observed from the flexural test results that sample N1 prepared with silane treated glass fiber and epoxy matrix had recorded the highest flexural strength of 176.58 MPa, whereas the sample N7 prepared with silane treated glass fiber/epoxy system with 6 wt.% of surface modified nanoclay had attained the lowest flexural strength of 114.15 MPa. There was a reduction of 45.3% reduction in flexural properties with the addition of 6 wt.% of nanoclay concentration. From the micrographs, Figures 4.7a and 4.7b for sample N1 it can been observed that insufficient bonding, matrix cluster and surface damage of glass fibers were noticed, however sample N1 had attained maximum flexural strength among all the other samples. From the SEM images, Figures 4.7m and 4.7n of sample N7 it can be observed that insufficient bonding, delamination and matrix cluster were noticed which could have attributed to the poor interfacial bonding strength leading to lowest flexural strength among all the samples. It can also be noticed from the test results that the addition of nanoclay concentration from 0-6 wt.% had shown gradual degradation in flexural properties of the nanocomposites.

From the above discussion, it was observed that the loss of flexural strength was mainly attributed due to the excessive reinforcement of nanoclay and the tendency for particle clumping in the matrix system. As the nanoclay concentration increases, the bonding characteristics are expected to be poor in the matrix due to the weak interaction between the matrix and the particle aggregates. These lumps act as stress concentration point and potential site for crack nucleation. This had led to restricting mobility of polymer chains under loading and thereby resulting in the reduction of flexural strength of the nanocomposite.
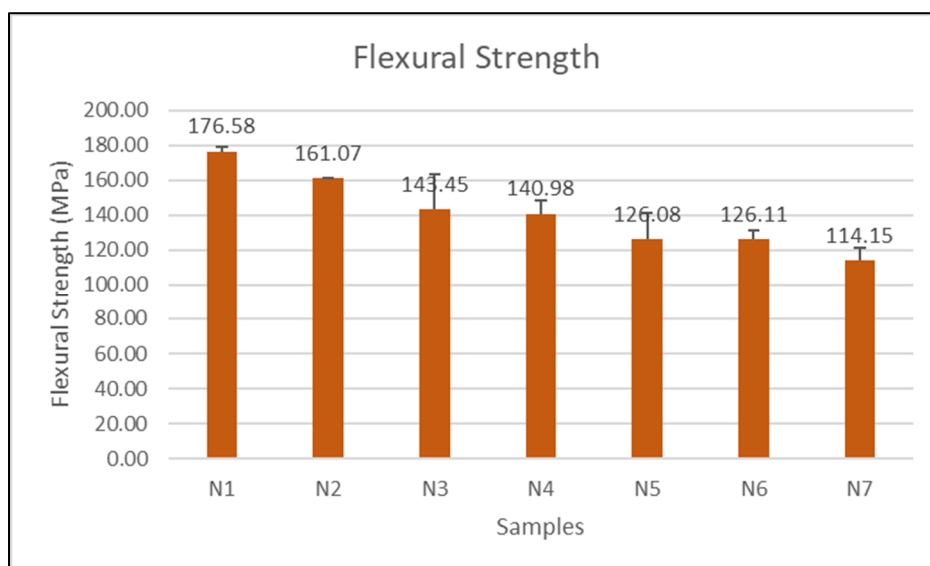
Figure 4.12: Flexural Strength Results for Nanoclay Concentration Effect

4.3.3.4 Impact Testing with the Nanoclay Concentration Effect

The impact test results for samples N1 to N7 were represented in Figure 4.13 for variation in nanoclay concentration effect. It had been observed from the impact test results that sample N7 prepared with epoxy, silane treated glass fiber and 6 wt.% of surface modified nanoclay concentration had recorded the highest impact strength of 267.03 KJ/m^2 whereas the specimen N1 prepared with epoxy and silane treated glass fiber had attained the lowest impact strength of 158.46 KJ/m^2. There was an increase of 68.5% in impact strength with the addition of 6 wt.% of surface modified nanoclay concentration. From the micrographs, Figures 4.7m and 4.7n of sample N7 it can be observed that insufficient bonding, delamination and matrix cluster were noticed, however sample N7 had attained the highest impact strength among all the other samples. On the other hand, from the micrographs Figures 4.7a and 4.7b of sample N1 it can be observed that insufficient bonding, matrix cluster and surface damage of glass fibers were noticed which could have been attributed to the drastic reduction in impact properties. It can also be observed from the impact test results that the addition of nanoclay concentration from 0-6 wt.% had shown gradual increase in impact strength of the nanocomposites but not consistently.

From the above inference, it was observed that in general the addition of nanoclay improved the absorbed energy when compared to the controlled sample. The nanoclay concentration improved the impact strength through enhanced interfacial bonding mechanism between the fiber and epoxy matrix with nanoclay by increasing the interfacial surface area of the constituents in the system and thereby increasing superficial area-volume ratio. As explained earlier in Chapter-2, based on the Faber and Evans model for the fracture toughness, the increase in fracture surface area led to the increase in fracture toughness which was also similarly reported by Ratna et. al [46]. Furthermore, it was also not possible to establish direct correlation between surface treatment, nanoclay addition and impact energy absorbed which was similarly reported by Ferreira et al. [10]. However, as the nanoclay concentration increases, the non-homogenous mixture of clay/epoxy resulted in the increased viscosity of the matrix system leading to agglomeration. This leads to processing difficulties and degassing, thereby leading to airgaps or voids which in turn acts as stress concentrators at some portion, affecting the impact properties of the nanocomposite.
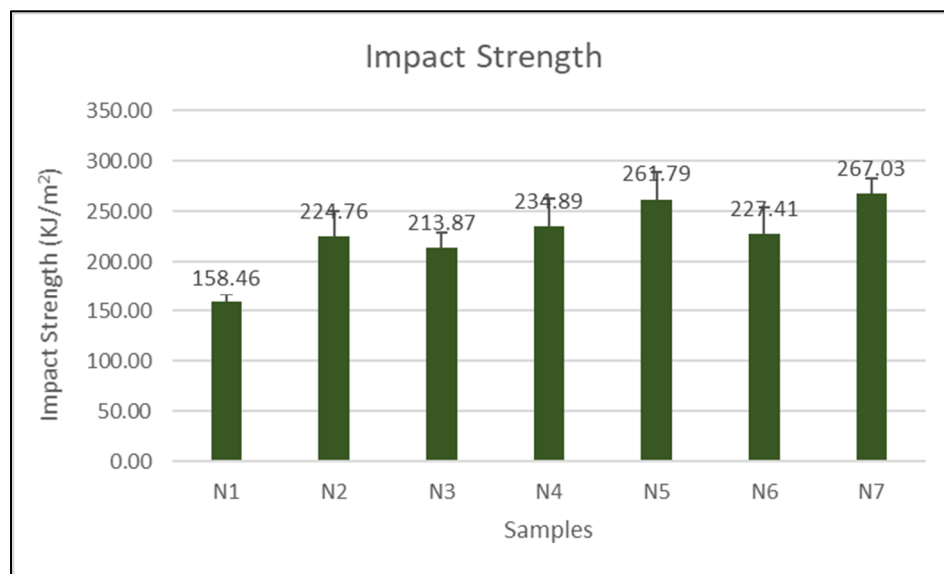

Figure 4.13: Impact Strength Results for Nanoclay Concentration Effect

Table 4.4: Mechanical Test Results for Nanoclay Concentration Effect

Sample	Description	Microhardness (HV)	Tensile Strength (MPa)	Flexural Strength (MPa)	Impact Strength (KJ/m^2)
N1	Epoxy+SGF+0% MNC	32.30	250.69	176.58	158.46
N2	Epoxy+SGF+1% MNC	47.00	319.86	161.07	224.76
N3	Epoxy+SGF+2% MNC	40.67	327.32	143.45	213.87
N4	Epoxy+SGF+3% MNC	35.20	318.68	140.98	234.89
N5	Epoxy+SGF+4% MNC	31.90	327.53	126.08	261.79
N6	Epoxy+SGF+5% MNC	28.00	340.08	126.11	227.41
N7	Epoxy+SGF+6% MNC	26.33	318.16	114.15	267.03

4.3.4 Summary of Nanoclay Concentration

An in-depth analysis related to the effect of nanoclay concentration on the epoxy composites towards the interfacial bonding strength in terms of surface hardness and mechanical properties of glass fiber reinforced polymer nanocomposites were dealt in this chapter. The vigorous finding from those analysis was to identify the effective nanoclay concentration that address the interfacial bonding strength through improved surface characteristics i.e. surface hardness with complementing other mechanical characteristics, demonstrated through the tensile, flexural and impact tests. In general, addition of nanoclay had shown improvement in surface hardness and tensile strength without compromising on flexural and impact properties but with further increase in nanoclay concentration had shown gradual decrease in surface hardness. The increase in microhardness of the nanocomposite was due to the enhancement of cross link density due to the formation of network like structure of intercalated platelets with epoxy resin molecules. With further addition of nanoclay concentration, the viscosity of the matrix increases thus making the fabrication process more difficult leading to the formation of voids. This non-uniform mixture of clay/epoxy suspension resulted in insufficient interfacial bonding which acted as stress concentrators leading to the reduction of mechanical performance in particular hardness. Nevertheless, it was revealed based on micrography and surface hardness analysis that epoxy, silane treated glass fibers with 1 wt.% of surface modified nanoclay (sample N2) had shown the most effective interfacial bonding performance in terms of surface hardness. Therefore, the threshold limit on the addition of nanoclay concentration was 1 wt. % to obtain the maximum hardness property of the nanocomposite and henceforth followed-up throughout the experiments.

4.4 Dispersion Mechanism Effect on Hardness In this section results were analysed to understand the behaviour of dispersion mechanism on the interfacial bonding in terms of surface hardness and to identify the effective dispersion mechanism. The speed for mechanical stirrer was varied between 125 rpm to 2000 rpm and the amplitude for ultrasonication process was varied in four steps between 20% to 100% where the experimental set-up and process conditions were followed according to section 3.2.5 in Chapter-3. Table 4.5 represents the mechanical test results obtained through the variation of the dispersion mechanism effect.

4.4.1 Surface Morphology Analysis

4.4.1.1 Surface Morphology Analysis for Samples using Mechanical Stirrer

Figure 4.14a and 4.14b represent the SEM images of sample D1 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay using mechanical stirrer at a speed of 125rpm. The micrograph reveals that there were clusters of matrix noticed in the composite material which could be due to the inadequate mixing of nanoclay with the epoxy resin. There were also lack of filling of matrix/bonding noticed in between the glass fibers which could be due to the increase in viscosity of the matrix material caused because of improper mixing of nanoclay in the epoxy matrix. The main reason for non-uniform dispersion could be due to the low speed of the mechanical stirrer that could not evenly disperse the nanoclay in the matrix system. There were minor surface damages noticed on the glass fibers but no signs of fragmentation of the glass fibers were observed.
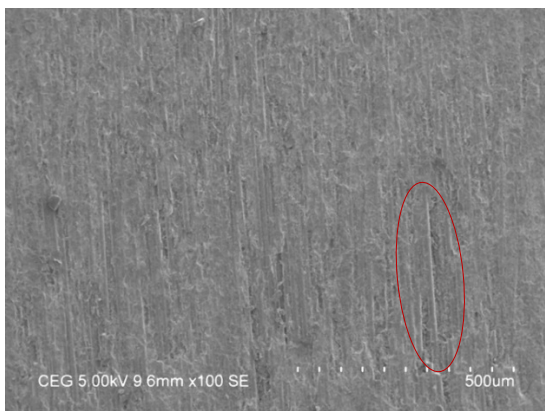

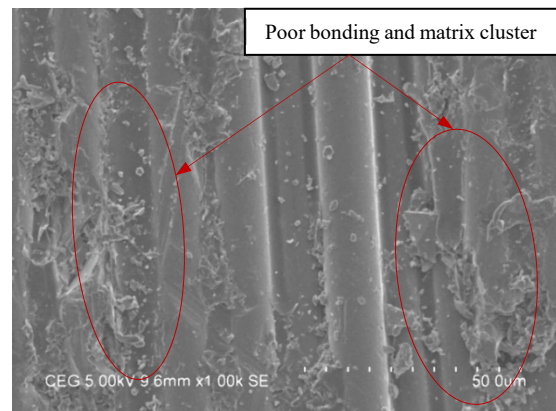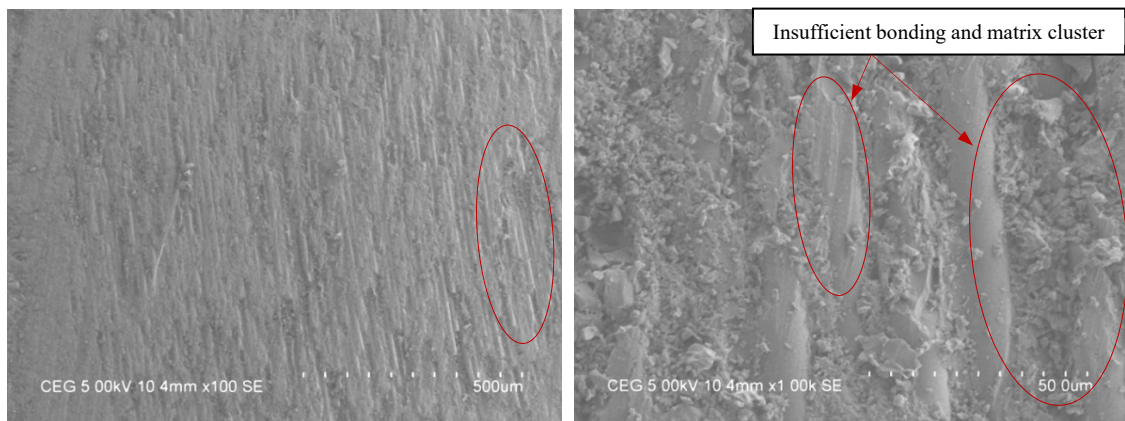**Figure 4.14a- Sample D1 (100x)**   **Figure 4.14b- Sample D1 (1000x)**

Figure 4.14c and 4.14d represent the SEM images of sample D2 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay using mechanical stirrer at a speed of 500rpm. From the micrograph it could be clearly seen that the surface of the glass fibers were damaged and fragmentation of the fibers were also noticed. The micrograph also reveals that there were clusters of matrix noticed in the composite material which could be due to the inadequate mixing of nanoclay with the epoxy resin. There were also lack of bonding noticed between the glass fibers which could be due to the insufficient mixing of nanoclay in the epoxy matrix. The main reason for non-uniform dispersion of nanoclay could be due to the lower speed of mechanical stirrer used for diffusing the nanoclay leading to the increase in viscosity of the matrix material.

Figure 4.14c- Sample D2 (100x)   **Figure 4.14d- Sample D2 (1000x)**

Figure 4.14e and 4.14f represent the SEM images of sample D3 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay using mechanical stirrer at a speed of 1000rpm. The micrograph reveals that there was minor surface damages of the glass fibers noticed and no significant break down of the glass fibers were found. In addition, clusters of matrix were not significantly noticed in the composite material. Good coupling between the glass fibers and matrix material could be observed, which could be due to the effective mixing of nanoclay into the epoxy matrix and no signs of agglomeration were noted in the micrograph.
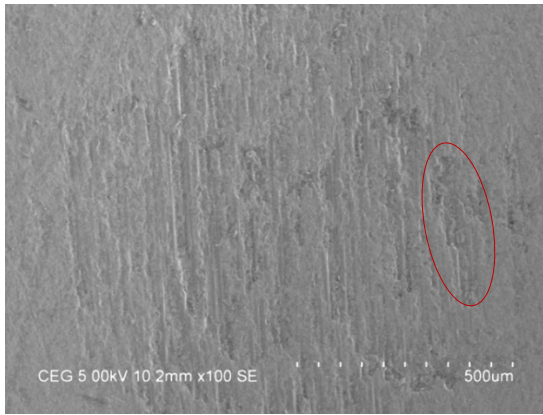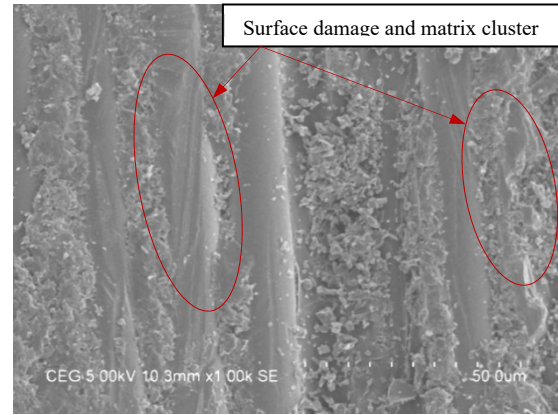
Figure 4.14e- Sample D3 (100x)   **Figure 4.14f- Sample D3 (1000x)**

Figure 4.14g and 4.14h represent the SEM images of sample D4 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay using mechanical stirrer at a speed of 2000rpm. The micrograph reveals that there was smooth blend of epoxy matrix with the glass fibers which could be due to the efficient bonding between the matrix material and glass fibers. The nanoclay distribution was uniform throughout the epoxy matrix system and no signs of agglomeration were observed. It can also be noticed that there were no clusters of epoxy matrix found which also indicates that the addition of nanoclay in epoxy matrix were effective due to the increase in the speed of the mechanical stirrer maintained during this sample preparation.
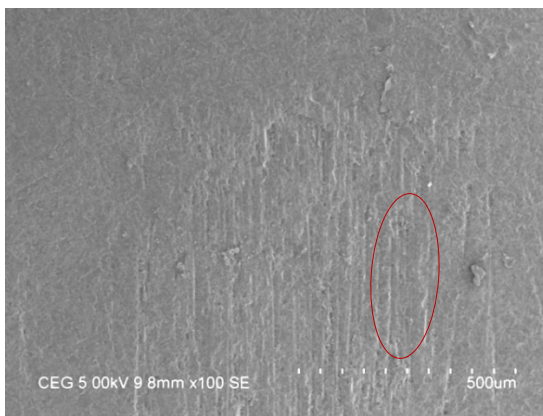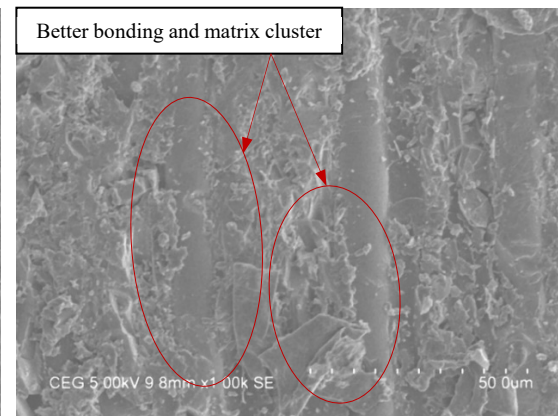

Figure 4.14g- Sample D4 (100x)   **Figure 4.14h- Sample D4 (1000x)**

4.4.1.2 Surface Morphology Analysis for Samples using Ultrasonication Process

Figure 4.14i and 4.14j represent the SEM images of sample D5 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay using ultrasonication process with 20% amplitude. The micrograph reveals that there were clusters of matrix noticed in the composite material which could be due to the inadequate mixing of nanoclay with the epoxy resin and the process of dispersing the nanoclay in matrix system was not effective. There were also lack of filling of matrix/bonding in between the glass fibers which could lead to the increase in viscosity of the matrix material because of the inadequate mixing of nanoclay in the epoxy matrix. The nanoclay distribution was not uniform throughout the epoxy matrix system and some signs of agglomeration were noted. The main reason for the insufficient bonding could be due to the inefficient dispersion of nanoclay caused mainly because of the low amplitude in the ultrasonication process.
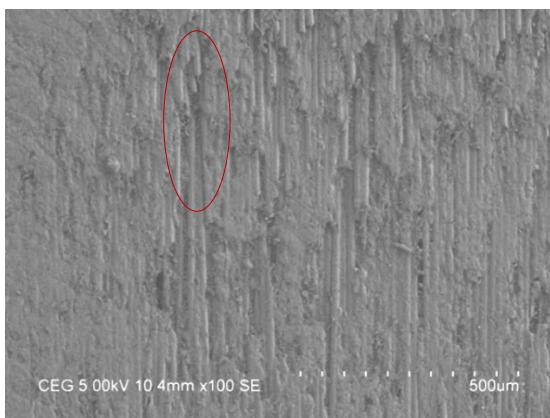

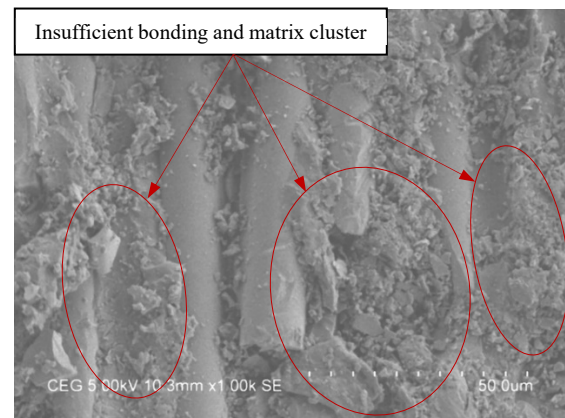**Figure 4.14i- Sample D5 (100x)**   **Figure 4.14j- Sample D5 (1000x)**

Figure 4.14k and 4.14l represent the SEM images of sample D6 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay using ultrasonication process with 40% amplitude. The micrograph reveals that there were noticeable fragmentation of glass fibers and surface damage on the glass fibers. In addition, there were clusters of matrix noticed in the composite material which could be due to the inadequate mixing of nanoclay with the epoxy resin. There were also lack of bonding in between the glass fibers occurred because of the inadequate mixing of nanoclay in the epoxy matrix and increase in viscosity of the matrix material. But the

nanoclay distribution were uniform in most of the locations and there was no significant agglomeration noticed.
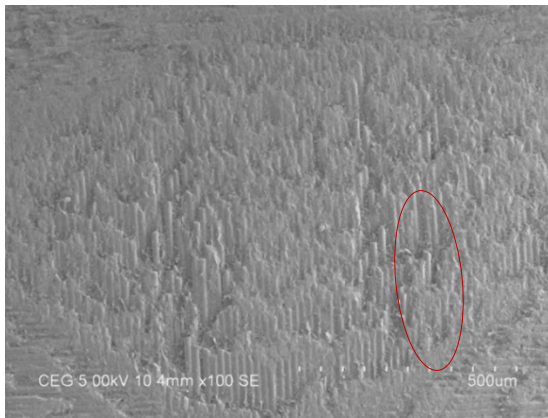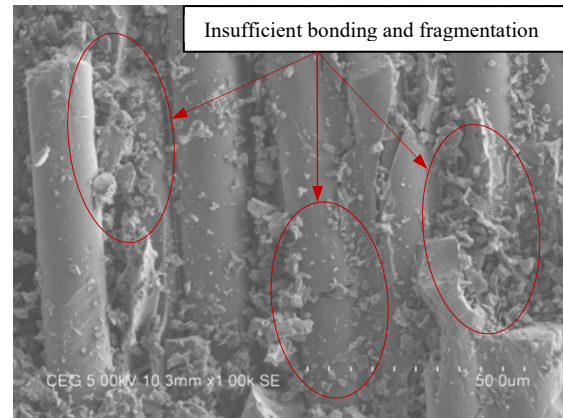

Figure 4.14k- Sample D6 (100x)

Figure 4.14l- Sample D6 (1000x)

Figure 4.14m and 4.14n represent the SEM images of sample D7 prepared with silane treated glass fibers, epoxy resin and with the addition of 1 wt.% of surface modified nanoclay using ultrasonication process with 80% amplitude. The micrograph reveals that there were noticeable breakdown of glass fibers and surface damage on the glass fibers. In addition, there were clusters of matrix noticed in the composite material which could be due to the inadequate mixing of nanoclay with the epoxy resin. There were also lack of bonding in between the glass fibers because of the inadequate mixing of nanoclay in the epoxy matrix. The nanoclay distribution were not uniform throughout the epoxy matrix system and signs of agglomeration were noted all over the composite material which also specifies that the ultrasonication process with 80% amplitude was not significant.
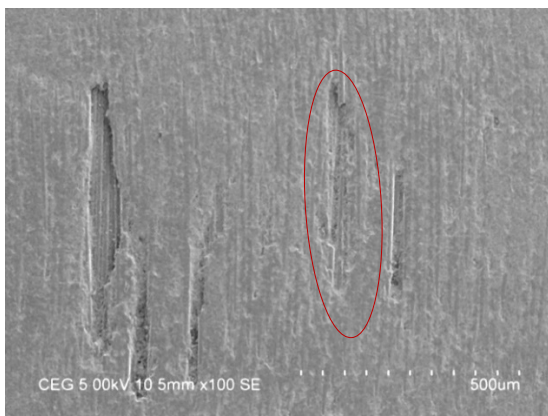

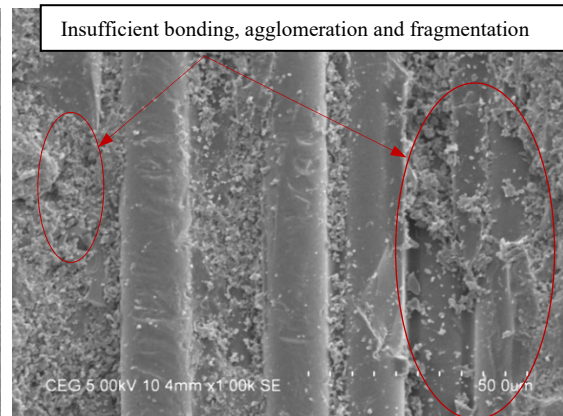**Figure 4.14m- Sample D7 (100x)**

Figure 4.14n- Sample D7 (1000x)

Figure 4.14o and 4.14p represent the SEM images of sample D8 prepared with silane treated glass fibers, epoxy resin and with 1 wt.% of surface modified nanoclay. In this sample, the amplitude of the ultrasonication process was set at 100% with a time period of 30 minutes. From the micrograph as highlighted, it was evident that there exists better bonding between glass fibers, epoxy matrix and nanoclay. It can also be noticed from the SEM images that there occurs good coupling between the glass fibers with the epoxy resin and the surface of the glass fibers were covered by epoxy matrix. The glass fibers were not fragmented and no signs of surface damage to glass fibers were observed. It was also noticed that the nanoclay has been uniformly dispersed in the epoxy matrix and no signs of agglomeration has been noticed in the epoxy resin. The micrograph also reveals that strong bonding between the fiber and matrix exists since traces of matrix were left on the glass fiber. The nanoclay clusters with nanosized diameters were found on the surface and the distance between the clusters are relatively large which was an evidence of good dispersion and exfoliation. The addition of nanoclay had contributed to significant increase in mechanical properties of tensile strength, impact strength, flexural strength and microhardness which was also due to the effective dispersion through the ultrasonication process and had also revealed an efficient load transferring between nanoparticles and matrix resin through the improvement of interfacial bonding strength.
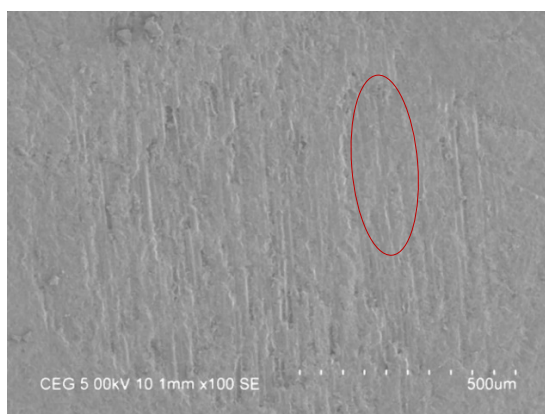

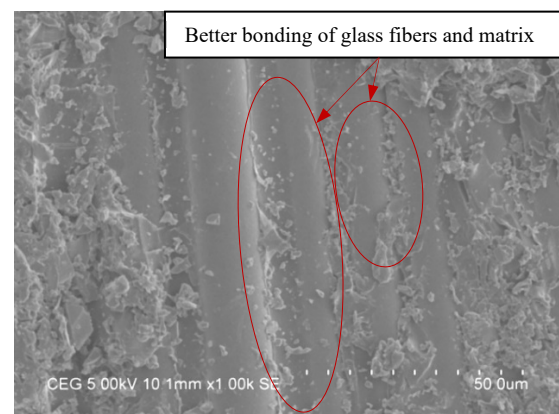**Figure 4.14o- Sample D8 (100x)**   **Figure 4.14p- Sample D8 (1000x)**

From Figures 4.15a to 4.15h it was observed from the microscopic images of the samples that in general the nanoclay distribution in the epoxy matrix was uniform and there were less or no significant agglomeration noticed in the nanocomposites depending on the dispersion process of nanoclay. For the samples prepared using ultrasonication

process with lower amplitude or by using mechanical stirrer with lesser speed there were considerable amount of fiber surface damage and fragmentation noticed. In general, it was also observed from the microscopic images that there was smooth adhesion between glass fiber and epoxy matrix in the composite. It can be concluded from the SEM analysis that epoxy resin penetrates between clay layers, some nanoclay were stripped and the orientation and structure of clay layers were changed. It was also possible to conclude that nanoclay acts as a bridge between the matrix and the reinforcing body and enhances the interfacial bonding ability. It was evident from the microscopic images that sample D8 prepared using the epoxy resin, silane treated glass fibers and with 1 wt.% of surface modified nanoclay using ultrasonication process with 100% amplitude exhibit the highest hardness and wear properties. Moreover this was further confirmed through the SEM images, revealing efficient load transfer between particle and matrix which was significantly affected by interaction and adhesion of the nanoclay particles with epoxy resin and glass fibers.
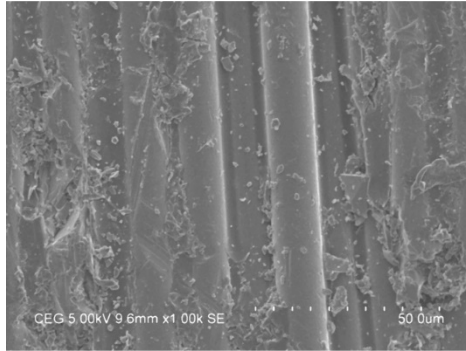
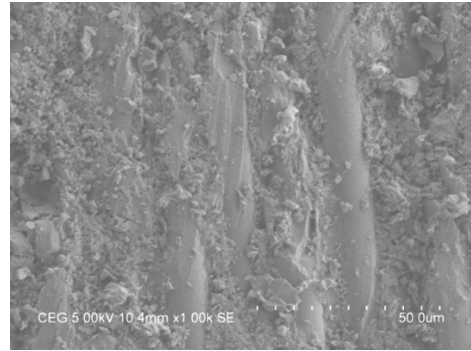**Figure 4.15a-Sample of 125rpm (D1)**
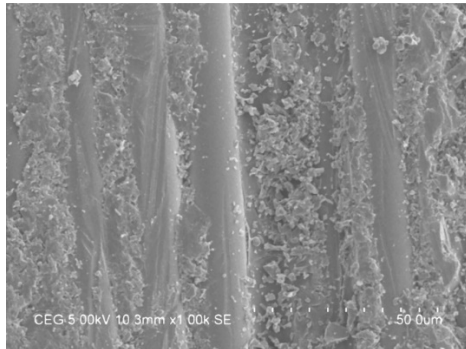

Figure 4.15b-Sample of 500rpm (D2)

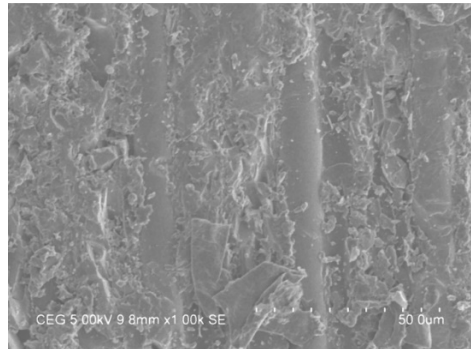**Figure 4.15c-Sample of 1000rpm (D3)**

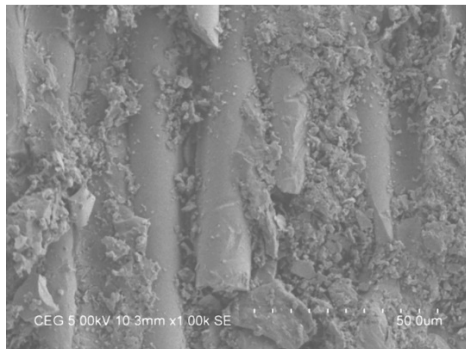**Figure 4.15d-Sample of 2000rpm (D4)**

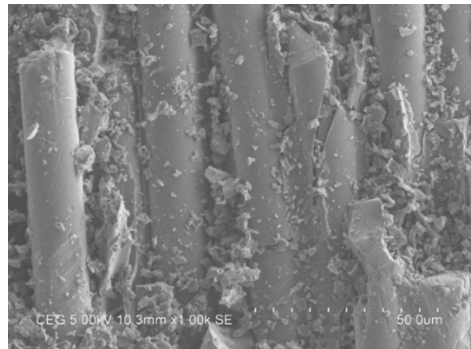**Figure 4.15e-Sample of 20% amp. (D5)**
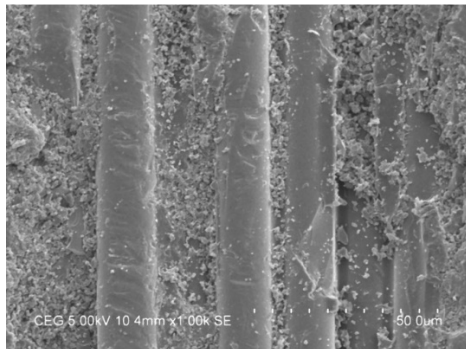

Figure 4.15f-Sample of 40% amp. (D6)
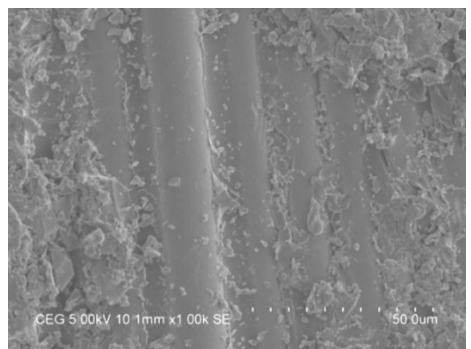

Figure 4.15g-Sample of 80% amp. (D7)

Figure 4.15h-Sample of 100% amp. (D8)

Figure 4.15a-4.15h – SEM images of Samples D1 to D8 (1000x)

4.4.2 Mechanical Testing for Dispersion Mechanism Effect

4.4.2.1 Microhardness with the Dispersion Mechanism Effect

The microhardness test results for samples D1 to D8 were represented in Figure 4.16 for dispersion mechanism effect. The test results indicated that the sample D8 using ultrasonication process with 100% amplitude had recorded the highest value of 47.00HV whereas the sample D3 using mechanical stirrer with 1000 rpm had achieved the lowest hardness of 23.93 HV. There was 96.4% increase in the hardness noticed due to the change in dispersion process from mechanical stirrer to ultrasonication. It was also noticed from the test results that the increase in the speed of mechanical stirrer did not show significant impact in the hardness of the specimen. In contrast, the increase in amplitude of the ultrasonication process had shown drastic increase in hardness value. From the microscopic images, Figure 4.14a to 4.14f and Figure 4.14i to 4.14n it was also evident that insufficient bonding, fragmentation, agglomeration, surface damage and cluster of matrix were noted in samples with either low rpm in mechanical stirring or lesser amplitude in ultrasonication process which had decreased the hardness value. In general, the samples using either the mechanical stirrer or ultrasonication, as the speed of the stirrer or amplitude increases the hardness of the specimen also increases. It could also be concluded from the hardness test results that effective dispersion of nanoclay in epoxy matrix plays a significant role in improving the interfacial adhesion between the glass fibers and epoxy matrix thereby increasing the hardness of the specimen.

From the above inference, it was observed that ultrasonication process was accompanied through heat transfer and localised heating of modified nanoclay platelets thereby providing temporary physical crosslink with the hardener. When the curing of the composite was carried out at elevated temperatures, the polymerisation of epoxy nanoparticles creates free radicals leading to an increase in cross link density at the interface formed by the nanoclay. The nanoclay acts as rigid connectors which results in better stress transfer in the system. In addition the functional group in silane through glass fiber treatment, react with inorganic clay and epoxy resin thus forming a network between nanoclay, silane and epoxy resin which enhances the interfacial bonding between the glass fiber, nanoclay and epoxy matrix. However with low speed or low amplitude, the inadequate dispersion of the nanoclay led to agglomeration which act as

stress concentration leading to the reduction in the hardness performance of the nanocomposite.
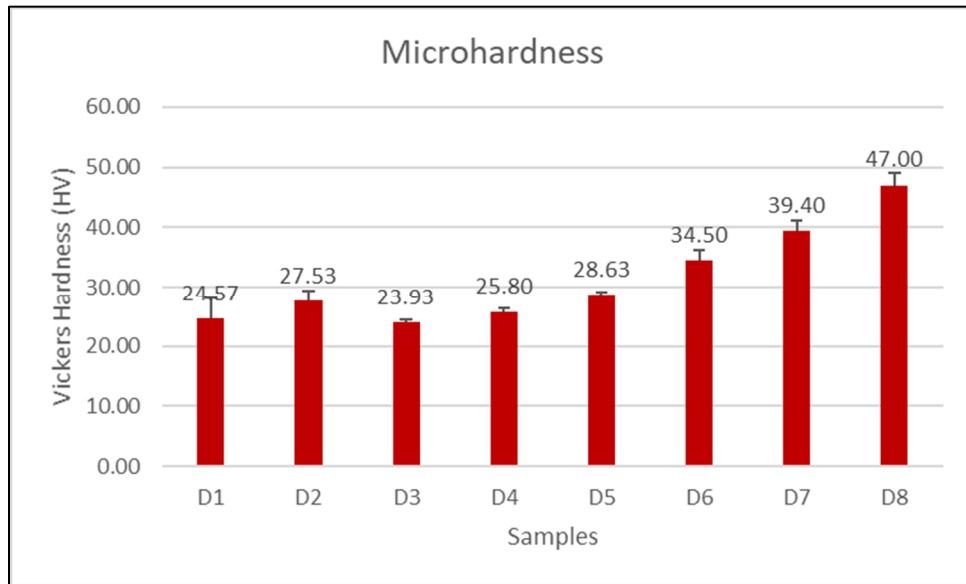

Figure 4.16: Microhardness Results for Dispersion Mechanism Effect

4.4.2.2 Tensile Testing with the Dispersion Mechanism Effect

The tensile test results for samples D1 to D8 were represented in Figure 4.17 for variation in dispersion mechanism effect. It had been observed from the test results that sample D3 prepared with epoxy, silane treated glass fiber and 1 wt.% of surface modified nanoclay using mechanical stirrer with 1000rpm had recorded the highest tensile strength of 388.51 MPa, whereas the sample D5 prepared using ultrasonication process with 20% amplitude had attained the lowest tensile strength of 301.71 MPa. There was an increase of 28.8% in tensile strength when comparing samples D3 and D5. From the SEM images, Figure 4.14e and 4.14f of sample D3, it can be observed that there exists good coupling between epoxy, glass fibers and nanoclay which could have attributed to the maximum tensile strength. From the SEM images, Figure 4.14i and 4.14j of sample D5 it was observed that lack of filling of matrix/bonding in between the glass fibers, nanoclay distribution was not uniform throughout the epoxy matrix system and some signs of agglomeration were noted, leading to the lowest tensile strength among all samples. It can also be noticed from the tensile test results that there was gradual increase in tensile strength through the variation in dispersion mechanisms of nanoclay in

particular when the amplitude of the ultrasonication process is being increased. From these test results, it can be concluded that effective nanoclay dispersion plays a vital role in the tensile strength of the specimen.

From the above discussion, it was noticed that effective dispersion of nanoclay particles through appropriate mechanism acted as an interface material between the fiber and the matrix resulting in the improvement on the mechanical performance of the nanocomposite. The uniformly dispersed nanoparticles modified the composite by improving the wettability of glass fiber and the polymer matrix which further act as a bridge between the glass fiber and epoxy thereby enhancing the interfacial adhesion between the epoxy resin and glass fiber. This has led to the restricting mobility of the polymer chain under loading, resulting in improved tensile strength. On the other hand, if the dispersion of nanoparticles were not effective then nanoclay clustering occurs leading to agglomeration effect. This agglomeration contributed to creation of stress concentration at various location in the laminated plates leading to the reduction in tensile strength.
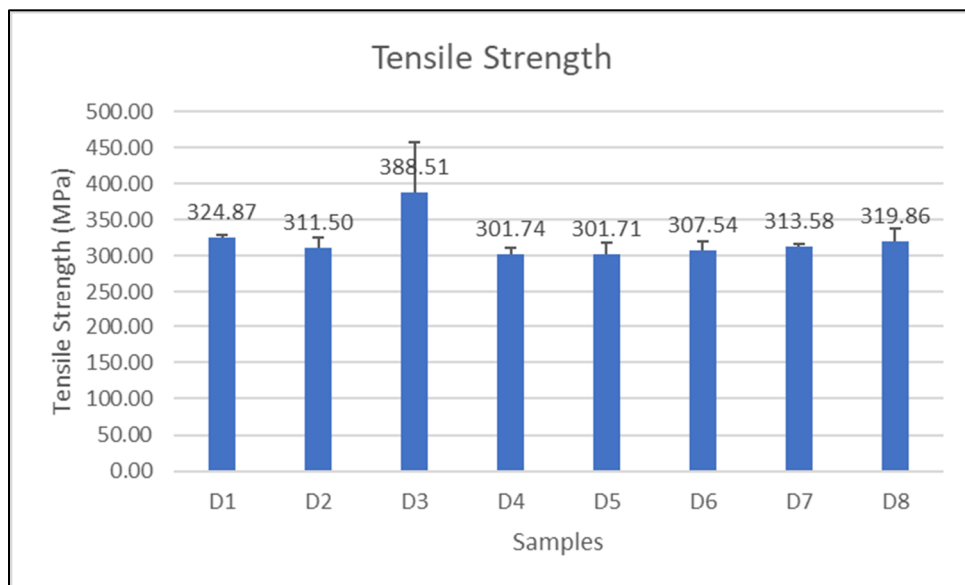

Figure 4.17: Tensile Strength Results for Dispersion Mechanism Effect

4.4.2.3 Flexural Testing with the Dispersion Mechanism Effect

The flexural test results for samples D1 to D8 were represented in Figure 4.18 for variation in dispersion mechanism effect. It had been observed from the flexural test results that sample D3 prepared with epoxy resin, silane treated glass fiber and 1 wt.% of surface modified nanoclay using mechanical stirrer at 1000 rpm had recorded the highest flexural strength of 193.96 MPa whereas the sample D4 prepared with silane treated glass fiber/epoxy system and 1 wt. % of surface modified nanoclay using mechanical stirrer at 2000rpm had achieved the lowest flexural strength of 148.77 MPa. There was 23.3% reduction of flexural properties from sample D3 to D4. From the SEM images, Figure 4.14e and 4.14f of sample D3, it has been observed that good coupling exists between the glass fibers and matrix material. The micrograph also revealed that there was only minor surface damages of the glass fibers noticed and no significant break down of the glass fibers were found which could have attributed to the maximum flexural strength. From the SEM images, Figure 4.14g and 4.14h of sample D4, it can be observed that smooth blend of epoxy matrix with the glass fibers exists which could be due to the efficient bonding between the matrix material and glass fibers. The nanoclay distribution was uniform throughout the epoxy matrix system and no signs of agglomeration were observed.

From the mechanical test results it can be observed that effective dispersion of nanoclay particles had improved the interfacial mobility through the enhancement of fiber/matrix adhesion which had contributed to the increase in flexural strength. In addition, the silane treatment of glass fiber also act as a bridge thereby providing mechanical interlocking as well as chemical bonding between the glass fiber, epoxy and the nanoparticles which in turn tailored the flexural strength of the composite. However, the nanoclay particles aids in filling up the cavities, if uniform dispersion is not achieved, then it acts as stress concentrators thereby reducing the flexural properties of the nanocomposite.
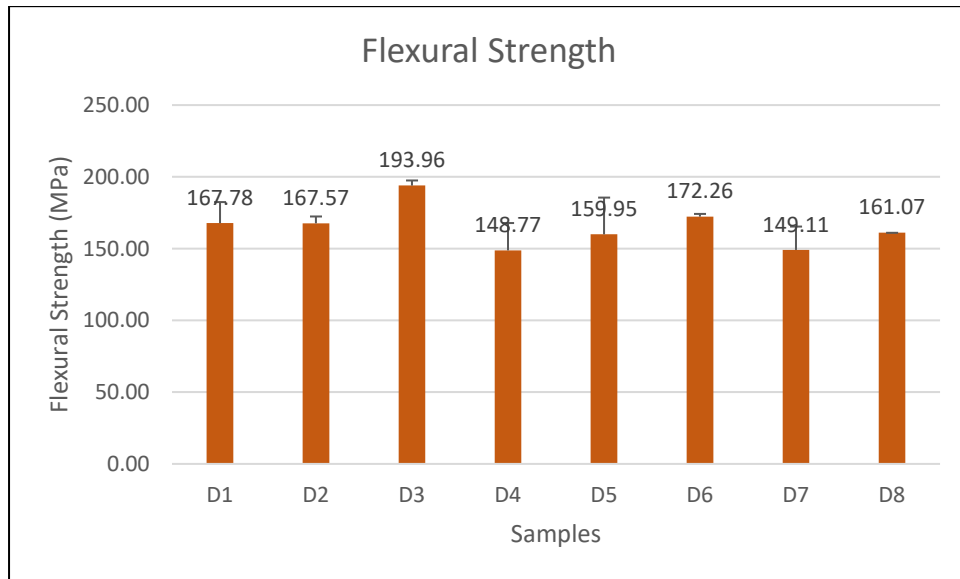
Figure 4.18: Flexural Strength Results for Dispersion Mechanism Effect

4.4.2.4 Impact Testing with the Dispersion Mechanism Effect

The impact test results for samples D1 to D8 were represented in Figure 4.19 for variation in dispersion mechanism effect. It had been observed from the impact test results that sample D1 prepared using epoxy resin, silane treated glass fiber and 1 wt.% of surface modified nanoclay using mechanical stirrer at 125 rpm had recorded the highest impact strength of 245.70 KJ/m^2, whereas the sample D4 prepared with silane treated glass fiber/epoxy system with 1 wt. % of surface modified nanoclay using mechanical stirrer at 2000rpm had achieved the lowest impact strength of 175.65 KJ/m^2. There was a reduction of 28.5% decrease in impact strength from sample D1 to D4. From the SEM images, Figure 4.14a and 4.14b of sample D1, it had been observed that lack of filling of matrix/bonding occurs between the glass fibers and minor surface damages were also noticed on the glass fibers but no signs of fragmentation on glass fibers were noticed. In spite of the defects observed, the impact test results had shown to be the maximum among all samples. From the SEM images, Figure 4.14g and 4.14h of sample D4, it has been observed that sufficient bonding exists between the epoxy, glass fibers and nanoclay. In spite of the improved bonding strength, the impact strength had been lowest among all the samples. It has also been observed from the impact test results that as the speed of the mechanical stirrer increases or amplitude of the

ultrasonication process increases the impact strength had not shown significant variation.

The above inference indicates in general that there is no significant trend noticed from the experimental test results. But with ultrasonication process it was observed that the impact properties are almost consistent. The impact strength behaviour can be explained through the Faber and Evan model as discussed in the previous section. When a growing crack meets nanoclay the crack gets deflected out of plane and when the crack propagates further and reaches further nanoclay, it gets twisted and tilted thereby increasing the fracture surface area leading to increased fracture toughness which was similarly reported by Ratna et. al [46]. In this observation even if the nanoclay particles are not uniformly dispersed due to lower speed or amplitude, and if the growing crack meets the nanoclay it gets deflected out of plane thereby increasing the impact strength. Furthermore, it is also not possible to establish an unequivocal relationship between surface treatment, nanoclay dispersion and impact energy absorbed which was similarly reported by Ferreira et al. [10].
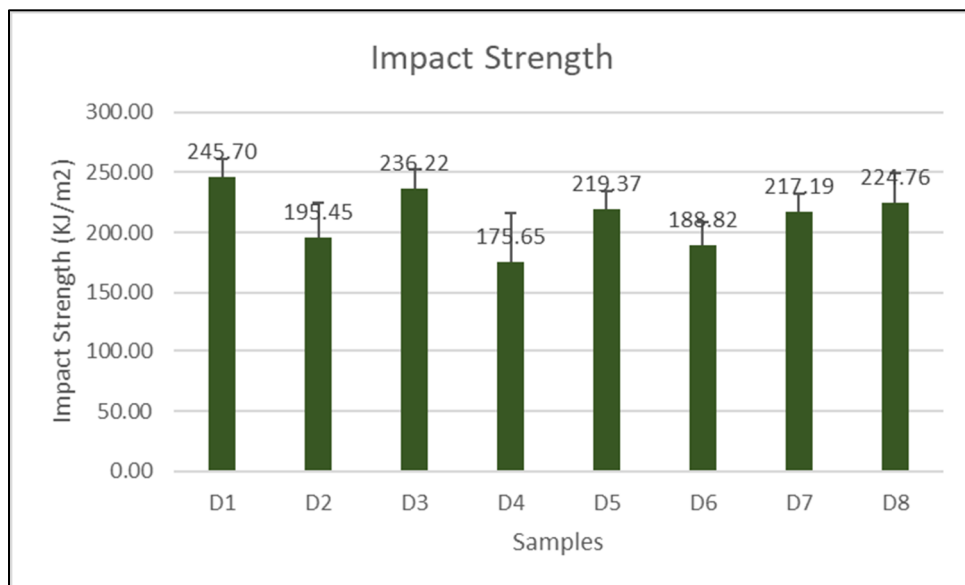

Figure 4.19: Impact Strength Results for Dispersion Mechanism Effect

Table 4.5:Mechanical Test Results for Effect of Variation in Dispersion Mechanism

Sample	Description	Mechanism	Parameters	Micro hardness (HV)	Tensile Strength (MPa)	Flexural Strength (MPa)	Impact Strength (KJ/m²)
D1	Epoxy+SGF+1% MNC	Mech. Stirrer	30 mins/125 rpm	24.57	324.87	167.78	245.70
D2	Epoxy+SGF+1% MNC	Mech. Stirrer	30 mins/500 rpm	27.53	311.50	167.57	195.45
D3	Epoxy+SGF+1% MNC	Mech. Stirrer	30 mins/1000 rpm	23.93	388.51	193.96	236.22
D4	Epoxy+SGF+1% MNC	Mech. Stirrer	30 mins/2000 rpm	25.80	301.74	148.77	175.65
D5	Epoxy+SGF+1% MNC	Ultrasonication	30 mins/20% Amp	28.63	301.71	159.95	219.37
D6	Epoxy+SGF+1% MNC	Ultrasonication	30 mins/40% Amp	34.50	307.54	172.26	188.82
D7	Epoxy+SGF+1% MNC	Ultrasonication	30 mins/80% Amp	39.40	313.58	149.11	217.19
D8	Epoxy+SGF+1% MNC	Ultrasonication	30 mins/100% Amp	47.00	319.86	161.07	224.76

4.4.3   Summary of Dispersion Mechanism

In this section 4.4, experimental analysis related to the effect of dispersion mechanism for nanoclay addition in the epoxy matrix towards the interfacial bonding in terms of surface hardness and mechanical properties of glass fiber reinforced polymer nanocomposites were discussed. The vital finding from those analysis is to identify the effective dispersion mechanism that address the interfacial bonding characteristics through improved surface characteristics i.e. surface hardness with complementing other mechanical characteristics, demonstrated through the tensile, flexural and impact tests. In general, samples prepared using ultrasonication process exhibit better tensile strength and hardness properties without compromising on flexural and impact properties. Nevertheless, it is revealed that based on the micrography and surface hardness analysis, dispersion process using ultrasonication with 100% amplitude sample (D8) had shown the most effective interfacial bonding performance in terms of surface hardness. Therefore, silane treated glass fiber with surface modified nanoclay utilising ultrasonication process with 100% amplitude was considered the effective dispersion mechanism and followed throughout the experiments.

During the dispersion mechanism of nanoclay particles due to the localised heating and through the heat transfer, temporary physical crosslink arises with the hardener. In addition to the dispersion process when the composite undergoes thermal cycle during post curing process, the polymerisation of epoxy nanoparticles creates free radicals

leading to an increase in cross link density at the interface formed by the nanoclay. The nanoclay particles being rigid connectors results in better stress transfer and increases the load carrying capacity of the nanocomposite. In addition, the functional group in silane react with inorganic clay and epoxy resin thus forming a network between nanoclay, silane and epoxy resin which enhances the interfacial bonding strength between the glass fibers, epoxy matrix and nanoclay. However if inadequate dispersion of the nanoclay arises due to the low speed of mechanical stirrer or lower amplitude of the ultrasonication process, agglomeration occurs which as a source of stress concentration lead to the reduction in mechanical performance of the nanocomposite.

4.5 Curing Temperature and Curing Time Influence on Hardness

In this section results were analysed to understand the behaviour of curing temperature and curing time influence on the interfacial bonding in terms of surface hardness and also to identify the effective curing temperature and curing time. The curing temperature was varied between 25°C to 125°C at an interval of 25°C for a period of 30 minutes and the curing time was varied for 30 minutes, 120 minutes and 480 minutes at curing temperature of 100°C where the experimental set-up and process conditions were followed according to section 3.2.6 in Chapter-3. The mechanical test results attained through the variation of curing temperature are presented in Table 4.6 and for variation in curing time are presented in Table 4.7.

4.5.1 Surface Morphology Analysis Surface Morphology Analysis for Influence of Curing Temperature

Figure 4.20a and 4.20b represent the SEM images of sample T1 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 25°C for 30 minutes. The micrographs reveal that there exists insufficient bonding between the glass fibers and epoxy matrix. In addition, there were clusters of matrix noticed in the composite material which could be due to the inadequate temperature for curing that attribute to the increase in viscosity of the matrix material. There were fragmentation of glass fibers noticed in the nanocomposite which could be due to the brittle nature of the fibers.
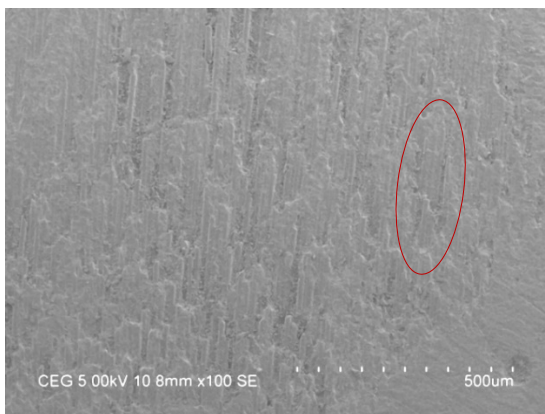

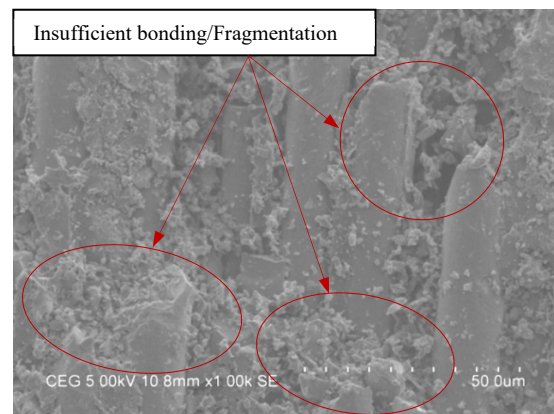**Figure 4.20a- Sample T1 (100x)**   **Figure 4.20b- Sample T1 (1000x)**

Figure 4.20c and 4.20d show the SEM images of sample T2 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 50°C for a time period of 30 minutes. The micrographs reveal that there were severe fragmentation and surface damage noticed on the glass fibers. There was also inadequate bonding between matrix and glass fibers due to the insufficient temperature maintained during curing period of the composite. It can also be noticed that clusters of matrix exist in the composite material which could be due to the unsatisfactory mixing of nanoclay with the epoxy resin.
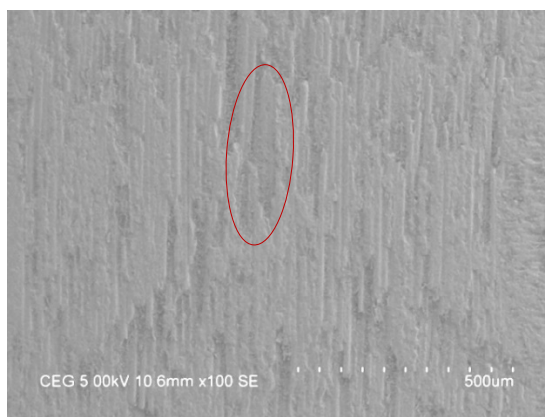

Figure 4.20c- Sample T2 (100x)   **Figure 4.20d- Sample T2 (1000x)**

Figure 4.20e and 4.20f illustrate the SEM images of sample T3 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 75°C for a time period of 30 minutes. The micrograph images reveal that there was an improvement in the interfacial bonding between the glass fibers and epoxy matrix when compared to sample T1 and T2. There were no signs of fragmentation of glass fiber noticed even though there were some surface damages of the glass fibers. The bonding between the glass fibers and matrix was smoothly blended and the amount of matrix clusters were reduced due to the effective mixing of nanoclay in the epoxy and due to the increase in the curing temperature of the glass fibers and epoxy matrix.
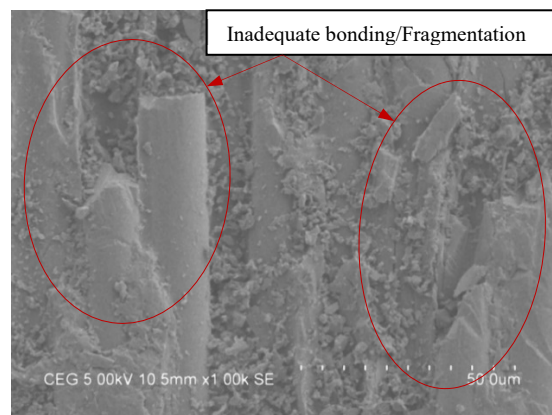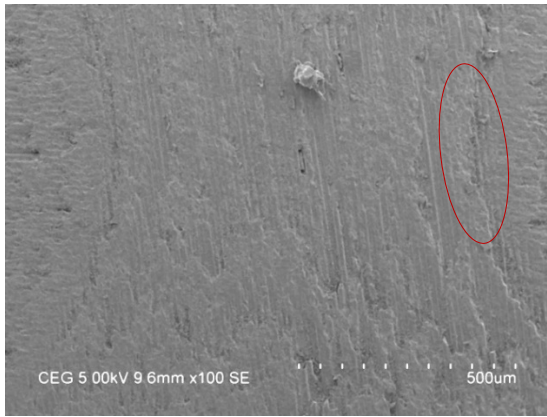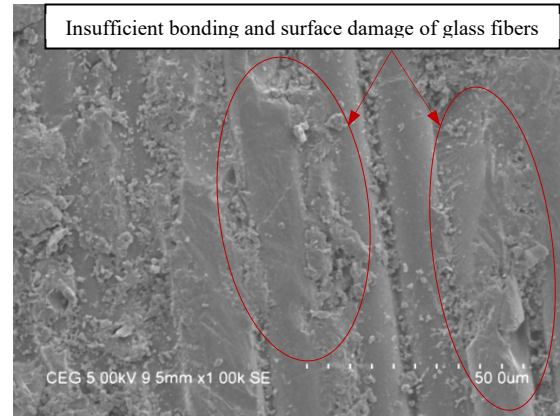
Figure 4.20e- Sample T3 (100x)   **Figure 4.20f- Sample T3 (1000x)**

Figure 4.20g and 4.20h depict the SEM images of sample T4 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 100°C for a time period of 30 minutes. The micrograph reveals that there exists better bonding between the glass fibers and epoxy matrix. The bonding between the glass fibers and epoxy matrix were smooth and no signs of agglomeration were noticed. In addition, there were no signs of surface damage and fragmentation of glass fibers in the nanocomposite. The increase in the curing temperature had shown significant improvement in the interfacial bonding of the glass fibers and matrix and no signs of agglomeration were noted.

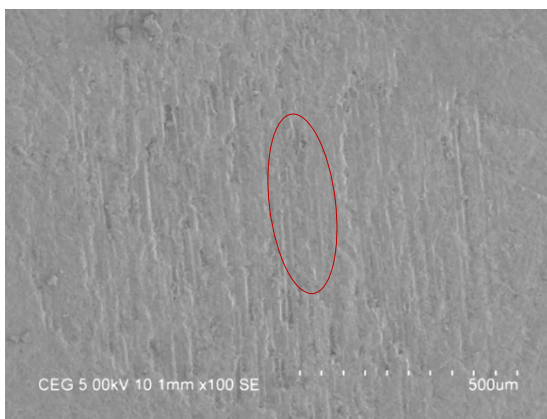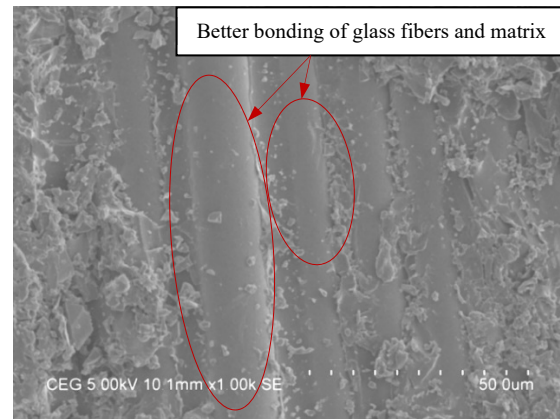**Figure 4.20g- Sample T4 (100x)**   **Figure 4.20h- Sample T4 (1000x)**

Figure 4.20i and 4.20j characterize the SEM images of sample T5 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 125°C for a time period of 30 minutes. The micrograph reveals that there exists insufficient bonding between the glass

fibers and epoxy matrix. There were clusters of matrix and fragmented glass fibers noticed in the composite material. It could be due to the increase in the curing temperature of the matrix material that caused the fragmentation of glass fibers and epoxy matrix. But the nanoclay distribution was uniform throughout the epoxy matrix system and no signs of agglomeration were noted in the nanocomposite.
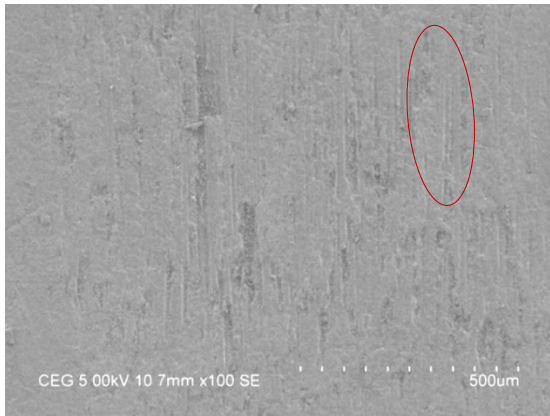
| **Figure 4.20i- Sample T5 (100x)** | **Figure 4.20j- Sample T5 (1000x)** |
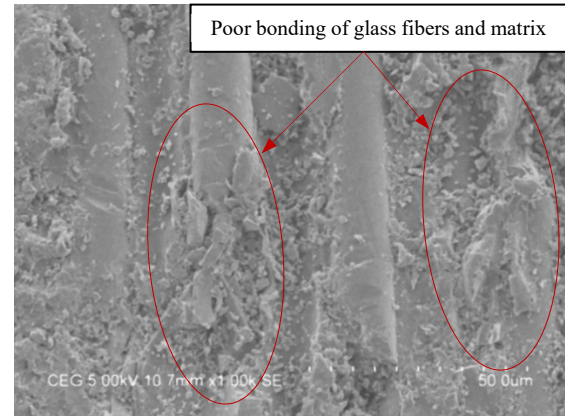
From the SEM images 4.21a to 4.21e it has been observed that for lowest as well as highest curing temperature there was an increase in fragmentation of glass fibers and lack of filling of matrix between the glass fibers. There also exists poor interfacial bonding between the glass fibers and epoxy for lowest and highest curing temperature. According to phenomenon of the fibers splitting and pulled-off, it can be concluded that the composites fabricated at moderate curing temperature at 75°C to 100°C have a better interface properties with a higher bonding strength. It can be observed that the grooves of the matrix were straight and their surfaces were smooth at 75°C and 100°C respectively. This phenomenon can be explained by the anisotropic thermal expansion coefficient of the glass fibers and the better liquidity of epoxy matrix at moderate temperature. During the fabrication process, the fibers would produce thermal deformation and are curved accompanied by the distorted grooves. Furthermore, due to the more sufficient wettability of the fibers, the thickness of the matrix between adjacent fibers are significantly enlarged with the increasing of curing temperature which were also similarly reported by Liu et. al [55].
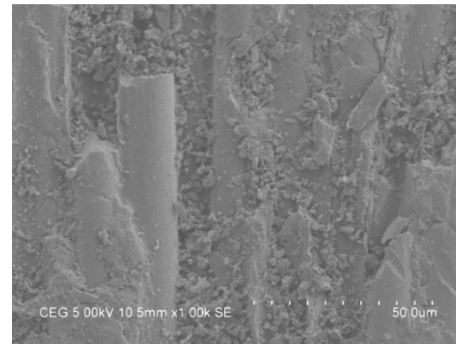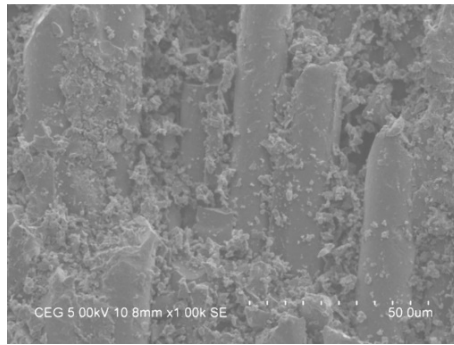
Figure 4.21a-Sample of 25ºC/30mins(T1) Figure 4.21b-Sample of 50ºC/30mins(T2)
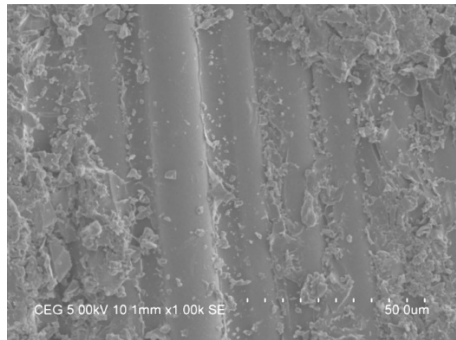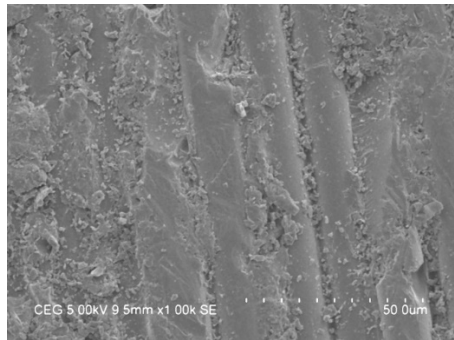
Figure 4.21c-Sample of 75ºC/30mins(T3) Figure 4.21d-Sample of 100ºC/30mins(T4)
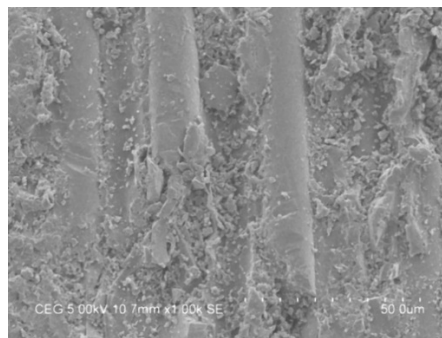
Figure 4.21e-Sample of 125ºC/30mins(T5)

Figure 4.21a-4.21e – SEM images of Samples T1 to T5 (1000x)

4.5.1.2 Surface Morphology Analysis for Influence of Curing Time Figure 4.22a and 4.22b depict the SEM images of sample C1 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 100ºC for a curing time of 30 minutes. The micrograph reveals that there exists improved bonding between the glass fibers and epoxy matrix. The bonding between the glass fibers and epoxy matrix were smooth and no signs of agglomeration were noticed. In addition, there were no signs of surface damage and fragmentation of glass fibers in the nanocomposite. The curing time of 30 minutes had shown

substantial improvement in the interfacial bonding characteristics of the glass fibers and matrix and no signs of agglomeration were noticed.
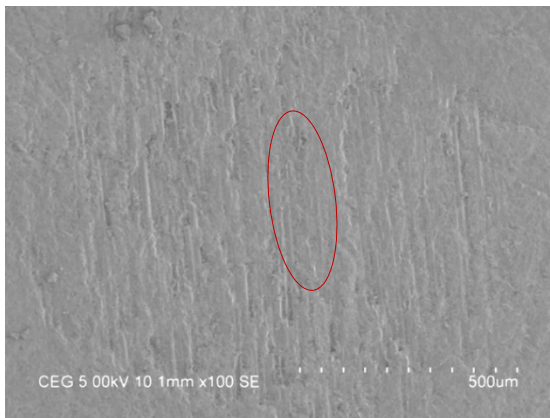
Figure 4.22a- Sample C1 (100x)   **Figure 4.22b- Sample C1 (1000x)**

Figure 4.22c and 4.22d represent the SEM images of sample C2 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 100°C for a curing time of 120 minutes. The micrograph reveals that there exists poor interfacial bonding between the glass fiber and epoxy matrix. The epoxy matrix has been delaminated from the glass fibers and shattered in pieces but no signs of surface damage of fibers were observed. It can also be noticed from the microscopic images that fragmentation of glass fibers were found. The delamination, fragmentation and surface damage noticed in the nanocomposite could be due to the increase in the curing time of the nanocomposite during the fabrication process.
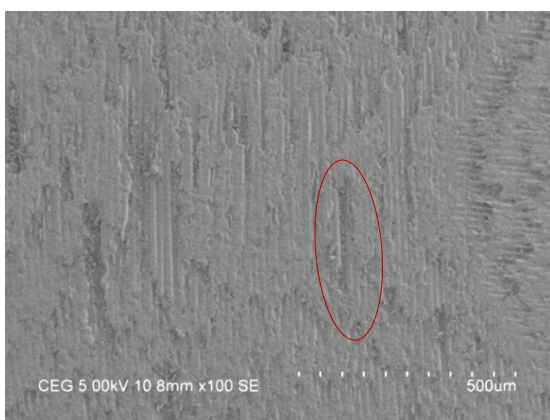
Figure 4.22c- Sample C2 (100x)   **Figure 4.22d- Sample C2 (1000x)**
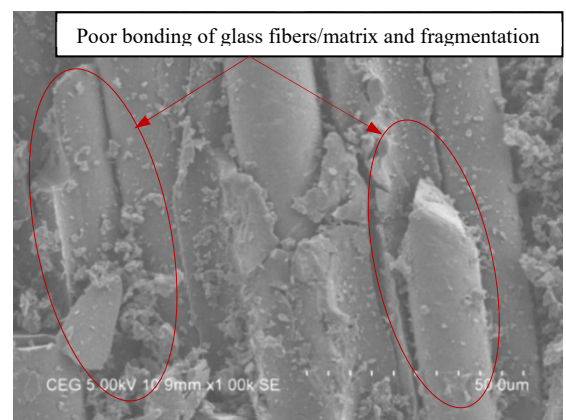
Figure 4.22e and 4.22f represent the SEM images of sample C3 prepared with epoxy resin, silane treated glass fibers with the addition of 1 wt. % of surface modified nanoclay where the curing temperature was maintained at 100°C for a curing time of 480 minutes. The images reveal that there was lack of bonding between glass fibers and epoxy matrix. It was also observed from the images that clusters of matrix were noticed in the composite material which could be due to the inadequate mixing of nanoclay with the epoxy resin. There were also lack of filling of matrix/bonding in between the glass fibers which could be due to the increase in viscosity of the matrix material caused because of insufficient mixing of nanoclay in the epoxy matrix. The lack of filler material and insufficient bonding could be due to the drastic increase in the curing time of the nanocomposite.
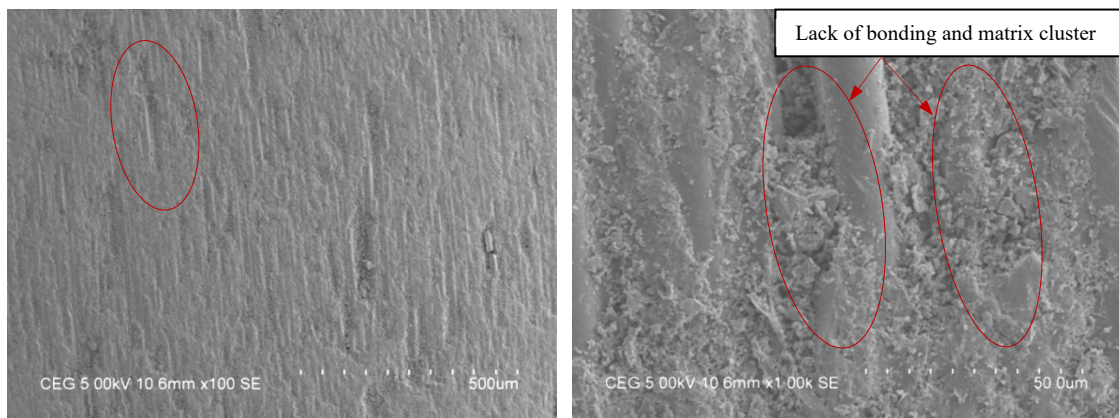
Figure 4.22e- Sample C3 (100x)   **Figure 4.22f- Sample C3 (1000x)**

From the SEM images 4.23a to 4.23c it has been observed that at higher curing time there was an increase in fragmentation of glass fibers and lack of filling of matrix in between the glass fibers. It has also been observed that at higher curing time there exists poor interfacial bonding between the glass fibers and epoxy matrix. As discussed in the previous section, during the fabrication process in particularly at longer curing period, the fibers would undergo thermal deformation and were curved accompanied by the distorted grooves. Furthermore, it was also observed from the literature review that longer curing time could be reduced by high cooling rate and de-molding temperature, however these methods leads to generation of internal stress between the layers of nanocomposites which should be incorporated in selection or design of appropriate post curing temperature and curing time which was also similarly reported by Charlotte et. al [57].
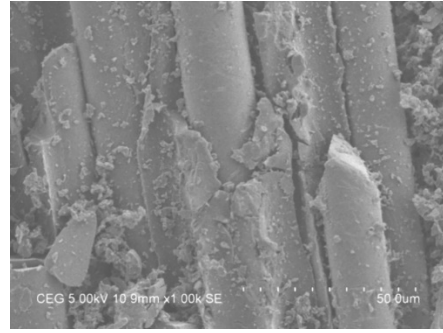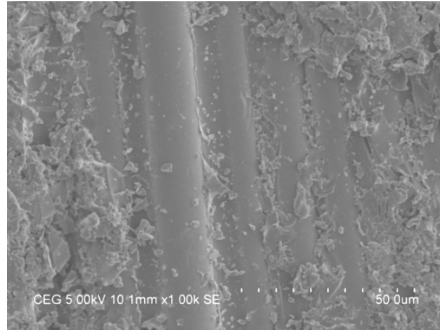
Figure 4.23a-Sample of 100ºC/30mins(C1) Figure 4.23b-Sample of 100ºC/120mins(C2)

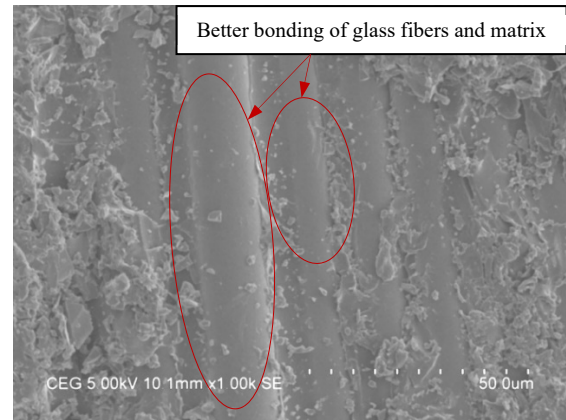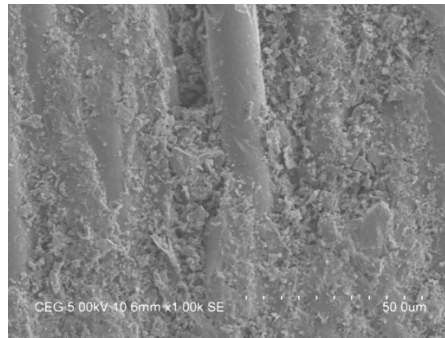**Figure 4.23c-Sample of 100ºC/480mins(C3)**

Figure 4.23a-4.23c – SEM images of Samples C1 to C3 (1000x)

4.5.2 Mechanical Testing for Curing Temperature and Time Effect

4.5.2.1 Microhardness with the Curing Temperature and Time Effect

The microhardness results for glass fiber reinforced nanocomposites are presented in Figure 4.24a for variation in curing temperature and in Figure 4.24b for variation in curing time.

For curing temperature effect, the test results indicated that the sample T1 with curing temperature of 25ºC with 30 mins had achieved the lowest hardness of 20.60 HV, whereas the sample T4 with curing temperature of 100ºC had recorded the highest value of 47.00HV, an increase by 128.2% from T1 to T4. It was also observed that the hardness value increased gradually as the curing temperature increased until 100ºC, but the hardness tends to decline with further increase of temperature. The above findings were also evident from the SEM images, Figure 4.20a to 4.20j where insufficient bonding, fragmentation and cluster of matrix were evident in samples T1, T2, T3 and T5 whereas

the sample T4 had shown better interfacial bonding between epoxy matrix and glass fibers resulting in better hardness properties.

Figure 4.24a: Microhardness Results for Curing Temperature Effect

For curing time effect, the test results indicate that the sample C1 with curing time of 30 minutes had recorded the highest hardness of 47.00 HV whereas the sample C3 with curing time of 480 mins had achieved the lowest hardness of 42.13 HV, a decrease of 11.6% in hardness from sample C1 to C3. Thus, as the curing time increased the hardness decreased. Nevertheless, microscopic images of Figure 4.22a to 4.22f had shown that as the curing time increased the fragmentation and insufficient bonding between the glass fiber and epoxy matrix also increased.
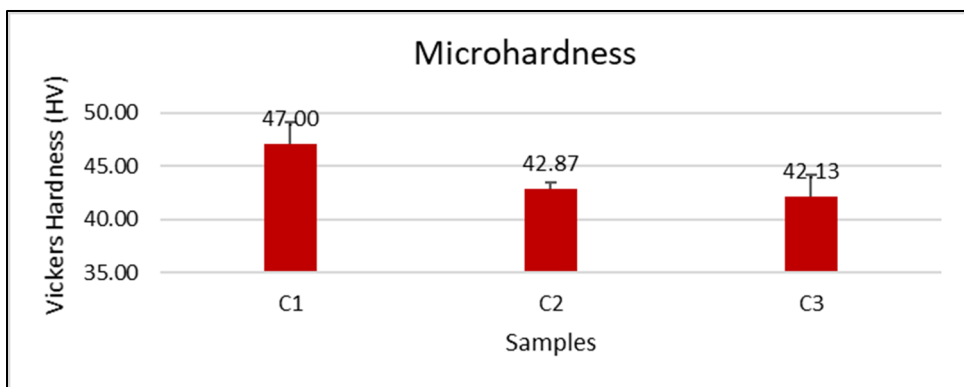
Figure 4.24b: Microhardness Results for Curing Time Effect

From the above discussion, it can be noticed that the hardness properties are greatly influenced by the curing temperature and curing time. As the curing temperature of the specimen increases the viscosity of the matrix reduces thereby increasing the wettability of the glass fibers with epoxy matrix. This in turn increases the interfacial properties thereby enhancing the interfacial bonding strength. In addition, the nanoclay aids in the improvement of the mechanical performance through the filling up the cavity which in turn reduces the stress concentration and the increase in hardness was due to the formation of network like structure of intercalated platelets with the epoxy resin that restricts the indentation. However, when the curing temperature or the curing time was increased beyond the curing temperature of 100ºC and with curing time of 30 minutes there occurs degradation in mechanical performance with severe damages to the epoxy and the resin. It was concluded that appropriate curing temperature and time need to be maintained to achieve the curing process to be complete.

4.5.2.2 Tensile Testing with the Curing Temperature and Time Effect

The tensile test results for glass fiber reinforced nanocomposites are presented in Figure 4.25a for variation in curing temperature and in Figure 4.25b for variation in curing time.

For curing temperature effect, the test results indicated that the sample T2 with curing temperature of 50ºC with 30mins had achieved the highest tensile strength of 345.38 MPa whereas the sample T4 with curing temperature of 100ºC had recorded the lowest value of 319.86 MPa. There was 7.9% decrease in the tensile strength noticed due to the increase in curing temperature from 50ºC to 100ºC. It was also noticed that as the curing temperature increased the tensile strength decreased gradually. From the microscopic images, Figure 4.20a to 4.20j it is observed that insufficient bonding, fragmentation and cluster of matrix were noted in the samples T1, T2, T3 and T5 whereas micrograph of sample T4 had shown better bonding between epoxy matrix and glass fibers.
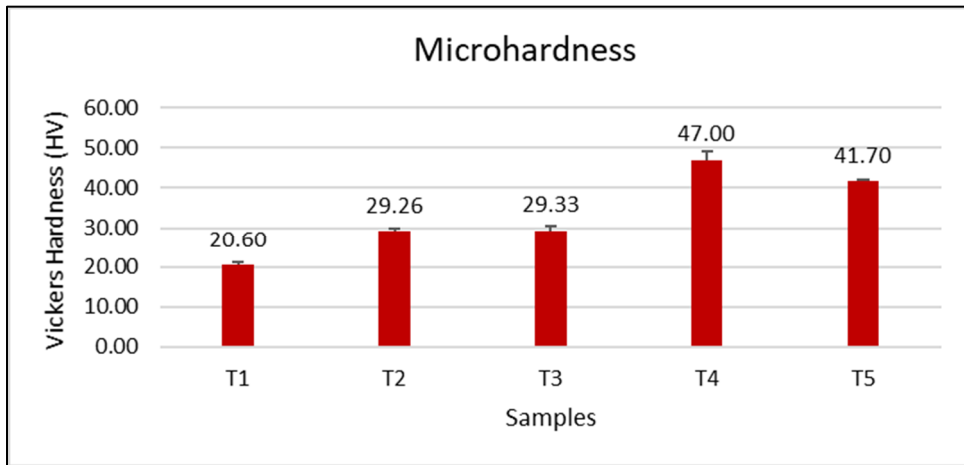
Figure 4.25a: Tensile Strength Results for Curing Temperature Effect

For curing time effect, the test results indicate that the sample C2 with curing time of 120 mins had achieved the highest tensile strength of 352.55 MPa whereas the sample C1 with curing time of 30 minutes had recorded the lowest tensile strength of 319.86 MPa. There was an increase of 10.2% in tensile strength due to the increase in curing time from 30 minutes to 120 minutes. However, with the further increase of curing time the tensile strength value declined by 3.3% in the sample C3. Nevertheless, based on the microscopic images of Figure 4.22a to 4.22f as the curing time increased the fragmentation and insufficient bonding between the glass fiber and epoxy matrix also increased.


Figure 4.25b: Tensile Strength Results for Curing Time Effect

From the above discussion, it can be observed that as the curing temperature or curing time is lesser, there was not significant improvement in tensile strength as the energy available was not sufficient enough to enhance the wettability of the fiber/matrix interphase. This could lead to weak interfacial adhesion between the glass fibers and the epoxy resin whereby resulting in the reduction of mechanical performance. At the same

time, if the curing temperature or time extends beyond the threshold limit then there arised degradation in tensile strength due to the damage caused to the glass fibers and the resin resulting in fragmentation and insufficient bonding between glass fibers and the epoxy resin.

4.5.2.3 Flexural Testing with the Curing Temperature and Time Effect

The flexural test results for glass fiber reinforced nanocomposites are presented in Figure 4.26a for variation in curing temperature and in Figure 4.26b for variation in curing time.

For curing temperature effect, the test results indicated that the sample T5 with curing temperature of 125°C had recorded the highest value of 213.26 MPa whereas the sample T4 with curing temperature of 100°C had the lowest flexural strength of 161.07 MPa. There was 32.4 % increase in the flexural strength recorded due to the increase in curing temperature. Regardless of flexural strength, the microscopic images of Figure 4.20a to 4.20j had shown fragmentation and cluster of matrix noted in sample T5 whereas the sample T4 had shown better bonding between epoxy matrix and glass fibers.
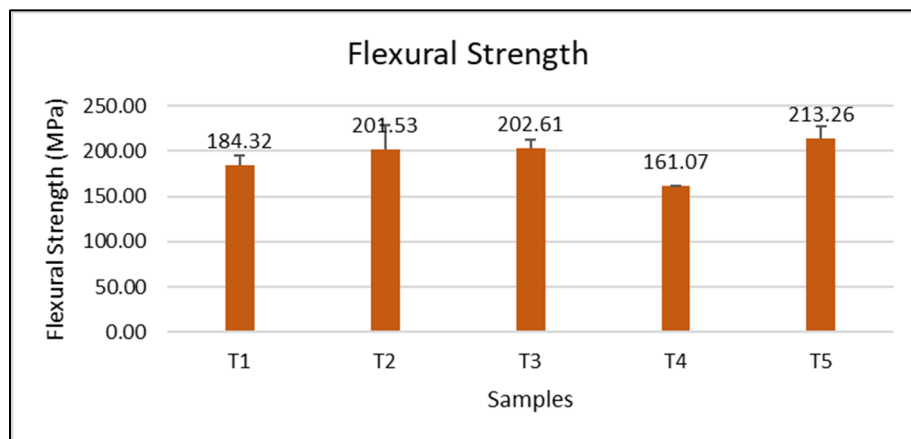
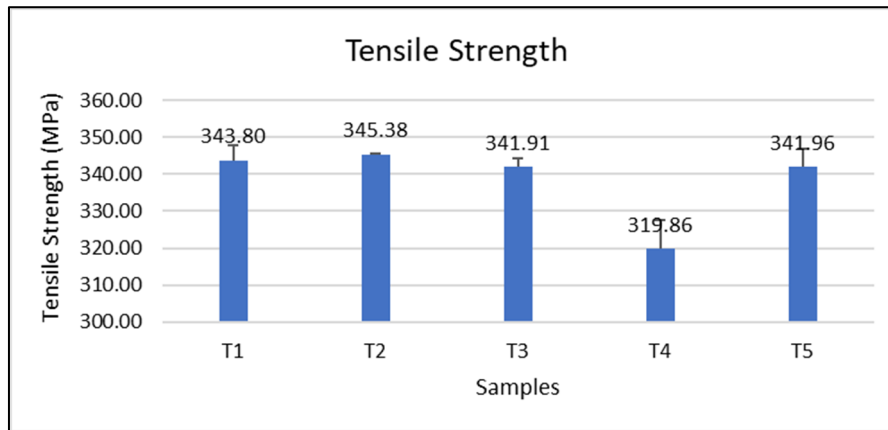**Figure 4.26a: Flexural Strength Results for Curing Temperature Effect**

For curing time effect, the test results indicate that the sample C2 with curing time of 120 minutes had recorded the highest flexural strength of 195.70 MPa whereas the sample C1 with curing time of 30 mins had achieved the lowest flexural strength of 161.07 MPa. There was an increase of 21.5% in flexural strength due to the increase in

curing time from 30 minutes to 120 minutes but as the curing time is further increased to 480 minutes the flexural strength tends to decrease. It can be noticed from the microscopic images of Figure 4.22a to 4.22f that as the curing time increased the fragmentation and insufficient bonding between the glass fiber and epoxy matrix also increased.
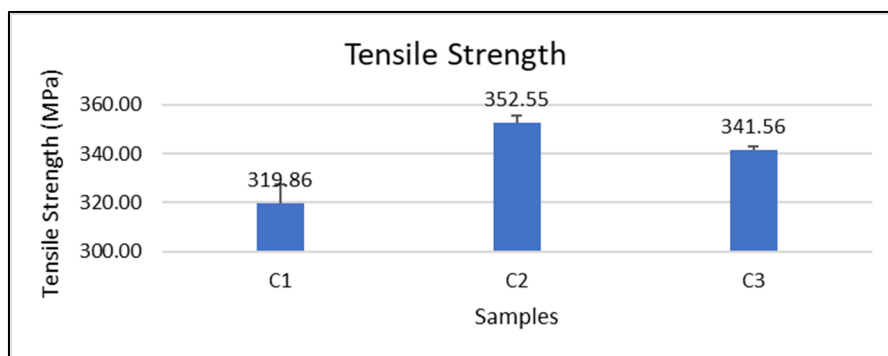

Figure 4.26b: Flexural Strength Results for Curing Time Effect

From the above inference, it can be observed that with lower curing temperature and curing time the energy provided was not sufficient enough for the wettability of the glass fibers and the epoxy matrix. This could significantly affect the interfacial properties by providing insufficient reinforcing effect between the constituents in the matrix system. When the curing temperature and time increased, the sufficient curing allowed the state of linkage to occur between the glass fiber and epoxy resin at elevated temperatures. This cross linkage in the thermosetting polymer led to the evolution of bond performance leading to the interfacial mobility between the glass fibers and epoxy resin thereby increasing the flexural strength of the nanocomposite. However, with further increase of curing temperature and time, there occurs degradation in flexural strength due to the fragmentation and severe damage to the glass fibers.

4.5.2.4 Impact Testing with the Curing Temperature and Time Effect

The impact test results for glass fiber reinforced nanocomposites are presented in Figure 4.27a for variation in curing temperature and in Figure 4.27b for variation in curing time.

For curing temperature effect, the test results indicated that the sample T2 with curing temperature of 50°C had recorded the highest value of 267.15 MPa whereas the sample T1 with curing temperature of 25°C with 30mins had achieved the lowest impact strength of 224.97 MPa. There was 18.7% increase in the impact strength noticed due to the increase in curing temperature from 25°C to 50°C. It was also noticed that as the curing temperature increased the impact strength decreased slowly. However, from the microscopic images of Figure 4.20a to 4.20j it can be seen that fragmentation and cluster of matrix were noted in sample T2 whereas the sample T4 had shown better bonding between epoxy matrix and glass fibers. Nevertheless, it is also observed that the impact strength of the specimens does not significantly vary from 50°C which in turn indicates that the effect of curing temperature has minor influence on impact properties of the nanocomposites.
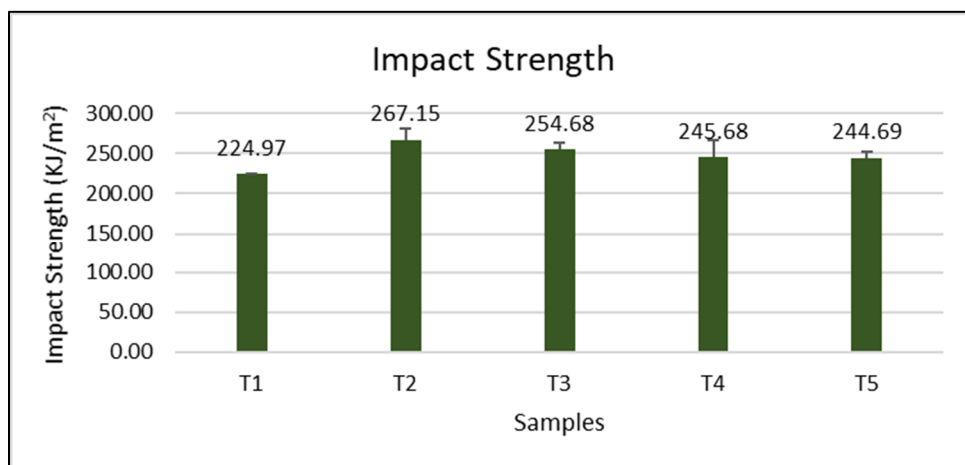
Figure 4.27a: Impact Strength Results for Curing Temperature Effect

For curing time effect, the test results indicate that the sample C3 with curing time of 480 minutes had recorded the highest impact strength of 271.02 MPa whereas the sample C1 with curing time of 30 mins had achieved the lowest impact strength of 245.68 MPa, which was an increment around 10.3%. However, fragmentation and insufficient bonding between the glass fiber and epoxy matrix were noticed with the increase of curing time as evident from the SEM images of Figure 4.22a to 4.22f.
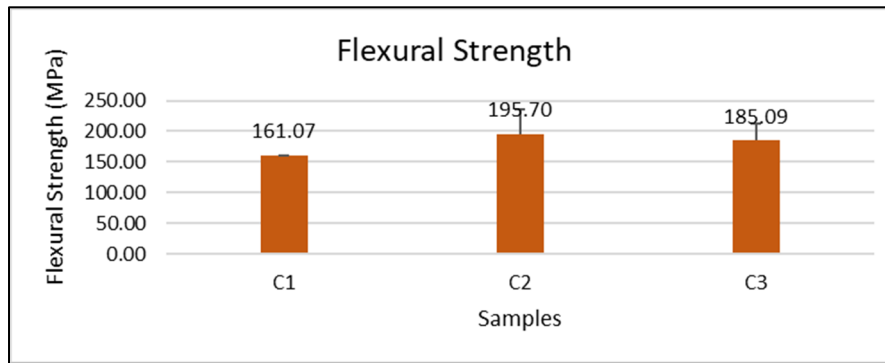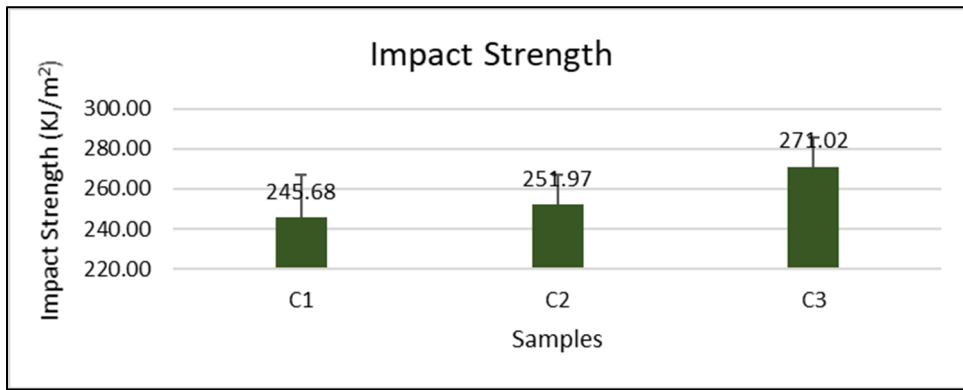
Figure 4.27b: Impact Strength Results for Curing Time Effect

From the above test results, it can be observed that curing temperature and curing time plays a significant impact on the mechanical performance of the nanocomposite. The increase in curing temperature and time had enhanced the interfacial properties to certain extent through the formation of crosslink between the polymers and the glass fibers thereby in addition nanoclay fill up the gaps in between them. As explained earlier in Chapter-2, when the nanocomposite was subject to impact loading and when a growing crack meets nanoclay the crack gets deflected out of plane and when the crack propagates further and reaches further nanoclay, it gets twisted and tilted thereby increasing the fracture surface area leading to increased fracture toughness which was similarly reported by Ratna et. al [46]. However, when the curing temperature or curing time was increased beyond 50°C and 120 minutes there raised degradation in impact properties due to the fact that there occurred severe physical damage to the constituents in the matrix system.

Table 4.6: Mechanical Test Results for Variation in Curing Temperature

Sample	Description	Curing Temperature	Curing Time	Micro hardness (HV)	Tensile Strength (MPa)	Flexural Strength (MPa)	Impact Strength (KJ/m²)
T1	Epoxy+SGF+1% MNC	25°C	30 mins	20.60	343.80	184.32	224.97
T2	Epoxy+SGF+1% MNC	50°C	30 mins	29.26	345.38	201.53	267.15
T3	Epoxy+SGF+1% MNC	75°C	30 mins	29.33	341.91	202.61	254.68
T4	Epoxy+SGF+1% MNC	100°C	30 mins	47.00	319.86	161.07	245.68
T5	Epoxy+SGF+1% MNC	125°C	30 mins	41.70	341.96	213.26	244.69

Table 4.7: Mechanical Test Results for Variation in Curing Time

Sample	Description	Curing Temperature	Curing Time	Micro hardness (HV)	Tensile Strength (MPa)	Flexural Strength (MPa)	Impact Strength (KJ/m²)
C1	Epoxy+SGF+1% MNC	100ºC	30 mins	47.00	319.86	161.07	245.68
C2	Epoxy+SGF+1% MNC	100ºC	120 mins	42.87	352.55	195.70	251.97
C3	Epoxy+SGF+1% MNC	100ºC	480 mins	42.13	341.56	185.09	271.02

4.5.3 Summary of Curing Temperature and Curing Time

Section 4.5 presented an experimental analysis on the effect of curing temperature and curing time of the glass fiber reinforced polymer nanocomposites towards the interfacial bonding in terms of surface hardness and other mechanical properties. The key objectives were to identify the effective curing temperature and curing time that address the interfacial bonding characteristics through improved surface characteristics i.e. surface hardness with complementing other mechanical characteristics, demonstrated through the tensile, flexural and impact tests. In general, samples prepared using higher curing temperature and curing time exhibit better tensile strength and hardness properties without compromising flexural and impact properties. However, it was revealed that based on the micrography and surface hardness analysis, sample (T4/C1) prepared with curing temperature of 100ºC and curing time of 30 minutes had shown the most effective interfacial bonding performance in terms of surface hardness. Therefore, epoxy with silane treated glass fiber and 1 wt. % nanoclay concentration using curing temperature of 100ºC and curing time of 30 minutes was considered the effective curing temperature and curing time and considered for validation using pin on disc wear test.

From the above discussion, it is evident that the mechanical performance of the nanocomposite significantly depends on the curing temperature and curing time of the specimen. The curing temperature accelerates the curing process whereby enhancing the bonding mechanism through the wettability of the fibers by resin as a result of lowered viscosity and improved mechanical interlocking between the fiber and resin. As glass fiber reinforced polymer nanocomposite is a thermosetting polymer, strong chemical covalent bond occurs which are mechanically stable whereby reducing the residual

stress. With curing temperature of around 100ºC there arises a state of cross-linked polymer network of the epoxy resin with fibers. However with either drastic increase of curing temperature above 100ºC or increase in curing time above 30 mins there arises degradation in mechanical performance with severe damages to the glass fiber and the resin.

4.6 Influence of Nanoclay Concentration and Silylation of Glass Fibers

A silane is a monomeric silicon chemical which is similar to hydrocarbon. Silane coupling agents has been used to achieve compatibility between inorganic fillers and organic polymer. Silane coupling agents are hybrid compounds whose molecules contain functional groups that bond with both organic and inorganic materials. They exhibit affinity towards both organic and inorganic surfaces (dual reactivity) and act as intermediary to form strong covalent bond between organic polymers (rubber, polymers and plastics) and inorganic fillers (fiberglass, fillers and metals). Due to this unique dual reactivity, silylating agent can be utilized for improving the adhesion between dissimilar materials. It is this characteristic that makes silane coupling agents to be utilized for improving the adhesion, mechanical strength of the composite, for resin modification and surface modification. Initially the silanes monomers to form reactive, hydrophilic, acidic silanol groups Si-OH followed by siloxane oligomers formation. Next, the oligomers or monomers silanol are physically absorbed to hydroxyl groups of glass fibers by hydrogen bonds on the surface. Finally under dehydration condensation reaction, a robust covalent bond -Si-O-Si- between silanols and hydroxyl groups of glass fibers are formed during the drying process. Moreover, covalent bonds enable a durable immobilization of the organic moieties in silane grafted products which prevent leaching into the surrounding solutions. In addition, the R' organofunctional group remains available can react with the polymer matrix, resulting in the formation of a network among silane, glass fiber and polymer through covalent bonding. Therefore, the resultant polymer composite exhibits a substantial improvement in mechanical properties including rheological properties whereby the compatibility between inorganic glass fiber and polymer matrices improved [7,12].

From the EDX analysis in section 4.3, it is revealed that the sodium plays a vital role for interfacial bonding in terms of surface hardness of the nanocomposite along the variation of nanoclay concentration. Hence, in this section, primary focus is on discussion of the sodium role. In Figure 4.28, it is clearly evident that increasing the concentration of nanoclay the hardness of the composite decreases except a threshold concentration of 1% nanoclay where the highest hardness observed. Similar trend follows for sodium weight concentration along the nanoclay concentration. Particularly for threshold 1% nanoclay where hardness sudden increase to 47 HV with the drastic

decrease of sodium to 0.22 % and rest follow gradual decline of hardness along the increment of nanoclay concentration i.e. trends of Na increase. This behavior is due to the silylation phenomena i.e. silane coupling agent which is highly influenced by the presence of sodium [7].

The higher sodium present in the nanoclay act as a negative catalyst i.e. retarder, however, appropriate sodium (Threshold value) contributes towards effective silylation process through enhancement of silane coupling agent to improve the interfacial bonding mechanism between glass fiber and epoxy matrix thereby improving the hardness performance. It is interesting to notice that as the nanoclay concentration increases, so do the sodium. Therefore, sodium act as retarder towards silylation process i.e. less silane coupling agent formation. Similar behavior observed for Daniel cell which is known as hydrogen polarization [82].
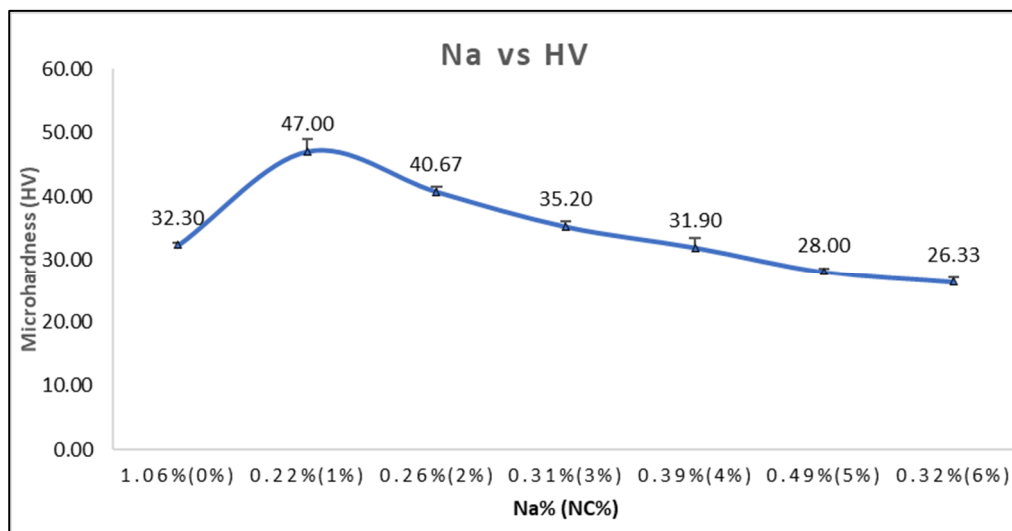
Figure 4.28 – Impact of Na with respect to Microhardness

Interestingly, it was also revealed that Na suppression influence significantly on the interfacial bonding in terms of radical variation in surface hardness through different compound formation which was supported by FTIR and XRD analysis which will be discussed in section 4.6.1 and 4.6.2. Figure 4.29 shows the coupling phenomenon between organic epoxy and inorganic glass fiber through silylation phenomena.
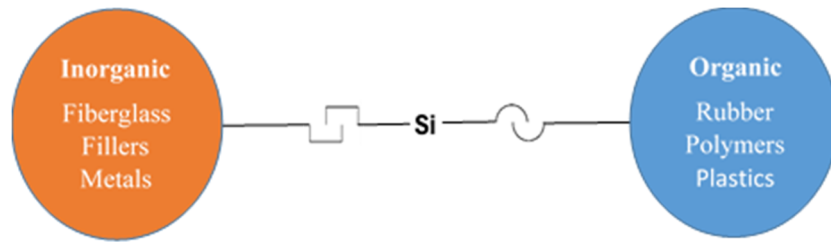
Figure 4.29 Silane Coupling Mechanism [65]

4.6.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The compounds formation due to interaction between the glass fibers, epoxy resin and nanoclay were investigated through FTIR analysis. The FTIR spectrum for the samples N1 to N7 are represented in Figure 4.30. It is clearly evident that three distinct group of spectrum were observed from the FTIR result which is due to formation of three different sets of compounds. Due to the interaction among the epoxy, glass fiber and small quantity of nanoclay forming similar group of compounds lead to shift in the vibration peaks of those samples N2(1% nanoclay) and N3(2% nanoclay) in similar pattern and finally attributed to similar characteristics spectrum. For larger quantity of nanoclay samples N4(3% nanoclay) and N5(4% nanoclay), similar behaviour of spectrum shifting is observed. Interestingly, for the largest quantity of nanoclay samples N6(5% nanoclay) and N7(6% nanoclay) characteristics follow control sample N1(0% nanoclay) and such behaviour can be attributed to the nanoclay polarization behaviour discussed in the section 4.6. It can be understood from the infrared test that the enhanced coupling agent of silane due to the nanoclay appropriate concentration interact with the functional groups in the epoxy resin and glass fiber, resulting in the change of the bonding which results the change of characteristic spectrum. These results conform with similar behaviour evident from the EDX analysis.
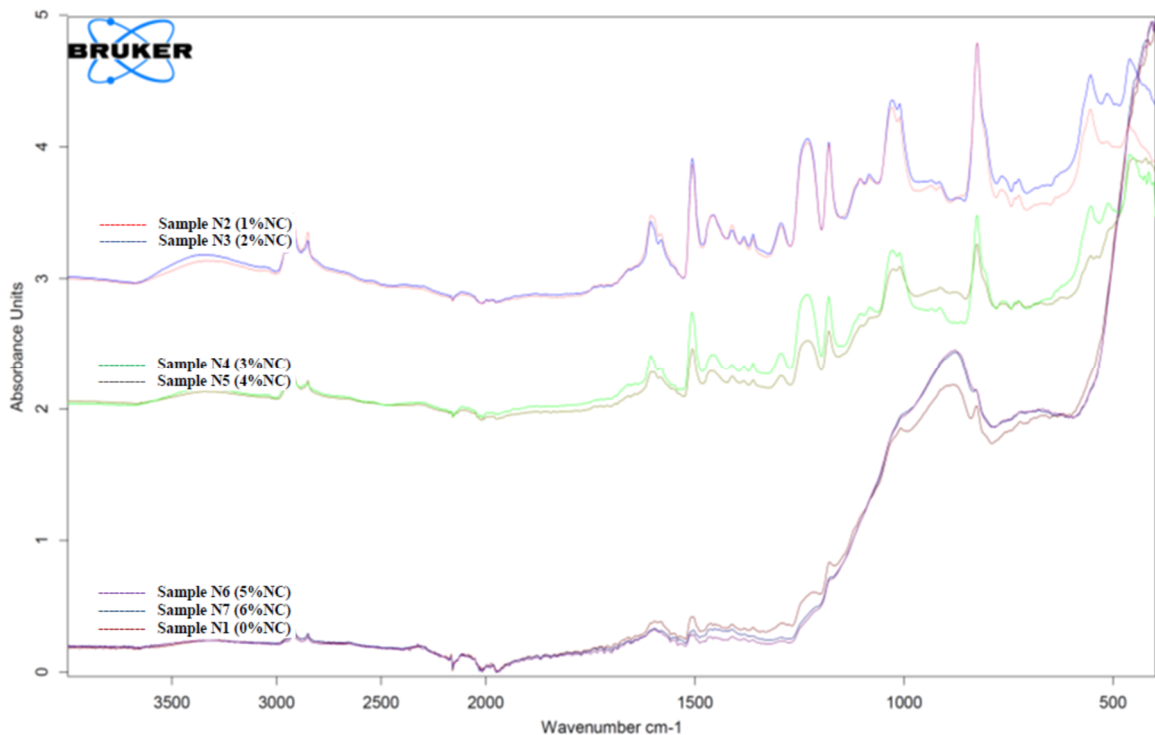
Figure 4.30 – FTIR Spectrum for Samples N1-N7

4.6.2 X-Ray Diffraction (XRD) Analysis

XRD technique is one of the versatile technique to investigate the crystallographic structure of hybrid nanocomposites. The three samples N1(0% Nanoclay), N2(1% Nanoclay) and N7(6% Nanoclay) were selected based on the hardness value of two boundary cases (N2 and N7) including a control sample (N1) as reference and analysed through scanning within the range between 0°-100° (as 2θ) without any background corrections. The Figure 4.31 displays the XRD pattern of diffraction characteristics peaks for the samples N1, N2 and N7. The reference patterns of samples obtained were identified by three distinct colours.
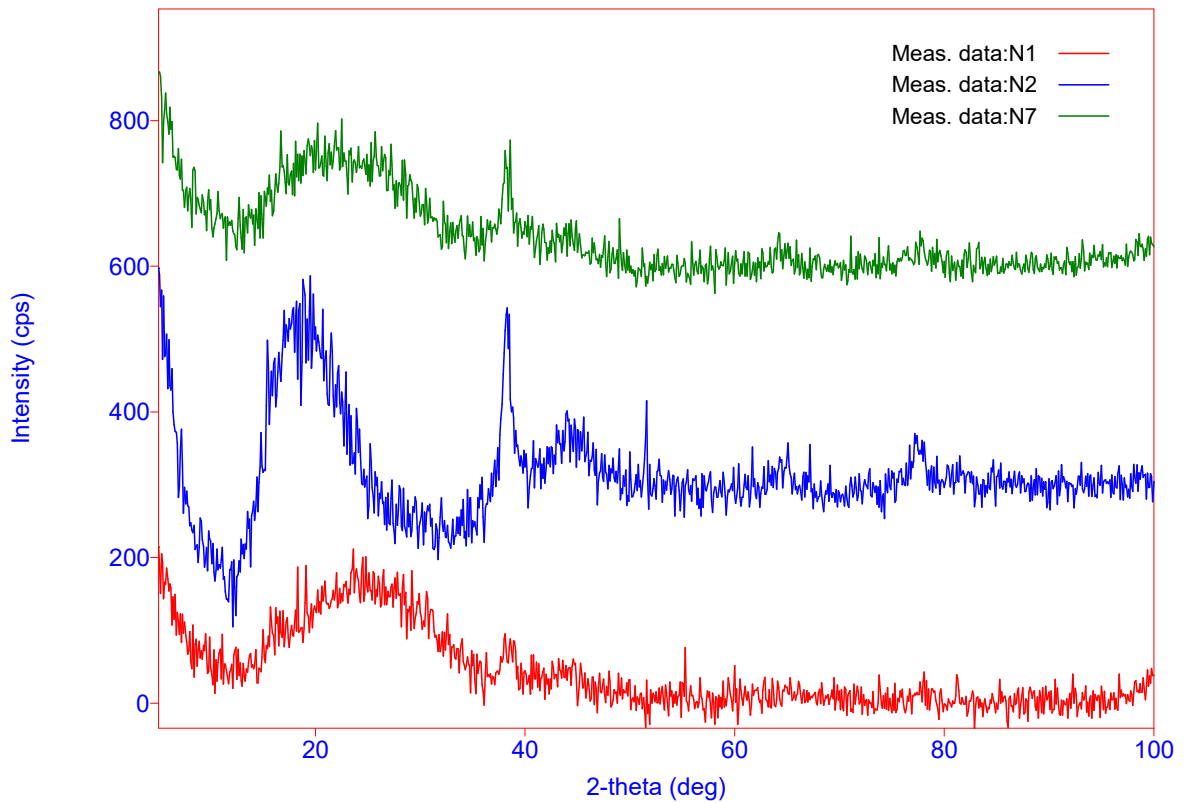
Figure 4.31 – XRD Pattern for Samples N1, N2 and N7

From the amorphous envelope, it is clearly evident that without any characteristics peak for the control sample N1, which indicate the absences of any crystal formation since in XRD analysis, amorphous materials do not produce any sharp diffraction peaks. Interestingly for the sample N7 shows similar amorphous envelope and the pattern

seemingly mostly amorphous region except a minor peaks which was insignificant to identify as any traceable crystal formation. On the other hand, in the case of sample N2, it is clearly evident of characteristics peaks from the crystalized region. This indicates the formation of intercalation structure of that composite. Such intercalated structure implies the strong interfacial bonding between the polymer matrix and the glass fiber hence resulted increase in surface hardness. The absence of sharp peaks for the XRD curves of samples N1 and N7 indicates formation of exfoliated structure in the composite which leads to weak interfacial bonding between the polymer matrix and glass fiber. Hence, eventually provide lower surface hardness. Such findings conform with the similarly report that non-intercalated structure could negatively affect the mechanical performance of the composite [45].

4.7 Wear Performance via Pin-on-Disc Test (Validation of Interfacial Bonding through Surface Hardness)

Wear and friction (Tribology) behaviour are one of the most characteristic features of polymer-metal components transferring load under sliding motion. The wear rate is affected by various operating parameters such as applied load, sliding distance, sliding velocity, temperature etc. The wear performance was carried out using pin-on-disc equipment to calculate the specific wear rate. The nanocomposite sample was selected based on the best hardness result achieved with complementing on tensile strength, flexural strength and impact strength. In order to validate the hardness reading achieved, the wear analysis was conducted.

4.7.1 Surface Morphology Analysis

Figure 4.32a and 4.32b represent the SEM images of sample N1(0% Nanoclay) prepared with epoxy resin and silane treated glass fibers. The micrographs indicate that there exists smooth adhesion between the glass fibers and epoxy resin. It can also be observed from the microscopic images that there were smearing and fracture of matrix in the composite. There were signs of fiber-matrix debonding observed but the surface of the matrix looks very smooth, which indicates that the bonding between the glass fibers and epoxy matrix was not sufficient enough to sustain the applied sliding load. In addition, there were no sign of glass fibers loosening observed in the micrograph.
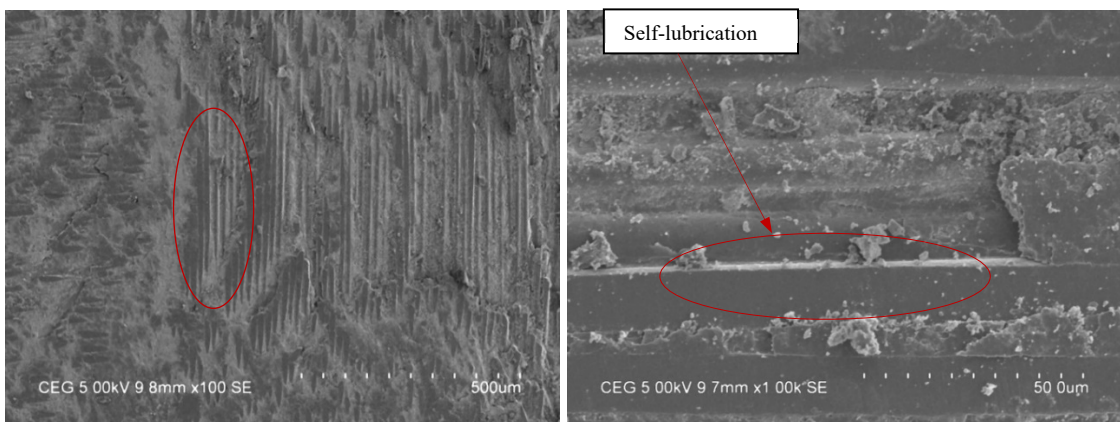
Figure 4.32a-Sample of wear for N1(100x)   Figure 4.32b–Sample of wear for N1(1000x)

Figure 4.32c and 4.32d represent the SEM images of sample N2(1% Nanoclay) prepared with epoxy resin, silane treated glass fibers with 1 wt.% of surface modified nanoclay. The micrographs indicate that there was smooth adhesion between glass fibers, epoxy resin and surface modified nanoclay. It can also be noticed from the microscopic images that the glass fibers were flexible due to silane treatment and no signs of agglomeration were noticed which could also lead to efficient bonding between epoxy, glass fibers and nanoclay. There were no signs of matrix fracture or delamination noticed in the micrograph. These will lead to effective load transfer between the glass fiber, nanoclay and epoxy resin which in turn will improve the interfacial bonding characteristics thereby improving the wear performance of the nanocomposites.
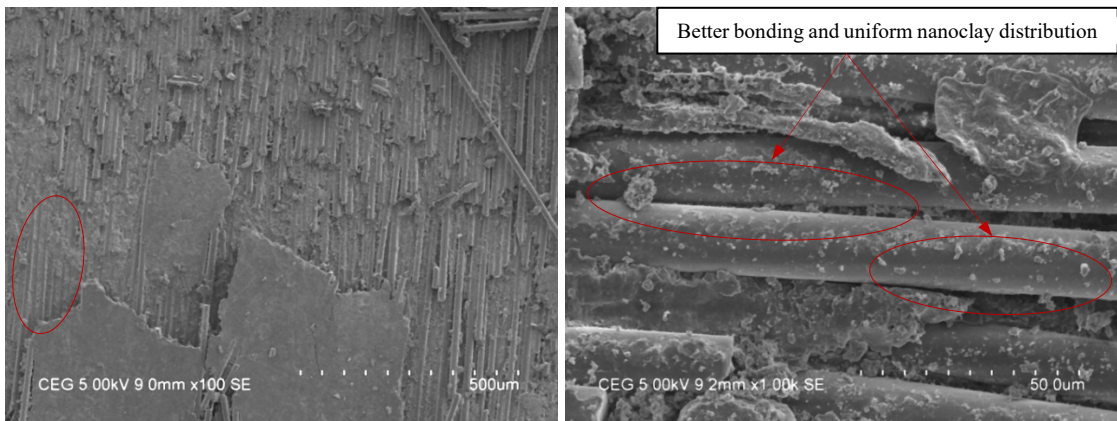
Figure 4.32c-Sample of wear for N2(100x)   Figure 4.32d–Sample of wear for N2(1000x)

Figure 4.32e and 4.32f represent the SEM images of sample N7(6% Nanoclay) prepared with epoxy resin, silane treated glass fibers with 6 wt.% of surface modified nanoclay. The micrographs indicate that there was delamination noticed between the glass fibers and epoxy matrix. The surface of the epoxy matrix at the delamination area were rough which indicates that the interfacial bonding between the glass fibers, nanoclay and epoxy resin were better with the addition of nanoclay. On the other hand it was observed that more glass fibers have been delaminated and may be removed during the process of applied load. Further, the microscopic images had shown signs of glass fibers fully detached from the matrix which specifies that the glass fibers are of flexible in nature due to silane treatment. There were no signs of agglomeration noticed and the nanoclay was uniformly dispersed in the epoxy matrix which indicates that the ultrasonication process used for nanoclay dispersion were effective.
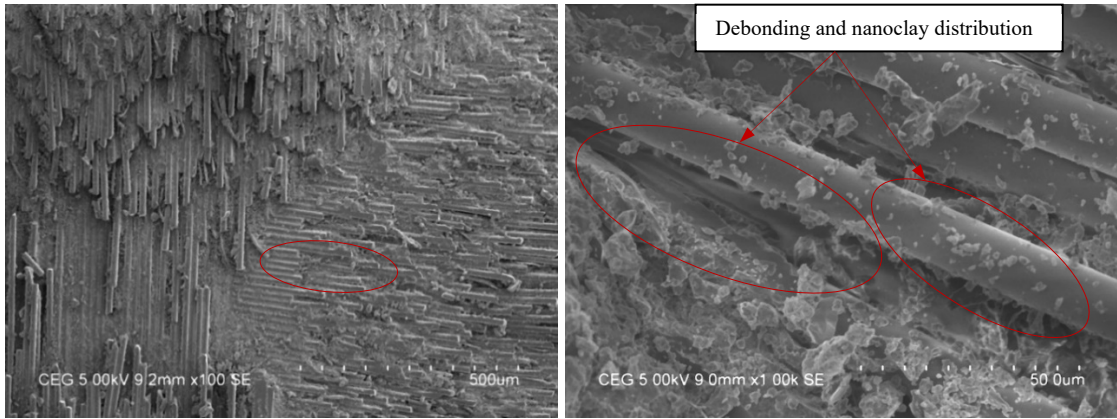
Figure 4.32e-Sample of wear for N7(100x)   **Figure 4.32f–Sample of wear for N7(1000x)**

Figure 4.33a to 4.33c represent the SEM images of the fractured surfaces of the samples N1, N2 and N7 on the worn surfaces after the pin-on-disc wear test. From the SEM images, it was evident that the interfacial bonding characteristics of silane treated glass fibers and epoxy matrix with 1 wt.% of nanoclay was better than the sample N1 and sample N7. In sample N2, the nanoclay particles had been uniformly distributed which could be mainly due to the ultrasonication process of dispersing the nanoclay in the epoxy system. The silane treatment of glass fibers had improved the interfacial adhesion between glass fibers and epoxy matrix which in addition has been further enhanced by the intercalation of the nanoclay. From the figure 4.33a, chipping of matrix was noticed and it had acted as self-lubrication in the wear process. The interfacial bonding characteristics of epoxy system with glass fibers and nanoclay had been quantitatively demonstrated through the microhardness values attained and validated through pin-on-disc wear analysis which was further qualitatively demonstrated by scanning electron microscopic analysis.
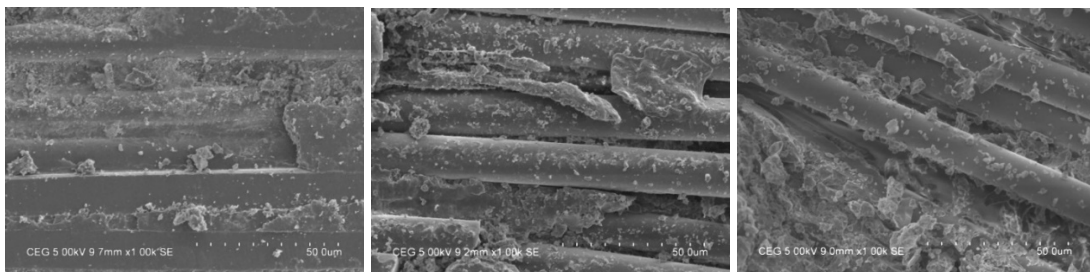
Fig.4.33a–Sample of 0% nanoclay(N1)   **Fig.4.33b–Sample of 1% nanoclay(N2)**   **Fig.4.33c–Sample of 6% nanoclay(N7)**

Figure 4.33a-4.33c – SEM images of Samples N1,N2 and N7

4.7.2 Wear Test Analysis

In previous sections, findings of experiments were analysed through different surface treatment of glass fibers and nanoclay, variation in nanoclay concentration, variation in dispersion mechanism as well as the variation in curing temperature and time of the glass fiber reinforced epoxy nanocomposites. From the experimental analysis, it was revealed that the sample N2 (1% nanoclay) which was prepared with epoxy resin, silane treated glass fibers with 1 wt. % of surface modified nanoclay had exhibited strongest interfacial bonding in terms of hardness among all the other samples without compromising on the other mechanical properties such as tensile strength, impact strength and flexural strength.

In order to validate this, the wear performance of nanocomposite samples N1, N2 and N7 were carried out through Pin-on-Disc wear analysis which was performed according to experimental procedure detailed in Chapter-3. Five samples were taken for each type of specimen and the average of the results have been recorded for final evaluation. The results are tabulated in the Table 4.8. From the experimental results shown in Table 4.8, it was noticed that sample N2 has the least specific wear rate when compared to samples N1 and N7 throughout all the applied loads of 30N, 60N and 90N. This finding was also in line with the microhardness value attained and discussed in section 4.3. This validates that the sample N2 (1 wt. % of nanoclay) had attained the highest hardness among the other samples and indicates that 1 wt.% nanoclay was the most effective concentration to enhance the interfacial bonding strength between epoxy matrix and silane treated glass fibers. Also, coefficient of friction for N2 was significantly lower compared to the sample N7 which was in line with the wear rate findings. Interestingly, for the case of N1, the coefficient of friction was lower compared to sample N2 despite of higher wear rate except for 90N applied load as shown in the Table 4.8.

The decreased wear rate was mainly due to the nanoclay addition that contributed to improvement in fiber-matrix interfacial strength followed by the reduction of stress concentration on the fibers and enhancement of wear performance. In addition the silane treatment of glass fibers and trimethyl stearyl ammonium modified nanoclay act as a bridge thereby providing mechanical interlocking between the glass fiber, epoxy resin

and nanoparticles which in turn enhanced the interfacial bonding strength. As hardness and wear performance complement each other, the validation result of wear performance attained was harmonised with the hardness result achieved too.

Table 4.8: Wear Test Analysis Results

Sample	Applied Load 30 N			Applied Load 60 N			Applied Load 90 N			Micro hardness HV
	Wear Loss (g)	Coeff. of friction (cof)	Wear rate mm^3/N-m x10^{-4}	Wear Loss (g)	Coeff. of friction (cof)	Wear rate mm^3/N-m x10^{-4}	Wear Loss (g)	Coeff. of friction (cof)	Wear rate mm^3/N-m x10^{-4}	
N1	0.005	0.187	1.3210	0.009	0.266	1.5860	0.003	0.292	0.3964	32.30
N2	0.002	0.257	0.5995	0.006	0.288	1.1990	0.002	0.243	0.2998	47.00
N7	0.008	0.381	2.2160	0.012	0.353	2.2160	0.011	0.376	1.5240	26.33

4.8 General Conclusion

This chapter presented an experimental analysis on the results and discussion related to the effect of surface treatment, nanoclay concentration, dispersion mechanism, curing temperature and curing time of the glass fiber reinforced polymer nanocomposites. The key issue is to address the interfacial bonding mechanism in terms of surface hardness and mechanical performance (tensile strength, flexural strength and impact strength). The morphological behaviour was analysed through the SEM and EDX analysis. The characterization was done using FTIR spectroscopy and XRD analysis. Finally, the validation of the hardness results was performed using pin-on-disc wear test. The major findings from the analysis was insufficient bonding, fragmentation, agglomeration, fiber pull out, excess resin and delamination of glass fibers which could have caused degradation in hardness and interfacial bonding strength of the nanocomposites. Based on the micrography and surface hardness analysis, it was revealed that sample prepared with epoxy resin, silane treated glass fiber and 1 wt. % of surface modified nanoclay using ultrasonication process with 100% amplitude and curing temperature of 100ºC through curing time of 30 minutes had shown the most effective interfacial bonding performance in terms of surface hardness.

The validation of the hardness performance was done using pin-on-disc wear test for three samples N1, N2 and N7 at three different applied loads of 30N, 60N and 90N with a sliding speed of 1m/s and at fixed sliding distance of 500 m. The test results had shown that the sample N7 had more wear rate followed by the sample N1. The sample N2 had the least wear rate among all three samples at all the applied loads which validated the findings from the hardness test. Finally, the worn surfaces of the samples N1, N2 and N7 were analysed using a scanning electron microscope which exhibit, particularly for N1 and N7 samples, various wear features such as matrix wear, fiber thinning wear, fiber breakage and fiber/matrix debonding. It was revealed that the nanocomposite with excessive nanoclay (in the case of sample N7) deteriorate the interfacial bonding characteristics which in turn reduced the wear resistance and hardness property of the nanocomposites. For sample N7, it was also evident that fiber pull out occurred followed by the fiber breakage. In general, for nanoclay samples N1, N2 and N7 the micrographs did not show major fiber failure instead it exhibited surface cracks and matrix cracking which was discontinuous but not catastrophic.

CHAPTER 5

CONCLUSION

5.1 General Conclusion

In this research work, the effects of fiber/filler reinforcement on the tribological behaviour of polymer nanocomposites were addressed to improve the interfacial bonding. The addition of nanoparticles as a filler material between glass fiber and epoxy matrix were one of the solutions to enhance the bonding i.e. provide improvement in mechanical and tribological properties of the composite. However, the diffusion of nanoparticles in the matrix hamper the formation of the well performed composite mainly due to agglomeration of nanoparticles which was addressed through different dispersion mechanism. Quantitative characterization of interfacial adhesion strength was done in evaluating the mechanical behaviour and capabilities of composite materials. The interfacial bonding quality ultimately dictates the mechanical and wear performance of glass fiber reinforced polymer composites.

The first objective was to study the effect of surface treatment of glass fibers and nanoclay on the mechanical performance, which was done through untreated, silane treatment and acid treatment of glass fibers. The nanoclay was used in untreated and trimethyl stearyl ammonium modified condition. The samples prepared using silane treated glass fibers exhibit better tensile strength and hardness properties. The silane treatment for the glass fibers as well as the surface treatment of the nanoclay act as a bridge thereby providing mechanical interlocking between the glass fiber, epoxy and nanoparticles which in turn enhanced the interfacial bonding strength. It was concluded that the sample S10 made with epoxy, silane treated glass fiber and 3 wt. % of surface modified nanoclay was considered as the appropriate sample, based on the hardness performance of 35.20 (28% increment) and microscopic analysis, for further evaluation in this research work.

The second objective was to find the threshold level of nanoclay which was performed by varying the nanoclay concentration from 0-6 wt. % of the epoxy matrix.

By observing the hardness, sample N2, with 1 wt. % of nanoclay concentration was sufficient for achieving the highest hardness of 47 HV (45.5% increment) and with further addition of nanoclay had shown linear reduction in hardness properties. The increase in microhardness of the nanocomposite was due to the enhancement of cross link density due to the formation of network like structure of intercalated platelets with epoxy resin molecules. This finding had led to the research of effective nanoclay concentration in achieving the hardness of the nanocomposite.

The third objective was to study the effect of dispersion mechanism which was performed through mechanical stirrer and ultrasonication process. The time period for both dispersion process was kept constant of 30 minutes and the nanoclay concentration was fixed at 1 wt.%. The speed for mechanical stirring was varied from 125 rpm to 2000 rpm and for ultrasonication process the amplitude was varied from 20% to 100%. The dispersion mechanism of nanoclay particles due to the localised heating and through the heat transfer, created temporary physical crosslink arises with the hardener. The nanoclay particles being rigid connectors results in better stress transfer and increased the load carrying capacity of the nanocomposite. The sample D8 prepared using ultrasonication process with 100% amplitude had achieved the highest hardness of 47HV (96.4% increment) and considered as the appropriate sample for further evaluation in this research work.

The fourth objective was to study the impact of curing temperature and curing time done through the variation of the curing temperature from 25°C to 125°C and the curing time from 30mins to 480mins. The increase in curing temperature and time had enhanced the interfacial properties to certain extent through the formation of crosslink between the polymers and the glass fibers, thereby in addition nanoclay fill up the gaps in between them. In conclusion, based on the hardness value of 47HV and surface morphology analysis, the specimen T4/C1 with curing temperature of 100°C and curing time of 30 minutes was considered as the best sample for further evaluation in this research work.

Finally, validation of the hardness performance was conducted using pin-on-disc wear test for three samples N1, N2 and N7 at applied loads of 30N, 60N and 90N with a sliding speed of 1m/s and at fixed sliding distance of 500 m. The test results had shown that the sample N7 had more wear rate followed by the sample N1. The sample N2 had

the least wear rate among all three samples at all the applied loads. The validation test results were also harmonized with the hardness reading achieved.

From the FTIR and XRD analysis, it was established that the appropriate nanoclay concentration enhanced the silane coupling agent by interacting with the functional group in the resin and the fiber and also aid the formation of intercalation structure of the composite which implied the strong interfacial bonding between the polymer matrix and the glass fiber hence resulted increase in surface hardness.

The sample N2 prepared by epoxy matrix and silane treated glass fibers with 1 wt. % of surface modified nanoclay concentration using ultrasonication process at 100 % amplitude for 30 minutes had attained the maximum hardness of 47HV. The curing temperature and curing time was maintained at 100°C for a period of 30 minutes. From the mechanical performance and morphological analysis, it was evident that the nanoclay concentration had improved the physical bonding between the epoxy matrix and silane treated glass fibers. However, in addition to physical bonding it was also evident that there exists chemical bonding which too have influenced the interfacial bonding between the glass fiber and epoxy matrix that had been further investigated and confirmed through FTIR and XRD analysis.

5.2 Specific Conclusion

A few significant parameters had been established in this research work. The effective surface treatment, nanoclay concentration, dispersion mechanism, curing temperature and curing time has been determined. A coherent relation between the nanoclay concentration and sodium suppression influence significantly on the interfacial bonding in terms of radical variation in surface hardness were also observed. In summary, this study had contributed to the following conclusion:

- The effective surface treatment for glass fibers were silane treatment and for nanoclay were trimethyl stearyl ammonium modified condition.
- The effective threshold nanoclay concentration were revealed at 1 wt. % of the epoxy matrix.
- The effective dispersion mechanism for nanoclay concentration were ultrasonication process with 100 % amplitude for a time duration of 30 minutes.
- The effective curing temperature and curing time were $100^{\circ}C$ for a duration of 30 minutes.

The hypothesis is that, the enhanced coupling agent of silane due to the nanoclay appropriate concentration interact with the functional groups in the epoxy resin and glass fiber, resulting in the change of the bonding.

5.3 Future Work

The following are the future works to further expand the research regarding interfacial bonding between epoxy matrix and glass fibers:
- To study the effect of interfacial bonding characteristics with different nanofillers.
- To investigate further with natural fibers (eco-friendly) and enhance the interfacial bonding strength.
- To optimize the parameters that influence the specific wear rate and coefficient of friction.

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