Master Thesis

Delamination Properties of Hierarchical Structured Carbon fiber Composites with Bio-inspired vertically aligned Nano-reinforcement

Submitted in Partial fulfilment of the requirements for the academic degree Dipl.-Ing in Biomedical Engineering (with focus on Biomaterials & Biomechanics)

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Vienna, May 2019
Affidavit

With this statement, I confirm that I wrote this thesis and performed the associated research myself, using the literature cited in this volume. I confirm that this work is original and has not been submitted elsewhere for any examination, nor is it under currently under consideration for a thesis elsewhere.

Vienna, May 2019

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Abstract

Composites materials often provide the best solution for structural applications, offering a good combination of mechanical properties and low weight. Carbon fiber reinforced polymer (CFRPs) composites are commonly used wherever high strength-to-weight ratio and stiffness (rigidity) are required, such as aerospace, superstructure of ships, automotive, sports equipment etc... However, typically in epoxy based CFRPs composite laminates, debonding between the carbon fiber and polymer matrix, delamination between the CFRP sheets and generally the relatively low toughness of composite laminates are often limitations. Many researchers tried to overcome this limitation by mimicking nature principles, leading to a new class of composites with improved toughness. Understanding the hierarchical structural elements in biological materials can serve for systematizing the development of bio-inspired materials with improved mechanical properties. The tubular structural element that is found in hierarchically organized chitin-based crab exoskeleton provides ductile attachment that helps to stitch the layers together and improves fracture toughness. In a similar fashion, producing carbon fiber composites that contain well sorted and oriented nano reinforcement elements such as carbon nanotubes (CNTs) or carbon nanofibers (CNFs) has great importance in utilizing the capabilities and exceptional properties of CNTs and CNFs. In this thesis, first, functionalized CNT/CNF were dispersed in epoxy resin using a Three Roll Mill. Then, carbon fiber reinforced polymers (CFRPs) with a mixture of epoxy thermosets and CNTs/CNFs as a polymer matrix were fabricated using layer-by-layer deposition method. Finally, delamination properties of hierarchically structured CFRPs with and without CNTs/CNFs were investigated to assess the mechanical properties. The vertically aligned CNT/CNF structures are expected to improve fracture toughness and energy absorption.

Keywords: Hierarchical composite material, Carbon fiber reinforced polymer (CFRP), carbon nanotubes (CNT), layer-by-layer disposition, fracture toughness,
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1. Introduction

1.1 Overview of composite materials

A composite material can be defined as a material that consists of two or more physically and/or chemically distinct materials and having bulk properties significantly different from those of any of the constituents. The concept of composite materials is ancient: to combine different materials to produce a new material with performance and efficiency unattainable by the individual constituents. An example is adding straw to mud for building stronger mud walls, steel rods in concrete, cement and asphalt mixed with sand, fiberglass in resin, etc. In nature, examples abound: a palm leaf, cellulose fibers in a lignin matrix (wood), collagen fibers in an apatite matrix (bone), etc. Generally, a composite material is composed of reinforcement (fibers, particles, flakes, and/or fillers) embedded in a matrix (polymers, metals or ceramics). The matrix holds the reinforcement to form the desired shape while the reinforcement usually improves the overall mechanical, electrical and/or thermal properties of the matrix. The region between the matrix phase and the dispersed (reinforcing) phase can be simply a surface (interface) or another phase (interphase) that can for example facilitate adhesion of the dispersed phase to the matrix polymer [1-2].

Composite materials are considered as today’s materials due to their outstanding properties and diverse applications. Composites are also regarded as tomorrow’s materials due to their potentials that they can offer in the future, such as in the areas of nanocomposites, functionally graded, smart and intelligent materials [3]. The present usage of composite materials is mainly driven by the aerospace sector, with a large percentage of the modern airplane structures, such as Boeing 787 or Airbus A380, being manufactured from carbon, glass, and aramid fibers [4]. Other major application areas of composite materials include the automotive industry, the marine industry, the construction industry, in the electrical and electronic systems, sports accessories, in implantable medical devices, in renewable energy sector such as in wind turbine materials etc. [5]. The benefits of composites are mostly in weight and strength, measured in terms of ratios such as stiffness/weight, strength/weight, etc. As a result of their large weight savings, strength improvements, anticorrosion and anti-vibration performances, composite materials can significantly lower fuel consumption in the automotive and aerospace industry. Advances in biomedical composites have been focused on the design of dental and orthopaedic implants, which are mainly structural applications. However, in the recent researches of biomedical composites, biocompatibility, precise property matching and mimicking natural
structures has been given more important focus besides the tremendous stiffness, strength improvement and the large weight savings [2]. For instance, conventional dental fillings, traditional drug delivery matrix, and metallic implants left their places to hybrid composite materials today. Due to their structurally multifunctional and versatile features, biocompatible polymer hybrid composite materials are widely used in the fields of biomedical implants, drug delivery systems, biomedical sensors, scaffolds, tissue engineering and regenerative medicine applications [6-8].

There are many ways to classify composite materials. Based on the type of matrix material composites can be classified as Polymer Matrix Composites (PMCs), Metal Matrix Composites (MMCs), Ceramic Matrix Composites (CMCs) and Carbon/Carbon Composites (C/Cs). Other group of composites are the hybrids which are comprised of two or more composite material systems or a combination of two or more different fibers. Based on the geometry of reinforcement (form of dispersed phase) composites can categorized as particulate reinforced composites, whisker/flakes reinforced composites and fiber reinforced composites. Furthermore, in accordance with the type of reinforcing fibers, composites can be classified as carbon fiber composite material; glass fiber composite materials; organic fiber composite materials; boron fiber or silicon carbide fiber composite materials and hybrid fiber composite materials [9-10].

1.1.1 Metal Matrix composites

Metal Matrix Composites (MMCs) are advanced class of structural materials consisting of non-metallic reinforcements incorporated into the metallic matrix. The common matrix materials are aluminium, titanium, copper, iron, lead, magnesium and super alloys whereas; the common reinforcement phase which can be either dispersed ceramics (i.e., oxides, carbides) or metallic phases (i.e., tungsten, molybdenum, lead). The main objective of using metal matrix composites system is to increase the service temperature or specific mechanical properties of structural components by replacing super alloys. MMCs are widely used in the primary and secondary members of aerospace structure, military airplanes, the automobile engine components, piston and rods, cutting tools and circuit breaker contacts. Metal matrix composite materials prepared by combining biodegradable metals with other materials play an important role in biomedical applications, especially for the support of load bearing tissues such as orthopedic, dental, and cardiovascular tissue [11-17].
1.1.2 Ceramic matrix composites

Ceramic matrix composites (CMCs) consist of ceramic fibres embedded in a ceramic matrix, forming a ceramic fibre-reinforced material with improved properties. The desirable characteristics of CMCs include high-temperature stability, high thermal shock resistance, low friction coefficient, high hardness, high radiation resistance, high corrosion resistance, non-magnetic and nonconductive properties. The ceramic fibers include carbides (e.g. SiC), nitrides (Si₃N₄), oxides (Al₂O₃), titanium boride (TiB₂), aluminium nitride (AlN), zirconium oxide (ZrO₂) and mullite (Al₂O₃·SiO₂). The most common CMCs are oxides such as alumina (Al₂O₃/Al₂O₃) or nonoxides such as carbon/carbon (C/C), carbon/silicon carbide (C/SiC), and silicon carbide/silicon carbide (SiC/SiC). Ceramic matrix composites are used in severe environments such as rocket and jet engines, gas turbines for power plants, heat shields for space vehicles, fusion reactor walls, aircraft brakes, heat treatment furnaces, etc. Ceramics have been successfully used for more than twenty years for orthopaedic prostheses, aluminium and zirconium oxides are currently accepted as biomaterials for joint prostheses. The main disadvantage of CMC is their brittleness (lack of toughness). However, failure of long-fiber CMCs is not catastrophic [18-20].

1.1.3 Carbon fibre reinforced carbon matrix composites (C/Cs)

Carbon fibre reinforced carbon matrix composites or the so called carbon-carbon (C/Cs) composites use the strength and modulus of carbon fibers to reinforce a carbon matrix to resist the rigors of extreme environments. As high temperature structural materials, C/Cs have been widely used in aeronautics and astronautics because of their remarkable mechanical, thermophysical, and tribological properties. Carbon-carbon composites are used in a variety of sectors requiring high mechanical properties at elevated temperatures such as furnace fixtures, heat shields, load plates and heating elements; good frictional properties for brake pads in high speed vehicles or high thermal conductivity for thermal management applications and also in X-ray targets. However, for extended life applications, these composites need to be protected against oxidation [21-23].

1.1.4 Polymer matrix composites (PMCs)

Polymer matrix composites (PMCs) consist of fibres/particles embedded in polymer matrices and constitute the most prominent class of composites with innumerable applications especially with respect to the manufacturing of lightweight structural part. In PMCs, a polymer matrix
material of either thermoset or thermoplastic and the reinforcements such as fibers (natural or synthetic) are the major components. The mostly used fibre materials are glass-, carbon- and aramid-fibres. Typical glass fibres are E-glass (electrically isolating), S-glass (high breaking resistance and toughness), M-glass (high modulus) and R-glass (resistance). Carbon fibres can be high strength (HST), high modulus (HM), high tenacity (HT) and intermediate modulus (IM) fibres. Polymer composite offers several advantages such as light weight, high specific strength and stiffness, good fatigue resistance and high damage tolerance, good damping characteristics, multi-functional performance, good processing technics etc. But besides this, they also have severe shortcomings with a major concern on their wave propagation response, damage modeling and detection, joining, fatigue life prediction, and pre-stress issues. Currently, polymer composite structures are widely used for manufacturing aeronautic components and are being extended to other industrial applications including railway, ship, automotive, civil engineering, and constructions [24-25].

The mechanical and physical properties of fiber reinforced composite materials are determined not only by the type of fiber, resin type and relative volume fraction, but also closely related with the direction of fiber arrangement, ply stacking sequence and layer number. Owing to the large freedom in the design of composite materials, various functional, multifunctional, smart and intelligent composite materials can be produced by compounding different materials of function [10]. Multifunctional materials such as nano-sized particles including CNTs, graphene, polyhedral oligomeric silsesquioxane (POSS), inorganic nanoparticles, silica and cellulose nanofiber can be used as reinforcing filler for fabricating polymer composites [25].

The manufacturing method for polymer matrix composites include injection molding, resin transfer molding, hand lay-up, spray-up, filament winding, compression molding, pultrusion, vacuum bagging, and autoclave molding, extrusion, out-of-autoclave process, calendaring, thermoforming, braiding, resin film infusion, vacuum infusion, automated tape layering, automated fiber placement and pulforming etc... In injection molding technique, pallets or granules comprising polymer (with chopped fibers) are melted and injected into a mold after being fed through a hopper. In the resin transfer molding (RTM), reinforcement (in the form of woven, continuous strand mat, unidirectional, cloth fabric or three-dimensional textile performs) is arranged to the intended configuration and placed dry in mold cavity and then a catalyzed resin is transferred into the closed mold via a sprue. In spray-up molding, a spray-gun is used to apply resin and reinforcement in the form of chopped roving [3, 24].
In hand lay-up method, first mold release agent is initially placed on the surface of the mold to prevent the component from sticking to the mold. Then, a gel coat made of a resin is placed on the mold surface. The purposes of this coat are to provide smooth and hard surface and to prevent the fiber from appearing on the surface of the mold. Then, fibers and matrix are laid one layer after the other to the desired thickness. The consolidation of composites to obtain fully wet-out of the fibers and removing of air are done by means of a roller. Finally, the composites are cured. Compression or press molding employs a mold of matched male and female dies to mold an intermediate or raw material such sheet molding compound (SMC) and bulk molding compound (BMC) using press machine. Two types of compression moldings are available namely hot press and cold press but hot press is more commonly used. Vacuum bagging technique is used to improve the quality of composite produced by wet lay-up technique. In this process, the laid-up mold is inserted into a bag made of flexible film and then air is evacuated, and pressure is applied. This forces resin into any remaining voids and ensure good adhesion between fiber and matrix. If the laid-up mold inserted into a special bag is placed in an autoclave for cure and consolidation under controlled heat and pressure, it is called autoclave molding [3, 24].

1.1.5 Multifunctional polymer nanocomposites

Multifunctional polymer nanocomposites fabrication by utilizing carbon fillers has attracted widespread attention. Among many carbon fillers, CNTs, carbon nanofibers (CNFs), POSS, graphite, graphene, and nanoclay are the most potential and promising nanofillers for developing hybrid nanocomposites with multifunctional applications. Graphene and CNTs are the most widely used carbon nanomaterials (CNMs) due to their unique morphology, structure, and physicochemical properties. All of them possess different spatial configurations of covalently bonded carbon atoms and are used extensively as multifunctional materials besides CNFs and cellulose nanofibers.

When the size of material decreases and enters in range of the nano-size, the main components of the material (atoms) act like an individual entities and start to concentrate on the surface producing enormous surface energy. For example, when the particle is 2nm in diameter, the surface atoms will occupy 80% overall [10]. The surface energy of engineered nanoparticles depends on the ratio of atoms at the surface relative to atoms in the interior (or the bulk), expressed as a surface-to-volume ratio, A/V. However, due to its energetically unstable condition, the produced surface energy of nano particles reduce by the naturally occurring...
processes of agglomeration (i.e., reducing the surface-to-volume ratio) and/or adsorption of molecules from the surrounding to lower surface energy. This strong aggregation leads the enlargement of particle size which leads to the loss of nano effect (any effects that the bulk form of the same material does not possess such as high surface energy, surface reactivity, high thermal and electric conductivity of nanotubes/fibers) of the particles [26].

If the agglomerates are avoided and can be dispersed in a matrix to form composite materials, so that single nano-metersized individual can be maintained instead of being aggregated (particles or objects of other shapes), it will play the nano-effects (any effects that the bulk form of the same material does not possess, for example, unusual strength, high surface energy, surface reactivity, high thermal and electric conductivity of nanotubes/fibers). This gives rise to several special performances including the surface and interface effects. As a result of the existence of these effects, nano-composite materials have not only excellent mechanical properties, but also produce the function of optics, nonlinear optics, photochemistry and electricity. In a polymer nanocomposite, if the nanoparticle is fully dispersed in the polymer matrix, the filler will play it nano effect and dictate the material properties. Therefore, the design of the nanoparticle is critical to nanocomposite structure, and careful understanding of nanoparticle chemistry and structure are needed [27].

1.2 Motivation and problem definition

To design bio-inspired fiber-reinforced composite structure with higher strength and fracture toughness, nature has offered us with scientific and technological clues from the formation of biological composites using common organic components [6]. Biological composites that require high strength, fracture toughness, energy absorption and crack deflection are organized as tubules or fibrous structures, designed with numerous aligned tubules or fibres that often exhibit hierarchy across multiple length scales. Understanding the desired orientation of the tubules or fibrous elements along with other co-existing hierarchical structures in biological materials can serve as a toolbox for systematizing the development of stronger bio-inspired nano-composite materials with improved mechanical properties. The hierarchically organized exoskeleton of sheep crab, Loxorhynchus grandis features vertically aligned tubular structures which provides ductile attachment to the Bouligand structured exocuticle and endocuticle by stitching the layers together and improves fracture toughness. In a similar fashion, producing carbon fiber composites that contain well sorted and oriented nano reinforcement elements
such as carbon nanotubes (CNTs) or carbon nanofibers (CNFs) has great importance in utilizing the capabilities and exceptional properties of CNTs and CNFs.

In order to fabricate high performance nano-composites, the fraction, the homogeneous distribution and proper orientation of the nanometer-sized reinforcement structural elements play a key role. As CNTs and CNFs are difficult to be uniformly dispersed within polymer matrix at a high mass fraction due to their strong tendency to agglomerate it is still a challenge to fabricate CNT/CNF composites that mimic the natural ones. Producing carbon fiber composites that contain well sorted and oriented nano reinforcement elements such as carbon nanotubes (CNTs) or carbon nanofibers (CNFs) has great importance in utilizing the capabilities and exceptional properties of CNTs and CNFs. Recent studies have shown that nano-composites with superior mechanical and electrical properties can be fabricated with relatively low concentration of nano-fillers by properly dispersing them using a three roll mill and aligning them in polymer resins through AC electric field [24-25].

1.3 Thesis goal

Due to the heterogeneous nature of composites, their fracture mechanisms are more complex. Typical defects of composite materials include fiber break, microcracks, delaminations, foreign objects, or contaminants, impact damage, and porosity or voids. An investigation of the fracture toughness and energy dissipation during delamination in hierarchical composite materials such as CFRPs with vertically aligned carbon nano tubes, as well as pure epoxy is a goal of this master thesis. The energy dissipation during delamination upon the application of opening load depends mostly on the adhesive and ductility properties of reinforcement material. The experimental work deals with pure epoxy and CNT/CNF reinforced epoxy under opening load. It aims to investigate the inter-laminar fracture toughness and associated energy dissipation. The results of this research are expected to prove that the resistance to delamination of carbon fiber reinforced composites can be improved by the proper dispersion and alignment of carbon nano tubes in the epoxy polymer matrix.

1.4 Structure of the thesis

This thesis is organized into multiple units. In chapter 1, background information about conventional and nano composite materials followed by the thesis objectives are discussed. In chapter 2, the hierarchically structured biological nano-composite material eg. cuticle of the crab exoskeleton is discussed. In chapter 3, the features of carbon nanotubes and carbon
nanofibers, their functionalization and potential application areas are presented. In chapter 4, first the dispersion technique of carbon nanotubes and carbon nanofibers followed by alignment techniques are discussed. Then, a literature survey on the mechanical properties of carbon fiber reinforced polymers with carbon nano tube or carbon nano fiber as reinforcement are discussed. In the last sections of chapter 4, the methods to determine the inter-laminar fracture toughness in CFRPs are discussed.

In chapter 5, first materials and the dispersion of carbon nanotubes/carbon nanofibers in epoxy resin using Three Roll Mill (TRM) method are discussed. Then, production of carbon fiber reinforced polymer, orientation techniques of CNTs/CNFs and the procedure of DCB and three-point bending (TPB) are presented. Chapter 6 covers presentation of experimental result on the delamination properties of carbon nanotube/fiber reinforced CFRPs composites. Comparison of the strength and fracture toughness of the nano reinforced CFRP with the reference material, SEM investigation of fractured surface has been also done. Finally, in chapter 7 conclusion and recommendation are given.
2. Hierarchically structured biological nano composites

In recent years, structural biological materials that exist in nature and the complexity, multifunctionality, and multiscale nature of their structure-property relationships has increasingly become a source of inspiration of materials scientists and engineers to create next-generation advanced structural and multi-functional hierarchically organized nanocomposite materials. Synthetic structural materials that take advantage of the mechanical design principles found in nature could transform many fields such as materials science and engineering [28-29].

There have been two approaches in generating bioinspired materials and structures. Traditional approach has utilized synthetic materials to produce performance that mimics biological materials. The current frontier in bioinspired materials goes further and uses bioinspired processes at the molecular level to generate new materials and structures. Such is the case of tissue engineering and other molecular-based approaches. The increased availability of nanoscale testing, characterization, and modelling methods continues providing the tools required for advancing our understanding of the behavior of structural biological materials and hence mimic the unique and defining features of biological materials such as hierarchical structure, self-assembly, multi-functionality and self-healing. As material selection reaches its limitations, engineers look toward nature’s example of structural optimization for the next generation of technology. Understanding the self-assembly and synthesis mechanisms of such biological structural composites can then provide clues in devising a biomimetic processing methods and generate new materials and structures [30].

Most biological materials with structural functions in the animal kingdom consist of an organic matrix of structural biopolymers like collagen and chitin which is modified and reinforced with different proteins and in many cases also with biominerals. The most prominent examples of such materials, like the bones of vertebrates, the exoskeletons of arthropods, and mollusk shells, are known to possess excellent mechanical properties (e.g., in terms of stiffness-to-density ratio and fracture toughness). It has been observed that the specific design and properties at the nanoscale contribute significantly to their macroscopic properties. However, since the properties at small length scales are experimentally hard to access due to methodological constraints, a multiscale modeling that can systematically describe and investigate materials properties from the atomistic scale up to the macroscopic level has become a major approach to tackle the structure-property relations of biological
organic/inorganic nanocomposites and has been applied to bone, mother of pearl, lobster cuticle, and related heterogeneous natural compounds [31-35].

Nature assembles weak organic and inorganic constituents into sophisticated hierarchical structures, forming structural composites that demonstrate impressive combinations of strength and toughness. For example, the strength of hard tissues such as shells, crab exoskeleton, nacre or bones is derived from the structure rather than through materials selection. In biological materials there are eight structural elements that are identified as the most common designs which can serve as a toolbox for systematizing the development of bioinspired design and hence bioinspired materials with improved mechanical properties, namely strength, wear resistance, stiffness, flexibility, fracture toughness, and energy absorption of different biological materials for a variety of functions. The structural design elements identified are: fibrous, helical, gradient, layered, tubular, cellular, suture, and overlapping [31-35]. In this section, hierarchical organization nature of structural biological materials such as crab exoskeleton is highlighted to illustrate the inherent interconnection between design of the structure and material in biological systems.

Fig. 2.1. Diagram of the eight most common biological structural design elements [31].
2.1 Cuticle

One of the defining features of organisms in the Arthropoda phylum is the cuticle, a tough and robust exoskeleton structure whose purpose is primarily to provide support and protection from predators and other environmental pressures. The cuticle is a multi-layered structure, consisting of an epicuticle, exocuticle (procuticle) and endocuticle (underlying epidermal tissue). A schematic depicting the hierarchical structure of the cuticle is shown in Fig.2.2. The procuticle features a well-defined hierarchical assembly of organic and inorganic constituents. At the nanoscale, proteins are often covalently associated with long-chain polysaccharide α-chitin molecules, forming nano-fibrils, which aggregate to form nanofibers. These nanofibers further self-assemble into bundles. The bundles then arrange themselves parallel to each other and form horizontal planes. These planes are stacked in a helicoid fashion, creating a twisted plywood structure. A stack of layers that have completed a 180° rotation is referred to as a Bouligand structure which is pierced by pore canals in the form of twisted ribbons with elliptical cross section. These structures repeat to form the exocuticle and endocuticle [32-33].

Fig.2.2. Schematic showing hierarchical structure of the cuticle of the crustacean [32].

The mechanically relevant exocuticle and endocuticle share the same basic microstructure, but the mineral content in the exocuticle is higher, the pore canals are smaller, and the pitch of
rotation of the chitin–protein fiber planes is also smaller compared to the endocuticle. In crab exoskeletons, the minerals are in the form of calcite or amorphous calcium carbonate, deposited within the chitin-protein matrix. The microstructure of the chitinous organic matrix provides numerous mechanical advantages whereas; the mineral component also plays a vital role in modifying the stiffness, strength, and hardness of the crustacean cuticle. Moreover, in the direction normal to the cuticle surface there are fibrous pore canal tubules interpenetrating the rotating fibers and serve as channels for transport of mineral ions and nutrition during periodic molting and growth. The helicoidal structure is one of the eight most common structural motifs among biological materials in a variety of animal taxa [32-33]. Cuticle is a highly hierarchical composite material that combines high mechanical strength with a high functional versatility. The building block of cuticle are the organic matrix and inorganic nano-particle. The organic matrix (chitin, proteins) which is the most parts of the cuticle is combined with inorganic nanoparticles. The inorganic nano-particle consists of amorphous or crystalline (calcite) CaCO$_3$ and CaCO$_3$ doped by Mg arranged according to the organization of the chitin-protein fibers.

At the atomistic scale, crystalline $\alpha$-chitin exhibits anisotropic character that respects the nature of the interatomic interactions which dominate along different directions. The response of chitin on stresses applied along the $c$-axis of the molecule is dominated by covalent bonds. Along the other two directions a hydrogen bond network is developed which is responsible for the cohesion of the anti-parallel atomic strings. The crystal response to deformations along the $a$ and $b$ directions is rather soft and of the same order of magnitude. The material stiffer along the $c$-axis. Thus, the anisotropy in the bonding character is expected to result in a highly anisotropic elastic matrix. With the obtained elastic properties at the atomistic scale (stiffness tensor of crystalline $\alpha$-chitin), one can derive the effective properties of a cluster of chitin-protein nanofibrils and also the up-scaled elastic parameters by employing the homogenization methods, taking into account experimental information about the actual composite hierarchy [35].

The arthropod cuticle has recently become a biological material of biomimetic interest for structural applications, due to the fact that the mechanisms by which nature develops strong and tough materials using relatively weak (chitin, proteins and calcium carbonate) constituents. Great progress has been made in mimicking its helicoidal structure and achieving the fracture-tolerant properties that this structure affords. Biomimetic helicoidal carbon fiber/epoxy composites fabricated using modern prepreg materials and industrial processing techniques
have already demonstrated the ability to surpass the performance of current aerospace and automotive design standards under impact loading [32].

There are also other biological materials that exhibit superior mechanical properties because of their hierarchical nature. For example, in nacre, the remarkable strength and fracture toughness is attributed to its well-ordered microstructure that features a brick-and-mortar-like arrangement of its inorganic constituent such as polygonal ceramic tablets that form the lamellae and organic constituents such as porous sheets that separate the lamellae. At the mesoscale, mineral nano-asperities coat the surface of aragonite tablets, providing roughness, and some of these asperities cross plate boundaries, fusing them together via mineral bridges. Nacre achieves its high strength because of its high volume fraction of stiff ceramic material whereas, nacre achieved its toughness from several mechanisms such as its crack deflection mechanism at the hard/soft interfaces between the ceramic tablets and organic matrix and the viscoplastic deformation of the inter-lamellar organic sheets allows for tablet sliding, providing ductility. Resistance to tablet sliding under tensile loading due to mineral nano-asperities on the surface of tablets, mineral bridging between tablet layers, and wavy tablet morphology provides an interlocking and strain hardening effect. Because of such remarkable mechanical performance, significant efforts have been taken to mimic its hierarchical structure [33].

Another example is given by bone: where the microstructure of compact bone shows a typical hierarchical architecture made from collagen fibrils and hydroxyapatite (HA) nanocrystals. The fibers generated from several packed collagen fibrils are arranged in parallel to form a lamella. Then, the lamellas are stacked into the osteons with a concentric laminated structure. The osteons are connected by a boundary, called the cement line, with higher mineralization and lower collagen content. Due to compact bone’s anisotropy, how it resists an advancing crack differs depending on the propagating direction. Bone is a tough material, however, due to cement lines having a weak crack bridging interface, the cracks propagate along a cement line faster resulting in poor toughness [34].
3. Carbon nanotubes (CNTs) and Carbon nanofibers (CNFs)

Materials in a form of fiber are of great practical and scientific importance. The combination of high specific area, flexibility, and high mechanical strength allow nanofibers to be used in our daily life as well as in fabricating tough composites for vehicles and aerospace. However, it is worthy to note the clear difference between the conventional carbon fibers (CF), the carbon nanotubes and carbon nanofibers (sometimes known as carbon filaments). As depicted in Fig.3.1, the conventional CF has diameters of several micrometres, while CNFs have diameters of 50-200 nm. Conventional CFs and CNFs differ in the microstructure of the carbon. Conventional CFs have the carbon layers preferably oriented along the fiber axis, whereas CNFs do not necessarily have this preferred orientation. Both CNTs and also CNFs have a hollow channel inside along the axis whereas the conventional CF does not have. CNFs are also to be distinguished from CNTs, which are smaller (1 nm scale) in diameter and have the carbon layer(s) in the form of concentric cylinder(s) along the nanotube axis. For a single-wall nanotube, there is only one carbon layer. CNF are much lower in cost and wider in availability than nanotubes [36-37].

Fig.3.1 Schematic of various types of fibrous carbons [36]

Generally, conventional carbon fibers are manufactured by a controlled pyrolysis of stabilized precursor such as a synthetic, semicrystalline organic polymer polyacrylonitrile (PAN), rayon (made from regenerated cellulose fiber) or meso-phase petroleum pitch with PAN based being the most common. Precursor fibers are first stabilized at about 200-400 °C in air by an oxidization process. The infusible, stabilized fibers are then subjected to a high temperature
treatment at around 1,000°C in an inert atmosphere to remove hydrogen, oxygen, nitrogen, and other non-carbon elements. This step is often called carbonization. Carbonized fibers can be further graphitized at an even higher temperature up to around 3,000 °C to achieve higher carbon content and higher young’s modulus in the fiber direction [38].

The main method currently used for production of CNFs is the catalytic thermal chemical vapor deposition (CVD). Alternatively, carbon nanofibers could be fabricated by the right combination of electrospinning of organic polymers and thermal treatment in an inert atmosphere. CNTs can also be prepared by catalytic growth with alternate methods include arc discharge and laser ablation. Some of the CNTs preparation methods are more effective than others but a problem that all methods face is the ability of the CNTs to self-align. Many applications of CNTs require controlled growth of aligned CNTs with surface modification. Controlled synthesis of well-aligned CNTs in predetermined patterns is particularly important in terms of fundamental studies and applications [39].

3.1 Carbon nanofibers (CNFs)

Carbon nanofibers are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates. Carbon nanofibers with graphene layers wrapped into perfect cylinders are called carbon nanotubes. CNFs can be defined as sp²-based linear filaments with diameter of ca. 100 nm that are characterized by flexibility and higher aspect ratio. These fibers possess outstanding thermal, mechanical and electrical properties and have attracted a great deal of attention [40].

Regarding the production of CNFs, the main method currently used is the catalytic thermal chemical vapor deposition (CVD), which consists in the decomposition of a C-containing gas (usually hydrocarbons or CO) over an elemental transition metal (Fe, Ni or Co) or alloy as catalyst at temperatures in the range of 500-1200 °C. The general mechanism for the catalytic growth of CNFs can be shortly described as: (i) decomposition of the hydrocarbon (or CO) on the metal surface, (ii) carbon dissolution and diffusion through the bulk of the metal and (iii) precipitation in the form of graphite at the other side of the metal particle. Generally, the structures of the CNF are governed by the shapes of the catalytic nano-sized metal particles. The growth mechanism has been proven as the deposition of the hydrocarbons dissolved in the metal particle and precipitated on the metal surface as graphitic carbon [40-41]. Alternatively,
carbon nanofibers could be fabricated by the right combination of electrospinning of organic polymers and thermal treatment in an inert atmosphere.

To fabricate the CNFs by the electrospinning method, the polymer nanofibers are required to be prepared as the precursors of the CNFs. The properties of the final CNFs are decided by the types of polymer solution and the processing parameters. PAN and pitches are the most frequently used polymers. In addition, polyvinyl alcohol (PVA), polyimides (PIs), polybenzimidazole (PBI), polyvinylidene fluoride (PVDF), phenolic resin and lignin were also used. Once the polymer nanofibers have been successfully prepared, a heat treatment will be applied to carbonize the polymer nanofibers to form CNFs. After the polymer nanofibers have been successfully fabricated, the carbonization process will be followed by heating the polymer nanofiber up to 1000 °C in a specific environment [41]. Electrospun-based nanofibers exhibited noticeable properties, such as nanosized diameter, high surface area and thin web morphology, which make them applicable to the fabrication of high-performance nanocomposites, tissue scaffolds and energy storage devices.

3.2 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are one of the allotropes of carbon with a nano-scale cylindrical structure of a graphene sheet. CNTs are members of the fullerene structural family, which also include spherical shaped buckyballs. The sp2 C-C bond of CNTs is considered one of the strongest in solid materials. Owing to their exceptional strength and stiffness, carbon nanotubes have been constructed with aspect ratio (length-to-diameter ratio) of many millions to one which is significantly higher than any other material [42-44].

3.2.1 Structure conceptualization and properties of CNTs

The hexagonal arrangement of atoms in carbon nanotubes and graphene sheets can be described in terms of the tube’s chirality or helicity, using the chiral vector, \( \vec{c}_h \), or the chiral angle \( \theta \). This implies that the nanotube is uniquely specified by the pair of integer numbers \( n, m \) or by its radius \( R = c_h / 2 \pi \) and chiral angle \( \theta \). The chiral vector, \( \vec{c}_h \), also known as the roll-up vector, is defined by the following equation [42-44].

\[
\vec{c}_h = n\vec{a}_1 + m\vec{a}_2,
\]

where the integers \( n \) and \( m \) are the number of steps along the unit vectors \( \vec{a}_1 \) and \( \vec{a}_2 \), as defined in Fig. 3.2. The chiral angle \( \theta \) determines the amount of twist of the carbon nanotube.
According to their chiral vector, \( \mathbf{C}_h \), carbon nanotubes are classified into three main categories namely zigzag, armchair and chiral. A chiral nanotube has unequal, non-zero \( m \) and \( n \) integers, i.e. \( n \neq m \neq 0 \) and the chiral angle \( \theta \) is between its two limits (\( 0^\circ < \theta < 30^\circ \)). Zigzag nanotube has a chiral angle which is equal to zero (\( \theta = 0^\circ \)) and unequal integers, i.e., \( n \neq m \), \( m = 0 \) whereas, the armchair nanotube has a chiral angle (\( \theta = 30^\circ \)) and \( n = m \neq 0 \).

Fig.3.2 Schematic view of a single-walled zigzag, armchair and chiral carbon nanotubes [42]

Besides chirality, carbon nanotubes can be classified as single-walled carbon nanotubes (SWCNTs) and multiple-walled carbon nanotubes (MWCNTs) depending on the number of layers. SWCNTs have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer. MWCNTs consist of multiple rolled layers (concentric tubes) of graphite with 0.34nm distance between each wall. The electrical conductivity of the chiral and zigzag SWCNTs show metallic semiconducting behaviour, whereas the armchair SWCTs and the MWCNTs show metallic behaviour and are considered conducting materials. Single-walled nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale currently used in electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors [42-45].

3.2.2 Carbon nanotubes Synthesis methods

Carbon nanotubes can be produced using various methods. The three main techniques are arc discharge, laser ablation and chemical vapour deposition (CVD). The common characteristic of these techniques is to provide energy to a carbon source for the creation of carbon atoms.
that generate CNTs. The energy source is current in an arc discharge, the high-intensity light from a laser in the laser ablation & heat from a furnace in CVD.

3.2.2.1 Arc discharge method

In arc discharge technique, a vapor is created by an arc discharge between two carbon electrodes with or without catalyst and then CNTs self-assemble from the resulting carbon vapour. Because the growth temperature of the arc-discharge method is higher than that of other CNT production methods, CNTs produced by arc discharge are highly crystalline and have fewer defects than nanotubes produced by other methods. However, it is hard to grow aligned carbon nanotubes by arc discharge [45-48].

3.2.2.2 Laser ablation technique

In the laser ablation technique, a high power laser beam impinges on a volume of carbon containing feedstock gas (such as methane or carbon monoxide). Since the energy density of lasers is much higher than that of other vaporization devices, the laser is suitable for materials with a high boiling temperature such as carbon. In this process, a piece of graphite is vaporised by laser irradiation under an inert atmosphere. The graphite vapor is converted into amorphous carbon as the starting material of SWCNTs and then results in soot containing CNTs which are cooled at the walls of a quartz tube. High-quality SWCNTs with minimal defects and contaminants can be produced using the laser-furnace method together with purification processes. Both arc discharge and laser ablation techniques are expensive due to the high power equipment so they are mainly used for SWCNTs production [45-49].

3.2.2.3 CVD technique

CVD is another popular method for producing CNTs in which a hydrocarbon vapor is thermally decomposed in the presence of a metal catalyst. Compared with arc-discharge and laser methods, CVD is a simple, easy to scale up and economic technique for synthesizing CNTs at low temperature and ambient pressure. CVD generally involves reacting a carbon containing gas (such as acetylene, ethylene, and methane) with a metal catalyst particle (usually cobalt, nickel, iron or a combination of these such as cobalt/iron or cobalt/molybdenium) in a tube furnace in which a catalyst material is present at sufficiently high temperature (600-1200°C) to decompose the hydrocarbon. CNTs grow over the catalyst and are collected upon cooling the system to room temperature. Currently, a CVD is the most widely used method to produce the CNTs [46-50].
In all the CNT preparation methods, the CNTs come with a number of impurities whose type and amount depend on the technique used. The most common impurities are carbonaceous materials such as graphite (wrapped up) sheets, amorphous carbon, smaller fullerenes, catalytic particle, metal particles and other types of impurities. The structure selective and size-selective separations techniques are employed to separate the CNTs from the impurities and to give a more homogeneous diameter or size distribution respectively. For example, in chromatography technique, CNTs are separated into fractions with small length and diameter distribution by allowing them to flow over a column made of a porous material by first dispersing or solvating them [39].

3.2.3 Functionalization of Carbon nanotubes

For a nanocomposite, a good dispersion of the filler within the host matrix and stabilizing the dispersion to prevent re-aggregation of the filler are very important. These tasks are particularly very challenging in case of nanofillers such as CNT since the extremely large surface area lead to strong tendency to form agglomerates. CNTs are very well known to form aggregates during compounding and hence various mechanical techniques have been used to overcome this problem. But the most effective way to resolve this problem is surface functionalization of CNTs. Surface functionalization helps in stabilizing the dispersion, since it can prevent re-aggregation of nanotubes and also leads to coupling of CNT with polymeric matrix. Coupling between CNT and polymer matrix is also very important for efficient transfer of external stress to nanotube. Even though, like graphite, CNTs are relatively nonreactive like graphite, the hydrophobic surfaces of carbon nanotubes adsorb a wide class of substances by $\pi-\pi$ and/or van der Waals interactions. Surface functionalization of carbon nanotubes can be classified as covalent functionalization and noncovalent functionalization [50-53].

In covalent functionalization chemical reactions are carried out which result in bond formation with the surface of nanotube sidewalls. Covalent functionalization of CNTs can be achieved by introducing some functional groups on the surface of CNTs by using oxidizing agents such as strong acids (HNO3/H2O2 and HNO3/H2SO4), which results in the formation of carboxylic or hydroxyl groups (-COOH, -OH) on the surface of nanotubes. Such functionalization improves nanotube dispersion in solvents and polymers and imparts high stability in polar solvents. Although surface functionalization leads to significant improvement in CNT dispersion and stress transfer, it also causes deterioration of intrinsic properties of CNTs. Alteration of CNT properties lead to poor reinforcement and conductivity. Hence, it becomes
obvious that dispersion and stabilization are not simple issues and compromises have to be made depending on the applications [50-53].

To employ CNT as effective reinforcements in polymer composites, proper interfacial adhesion between polymer and CNTs is most important issue. As discussed in the previous sections, the chemical functionalization of MWCNT surfaces increases the compatibility between epoxy matrix and CNT due to the formation of an interface with stronger interconnections. -COOH functionalization of MWCNTs helps to achieve better interfacial reaction between MWCNTs and the epoxy matrix resulting in better dispersion. This better dispersion of MWCNTs effects the improvement of mechanical properties of polymeric composites. COOH in MWCNTs creates interconnection with polymer matrix and therefore make the nanocomposites more resistant to chemical attack [50, 67].

![Chemical functionalization of MWCNT](image)

**Fig. 5.2: Chemical functionalization of MWCNT**

### 3.2.4 The potential application areas of Carbon nanotubes

The potential applications of carbon nanotubes include as additives in polymers; nanotube composites (by filling or coating); nanoprobes for STM, AFM, and EFM tips; catalysts; electron field emitters for cathode ray lighting elements; flat panel display; gas-discharge tubes in telecom networks; electromagnetic-wave absorption and shielding; energy conversion; lithium-battery anodes; hydrogen storage; nanolithography; nanoelectrodes; drug delivery; sensors; supercapacitor and reinforcements in composites. With its superior material properties, CNT can also function as quantum wire and a critical material for the integrated circuit interconnection. It is now a widely-shared view that carbon-based materials are likely to be a major field in the twenty first century technology [54-55].
4. Carbon Fiber Polymer Composites (CFRP)

The conventional CFRPs composites consist of carbon fibres embedded in polymer matrices. CFRPs constitute the most prominent class of composites with innumerable applications especially with respect to the manufacturing of lightweight structural part. Currently, CFRP composites are replacing the metallic components in aviation, naval and automotive industries. The structural performance of a fiber-reinforced polymer composite depends on the fracture resistance to crack propagation. Improving the brittle fracture nature of the epoxy matrix and debonding between the carbon fiber and polymer matrix not only improves the interlaminar fracture toughness of CFRP but also the compressive strength, the fatigue life and impact performance. To extensively use fiber reinforced polymer matrix composites in structural applications, many nano-fillers (carbon nanotubes, nanoclays, etc.) have been incorporated into the traditional polymers to enhance their mechanical properties and add multi-functionality. Mechanical properties of carbon fibers reinforced polymer composites depend on the fiber, matrix and the interface between them. Researchers have been investigating various organic and inorganic nanoparticles as reinforcement of composites to enhance the mechanical properties and thermal stability. Significant development in the use of nanoparticles for modification of epoxy matrix has led to improved mechanical properties of the CFRP composites. Among the nanoparticles, carbon nanotubes CNTs and CNFs are the strongest materials and are most widely used because of their strong interfacial interactions and excellent stress transfer properties. Due to the high specific strength and modulus along with low density, the use of CNTs for modification of epoxy matrix has led to improved mechanical properties of the CFRP composites. However, to employ CNT as effective reinforcements in polymer composites, proper interfacial adhesion between polymer and CNTs is most important issue [56-59].

4.1 Dispersion techniques of CNTs/CNFs

Advances in functionality and reliability of CNT/polymer composite materials require careful formulation of processing methods to ultimately realize the desired properties. Many research efforts have been directed towards producing CNT/polymer composites for functional and structural applications. However, in spite of decades of research, the full potential of employing CNTs as reinforcements has been severely limited. This is primarily due to the strong interaction forces that cause the formations of bundles and clusters in as-produced CNTs. Conventional methods of producing a composite involves directly mixing as-produced CNT
fillers into a polymer matrix. The dispersion and arrangement of CNTs in the matrix (including their potential uniaxial alignment) hold a central role in controlling the properties of the resulting composites. The overall performances of the CNT/CNF enhanced CFRP composites are largely governed by the dispersion of the CNT/CNF in the polymer matrix; the dispersion technique plays a key role in the fabrication of CNT/CNF enhanced CFRP composites. The agglomeration behavior of CNTs is known to affect the mechanical, rheological, thermal, and electrical properties required for their diverse applications. The hydrophobic nature of CNT sidewalls and the strong interactions between individual tubes can lead to the congregation of CNTs in bundle-like shapes. To achieve an optimal dispersion of CNTs, the matrix should be compatible enough to wet the hydrophobic surfaces without inducing CNT aggregation. Hence, dispersion is one of the most important factors to consider in the fabrication of CNT/polymer nanocomposites. The strong tendency of CNTs to aggregate due to strong van der Waals interactions prevents their utilization as the ultimate nanomaterial. Successful dispersion of CNTs could lead to the diameter and/or chirality-selective separation of individual CNTs. Disaggregation and uniform dispersion are critical challenges that must be met, since carbon nanotubes tend to self-associate into micro-scale aggregates. Hence, the thermodynamic drive toward aggregation must be overcome. The two distinct approaches for dispersing carbon nanotubes are the mechanical method and methods that are designed to alter the surface energy of the solids, either physically (non-covalent treatment) or chemically (covalent treatment) [51-53, 60].

4.1.1 Chemical methods

The chemical inertness of CNTs hampers their processability and this has impeded the full-realization of their potential. Chemical surface functionalization of CNTs has been shown to improve their chemical compatibility with the target medium (solvent or polymer solution/melt), that is, to enhance wetting or adhesion characteristics and reduce their tendency to agglomerate. However, aggressive chemical functionalization, such as the use of neat acids at high temperatures, might introduce structural defects resulting in inferior properties for the tubes. The chemical dispersion approaches include: solvent dispersion, polymer-assisted dispersion, surfactant-assisted dispersion (a noncovalent treatment by using different surfactants for creating stable dispersions through van der Waals interactions, π-π stacking, and hydrophobic interactions) and biomolecular dispersion (using biomolecules such peptides, proteins, DNA, and RNA to maintain the stable dispersion of CNTs through the interaction on their surface). In solvent dispersion, the application of a solvent to the oxidized nano carbons
induced much stronger repulsion between them as compared to pristine nano carbons which helped maintain a stable dispersion. In polymer-assisted dispersion several methods including solution mixing, melt mixing, electrospinning, in situ polymerization, liquid crystalline phase-induced methods, and chemical functionalization have been adopted to achieve a stable dispersion of nanotubes in the polymer matrix [51-53].

4.1.2 Mechanical methods

Depending on their synthesis method, the as-produced CNT have different length ranges, and often contain defects in their walls, hence are not completely straight over their contours. Furthermore, they are rarely present in isolated entities but instead are found in bundles or clusters. The incorporation of CNTs into a polymer matrix leads to an exceptionally large quantity of agglomerated particles resulting in the difficulties to uniformly disperse these particles. Some of the mechanical techniques used for CNT dispersion in polymer matrix are ultrasonication, three roll mill, ball milling and extrusion. Generally, a mixing process by using external forces (e.g., through the rotation of a mixer blade, or cavitation in ultrasonication), generates the local shear stresses that are ultimately responsible for dispersion of nano fillers in the matrix [60-61].

Sonication/ultrasonication is a mechanical method that is frequently employed in combination with surfactants to break, disperse, or de-bundle CNT aggregates or bundles in the dispersing process. In ultrasonication techniques ultrasound energy is applied to agitate particles in a solution for various purposes. The principle of this technique is that when ultrasound propagates via a series of compression, attenuated waves are induced in the molecules of the medium through which it passes. The production of these shock waves promotes the “peeling off” of individual nanoparticles located at the outer part of the nanoparticle bundles, or agglomerates, and thus results in the separation of individualized nanoparticles from the bundles. The sonication time and sonication energy are parameters that identify the degree of CNT dispersion [60-62].

Three roll mill (also known as the calendar) dispersion technique employs a shear force created by rollers to mix, disperse or homogenize viscous materials. In calendering, the adjacent cylinders rotating at different velocities are utilized to impart high shear stresses. The material is fed and pre-dispersed in the first gap, pre-dispersed, and then transported by middle roller it into the second gap where the material is dispersed to the desired degree of fineness. Upon
exiting, a knife blade then scrapes the processed material off the apron roller. This milling cycle can be repeated several times to maximize dispersion. The narrow gaps between the rollers, combined with the mismatch in angular velocity of the adjacent rollers, result in locally high shear forces with a short residence time. Unlike other mills, which rely on compressive impact as well as shear, calendering results in nearly pure shear. Because the mixture must pass through the gap, the process also uniformly shears the entire volume. For dispersing nanotubes, high shear stresses break-up and untangle nanotubes while short residence time limits nanotube breakage. One of the unique advantages of this technique is that the gap width between the rollers can be mechanically or hydraulically adjusted allowing to get a controllable and narrow size distribution of particles in viscous materials. A high shear stress is required to disentangle CNT bundles and distribute the dispersed CNT into polymer matrix, while a short residence time will likely limit the breakage of individual nanotubes [60-63].

Fig. 4.1. Schematic showing the working mechanism of a Three Roll Mill (TRM) machine that is used for dispersion of CNTs/CNFs into a polymer matrix [60]

Ball milling is a type of grinding method used to grind materials into extremely fine powder. Ball milling of carbon nanotubes (CNTs) in the dry state is a common way to produce tailored CNT materials for composite applications, especially to adjust nanotube lengths. CNTs are filled together with steel balls into a rotating barrel for the milling process resulting in the grinding of the CNT material to the necessary fineness by friction and impact with the tumbling balls. Different materials, including ceramic, flint pebbles and stainless steel, are used as balls. Industrial ball mills can operate continuously to feed materials at one end and discharge them at the other end. Ball milling of CNTs in the presence of chemicals not only enhances their...
dispersibility, but also introduces some functional groups onto the CNT surface. However, ball milling also causes contamination or damage on CNTs surfaces and results in a degradation of CNTs properties [59-65].

Another mechanical dispersion technic is extrusion. It is a popular technique to disperse CNTs into solid polymers like most thermoplastics, where thermoplastic pellets mixed with CNTs are fed into the extruder hopper. Twin screws rotate at high speed create high shear flow, resulting in dispersion of CNT agglomerates and mixing them with the polymer melt. This technique is particularly useful to produce CNT/polymer nanocomposites with a high filler content [60].

4.2 Alignment of CNTs/CNFs in nanocomposites

The superior intrinsic properties of CNTs offer exciting opportunities for new nanocomposites. However, the limitation for some potential applications of CNTs come from the fact that randomly oriented nanotubes embedded in polymer matrices have exhibited substantially lower mechanical, electrical and thermal conductivities than expected. The orientation and arrangement of carbon nanotubes (CNTs) in composite structures is a challenging issue. In fact, if nanocomposites with an adjusted arrangement and desired distribution of CNTs could be produced, then our expectations about the properties of CNT nanocomposites could be fulfilled. Therefore, methods by which the arrangement of CNTs can be controlled and adjusted are of great importance. Carbon nanotube alignment can be achieved using different in-situ and ex-situ methods. In the in-situ method, alignment of CNT is done during growth (during synthesis of CNTs) where the regular placement of catalyst nanoparticles on the substrate leads to growth of CNT masses in regular rows. In ex-situ orientation (post growth) processes, the CNTs are initially produced using conventional methods. Then, by applying a distinct process, they are arranged for a specific purpose. It is reported that orientation and alignment of CNTs embedded in the epoxy the aforementioned methods increased and showed improvement in mechanical properties of the resulting nanocomposites. Some CNT alignment techniques include: dielectrophoresis (DEP), polymer film stretching, fracture stretching, friction orientation (doctor blade or tape casting technique), electrospinning (ES), fiber drawing, spray winding and layer-by-layer deposition, Inert gas flow method, Liquid crystal (LC) method and filtration method [52, 66].
4.3 Mechanical properties of CNT/CNF enhanced CFRP composites

Mechanical properties of carbon fibers reinforced polymer composites depend on the fiber, matrix and the interface between them. Researchers [67-73] have been investigating various organic and inorganic nanoparticles as reinforcement of composites to enhance the mechanical and thermo-mechanical properties. Significant development in the use of nanoparticles for modification of epoxy matrix has led to improved mechanical properties of the CFRP composites. Among the nanoparticles, carbon nanotubes CNTs and CNFs are the strongest materials and are most widely used because of their superior strength to weight ratio, higher stiffness, strong interfacial interactions and excellent stress transfer properties. Due to the high specific strength and modulus along with low density, the use of CNTs for modification of epoxy matrix has led to improved mechanical properties of the CFRP composites.

The study [67], has found that enhancement of the mechanical properties of CFRP composites can be achieved by the modification of matrix properties through the use of nano reinforcing materials such as CNT or nanoclays. In the study, carbon fiber reinforced epoxy composites were modified with 0.3 wt. % COOH-MWCNTs. The techniques used for dispersion are mechanical stir, ultrasonication and three roll mill shear dispersion. Then, after CNT/CFRP composite were manufactured through hand lay-up process and compression molding technique, a three-point bending test (TPB), dynamic mechanical analysis (DMA) and low velocity impact test (LVI) were conducted. The TPB test result showed that with addition of nanoparticles the flexural strength and modulus of all the samples increased by 20% and 15% respectively compared to the control one. The result of DMA test performed in three-point bending mode showed that COOH-CNT/CFRP composites possess higher storage modulus, high loss modulus and dumping properties. Similarly, the load versus displacement result of the LVI test conducted by impacting the sample with specific amount of energy proved that the COOH-CNT modified CFRPs possess higher amount of absorbed energy.

In the study [68], the mechanical properties such as the flexural modulus and flexural strength of CFRPs have been investigated by adding 0.7%wt of MWCNT, 0.7 %wt of NH2-MWCNTs or CNF to epoxy resin and compared with the CFRPs produced with neat epoxy during lamination. After conducting a four-point bending test, the flexural modulus was improved by +6 %, +13 % and +14 % by the addition of 0.7 %wt MWCNT, NH2-MWCNT and CNF respectively whereas, the flexural strength of the CFRPs was improved by +10 %, +18 % and +14 % by the addition of 0.7 %wt MWCNT, NH2-MWCNT and CNF respectively. The study
showed that epoxy resin matrix mixed with functionalized CNTs have better load transfer capability compared to the epoxy matrix mixed with non-functionalized CNTs.

In another research [69], the delamination toughness and damage-sensing capability of an aligned carbon nano-fibres (CNFs) in the matrix of a glass-fibre reinforced polymer (GFRP) composite have been investigated. The CNFs are added to the epoxy resin and alignment of the CNFs has been done using an alternating current (AC) electric field, applied across the GFRP sheet throughout the matrix-curing process. Investigation of the mode I crack growth resistance (R curve) behaviour of the CNF/CFRP composites under quasi- static loading using TPB test shows that the value of the interlaminar fracture toughness, \( G_{\text{ICI}} \), increased over the initial 10 to 15 mm of delamination growth and then reached steady-state propagation (\( G_{\text{ICSS}} \)) value. The result also shows that, the presence of randomly-orientated CNFs in the GFRP composite results in 50% and 25% increases in average values of the crack initiation (\( G_{\text{ICI}} \)) and steady-state (\( G_{\text{ICSS}} \)), interlaminar fracture toughness respectively, compared to the GFRP composites without alignment of CNFs. Furthermore, the presence of aligned CNFs in the GFRP composite further increases the values of \( G_{\text{ICI}} \) and \( G_{\text{ICSS}} \), by about 100% and 80% compared to the GFRP composite without CNFs. The study also reported that using the aligned CNFs in the epoxy matrix enhances the damage-sensing capacity of the GFRP composite which is attributed to the greatly increased out-of-plane electrical conductivity of the aligned CNF/CFRP composite compared the randomly oriented.

In another study [70], the results of the fracture toughness of carbon fiber polymer composites with the adhesive layer comprising of unmodified epoxy or epoxy nanocomposites containing randomly-oriented or aligned CNFs are presented. To disperse the CNF in epoxy resin, has been done using three-roll mill. After conducting a DCB test, the result shows that an increase in the value of the fracture energy was observed for all the epoxy nanocomposites with concentration of CNF 0.1\%, 0.4 \%, 0.7 \% and 1.6 \% in weight fraction. For the nanocomposites, the fracture energy increases almost linearly with the increase in concentration of CNFs. In addition, greater improvement in the fracture energy was consistently measured for samples containing aligned CNFs, with their orientation normal to the direction of crack growth. Further, compared to the nanocomposites containing randomly-oriented CNFs, the alignment of the CNFs resulted in a consistent rise of about an additional 25% increase in the fracture energy for the concentrations investigated at, and below, 1.0 wt\%. However, a further increase in the concentration of the CNFs to 1.6 wt\% showed a relatively
small difference between the fracture energies of the aligned and randomly-oriented CNF nanocomposites explained by the lack of free space available for the rotation and alignment of the CNTs in the epoxy when a relatively high concentration of nanofiller was present.

In [71], the interlaminar fracture toughness of CFRP laminates using cup-stacked carbon nanotubes (CSCNTs) as nano reinforcement have been investigated for six types of CFRP composites such as (a) CFRP without CNT (control), (b) CFRP using 5 wt% CNT-dispersed epoxy, (c) CFRP using 5 wt% CNT-dispersed epoxy with 10 g/m² sprinkle of AR10 CNT between layers, (d) CFRP using 5 wt% CNT-dispersed epoxy with 10 wt% AR10 CNT-dispersed film between layers, (e) CFRP using 5 wt% CNT-dispersed epoxy with 10 g/m² sprinkle of AR100 CNT between layers, and (f) CFRP using 5 wt% CNT-dispersed epoxy with 10 wt% AR100 CNT-dispersed film between layers. The dispersion of CSCNT in epoxy were done using the planetary mixer followed by wet mill with ceramic beads. In both mode-I and mode-II tests, all CNT-dispersed CFRP laminates exhibit higher fracture toughness, and specifically, CNT-dispersed CFRP laminates with thin epoxy interlayers containing short CNTs have three times higher fracture toughness than CFRP laminates without CNT. The results of DCB and ENF tests exhibit similar improvement of fracture toughness by using CSCNTs.

The reinforcement effects of epoxy/MWCNT and epoxy/VGCF in the bulk composites and at the interface of conventional CFRP laminates have been investigated in [72]. For VGCF, three area densities, i.e., 10, 20 and 30 g/m² at the interface, are used. For MWCNT, 5, 10 and 20 g/m² are used. To produce the interface of CFRP composites a simple powder method (using a sifter with mesh size about 70 µm in zigzag pattern spreading path) is used to add MWCNT or VGCF at the interface between CFRP prepreg. Then, the 14 layered CFRP laminates, with and without VGCF or MWCNT at the middle interface have been fabricated in autoclave. The results of the DCB test using cross head speed of 0.5mm/min indicate that the Mode-I interfacial mechanical properties are significantly improved where, VGCF was more efficient than MWCNT. The graph of $G_{IC}$ versus area density of nanofiller at interface shows 95.5% and 58.4% increases in $G_{IC}$ for 20 g/m² of VGCF and 10 g/m² of MWCNT, which is the maximum value of all that can be considered as the optimal addition amounts. For higher amount of nano filler (egg. 30 g/m² of VGCF and 20 g/m² of MWCNT) a good dispersion becomes difficult which results in fracture surface with large void. In the study, a bulk composites of epoxy/VGCF and epoxy/MWCNT composites with 2, 4 and 6 wt.% VGCF and 2, 3 and 4 wt.%
MWCNT additions respectively were also investigated under tensile and single edge notch blend tests. The results showed that largest increases of 31% and 36% in Young’s modulus occur at 4 wt.% loading for epoxy/MWCNT and at 6 wt.% loading for epoxy/VGCF, respectively compared to the neat epoxy. In case of tensile strength, the highest increases are 14.1% for epoxy/MWCNT at 4 wt.% loading, and 23.1% for epoxy/VGCF at 4 wt.% loading compared to the neat epoxy. Regarding the $G_{IC}$ value, a remarkable increase of 85.5%, were observed for 2 wt.% loading of MWCNT.

In [73] a DCB tests have been carried out in order to evaluate the Mode-I interlaminar fracture toughness of five CFRP specimens with a fixed amount of VGCF addition i.e., CFRP, CFRP/VGCF(10 g/m$^2$), CFRP/VGCF(20 g/m$^2$), and CFRP/VGCF(30 g/m$^2$). The result of $G_{IC}$ shows that all CFRP/VGCF laminates possess higher $G_{IC}$ compared to the base CFRP laminates. Especially, CFRP/VGCF(20) exhibits the highest values of Mode-I fracture property, where $G_{IC}$ is 95% greater than those of the base CFRP laminates. However, when the area density increases up to 30 g/m$^2$ for CFRP/VGCF(30), the $G_{IC}$ decrease, which is even lower than those of CFRP/VGCF(10). This result confirms that the reinforcement and toughening effects of VGCF interlayer depend on the area density of VGCF, which do not certainly increase as the addition amount of VGCF increases. Hence, there should be an optimal addition amount of VGCF to achieve the maximum reinforcement and toughening effects.

### 4.4 Methods to determine Inter-laminar fracture toughness of CFRPs

Due to the increased application of composite materials in a wide range of high-performance structures, intensive experimental and theoretical studies of failure analysis and prediction are being conducted. When designing a structure against fracture, there are three critical variables that must be considered: stress, flaw size, and toughness. Fracture mechanics provides mathematical relationships between these quantities. The stress and flaw size provide the driving force for fracture, and the fracture toughness is a measure of the material’s resistance to crack propagation. Fracture occurs when the driving force reaches or exceeds the material resistance. Several parameters are available for characterizing the fracture driving force. The stress-intensity factor $K$ and the energy release rate $G$ are suitable parameters when the material is predominately elastic. The $J$ integral and crack-tip-opening displacement (CTOD), are appropriate driving force parameters in the elastic-plastic regime. The mechanical performance of composites is typically dominated by the formation of delaminations. Delamination is a critical failure mode, as it typically leads to other structural problems such as premature...
buckling of the laminate, excessive vibration, intrusion of moisture, strength and/or stiffness degradation, and/or loss of fatigue life.

![Basic delamination modes](image)

**Fig.4.5. Basic delamination modes**

Accurate prediction of delamination initiation and propagation is therefore necessary for the design and analysis of robust composite structures. Delamination fracture may occur under three different loadings, referred to as opening or peel mode (mode I), the in-plane shear mode or sliding shear mode (mode II), and the out of plane shear mode or twisting shear mode or tearing mode (mode III) as shown in Fig.4.5. As long as nonlinear material deformation is confined to a small region surrounding the crack tip, delamination analysis of composites is typically carried out with the use of linear elastic fracture mechanics (LEFM). According to LEFM, delamination growth is predicted when the available surface energy exceeds the fracture toughness. The fracture toughness is defined as the energy required to create a new unit of surface area, commonly regarding to as the critical strain energy release rate. Several parameters are available for characterizing the fracture driving forces (the stress and the flow size). In Mode I fracture of elastic media (LEFM), the most common fracture parameters that used for fracture prediction and toughness characterization are the mode I energy release rate, $G_I$, the Mode I stress intensity factor, $K_I$, and the path-independent $J$-integral. The critical value of these parameters, i.e., their values at the instant that crack growth initiates, is called the fracture toughness and is generally assumed to be an intrinsic material property and is determined by experiments [74-75]. The energy release rate is defined as the decrease in total potential energy per unit area of crack extension. For pure mode I loading, the mode I energy release rate, $G_I$, is therefore given by:

$$G_I = \frac{P^2}{2b \partial a}$$  \hspace{1cm} (4.1)
where P is the magnitude of the applied load, a is the crack length, b is the width of the body and C is the compliance of the body which depends on P which is the magnitude of the applied load (P) and the associated displacement (δ) and can be given as C=δ/P.

4.4.1 The Mode I Interlaminar fracture toughness testing

The mode I delamination toughness is usually measured using the double cantilever beam (DCB) test, which was standardized for fiber reinforced composites by ASTM D-5528. A schematic of the DCB test is shown in Fig.4.6, where the specimen thickness is represented by h, the crack length is given by a, and the applied load is given by P [77]. For the linear elastic case under consideration, a variety of data reduction methods are available for DCB tests to determine the interlaminar fracture toughness. Those are the beam theory method (with corrections for load-blocks), the experimental compliance calibration method and the modified compliance calibration method as described by ASTM D5528. The $G_{IC}$ values determined by these three methods differed by not more than 3.1 %, none of the them were superior to the others. However, MBT method is recommended as it has yield the most repeated values of $G_{IC}$ for 80% of specimen tested during ASTM round robin testing [78].

![Fig.4.6: Schematic of specimen and loading block for DCB test](image)

4.4.1.1 The Compliance Calibration (CC) Method

The compliance calibration approach uses compliance versus crack length relationship which is determined in the experiments by loading and unloading the specimen at various crack lengths. The compliance at each crack length is determined from the slope of the load versus displacement data. A least squares curve fit is performed on points in the plot of compliances versus crack lengths using an empirical power law as follows [75]:

$$C = Ra^n$$  \(4.2\)
where $R$ and $n$ are constants. Substitution of equation (4.2) into equation (4.1) gives an expression for calculation of the fracture toughness as follows:

$$G_{IC} = \frac{nP_c R a^{n-1}}{2b}$$

(4.3)

where $P_c$ is the critical load used for the toughness definition. The above equation can also be represented in another form by substituting the relation $C = \delta_c / P_c$ into equation (4.3) and the Mode I interlaminar fracture toughness $G_{IC}$ is determined as follows [77-78]:

$$G_{IC} = \frac{nP_c \delta_c}{2ba}$$

(4.4)

Here $\delta_c$ is the crack opening displacement at the onset of fracture. The compliance calibration method generates a least squares plot of $\log(C)$ versus $\log(a)$ using the visually observed delamination onset values and all the propagation values. A straight line is drawn through the data that results in the best least-squares fit. The exponent $n$ from the slope of this line is calculated according to $n=\Delta x/\Delta y$ where $\Delta y$ & $\Delta x$ are increment value of $y$ & $x$ respectively.

**4.4.1.2 The Modified Compliance Calibration (MCC) method**

In this method generate a least squares plot of the delamination length normalized by specimen thickness $(a/h)$ as a function of the cube root of compliance $C^{1/3}$. Using the visually observed delamination onset values and all the propagation values and the slope of this line represented by $A_1$, the Mode I interlaminar fracture toughness will be given as:

$$G_I = \frac{3P_c^{2/3} C^{2/3}}{2A_1 b h}$$

(4.4)

**4.4.1.3 The Modified Beam Theory (MBT) method**

The beam theory expression for the strain energy release rate of a perfectly built-in double cantilever beam is as follows:

$$G_I = \frac{3P \delta}{2ba}$$

(4.5)

In practice, this expression will overestimate $G_I$ because the beam is not perfectly build-in where rotation may occur at the delamination front. One way of correcting for this rotation is to treat the DCB as if it contained a slightly longer delamination $a+\Delta$ where $\Delta$ may be determined experimentally by generating a least squares plot of the cube root of compliance, $C^{1/3}$ as a function of delamination length. The values used to generate this plot should be the load and displacements corresponding to the visually observed delamination onset on the edge and all propagation values. The Mode I interlaminar fracture toughness will be [77]:

$$G_I = \frac{3P \delta}{2b(a+|\Delta|)}$$

(4.6)
4.4.2 The Mode II interlaminar fracture toughness testing

The double cantilever beam (DCB) test method is an international standard for mode I interlaminar fracture testing of fiber reinforced composites and has been used widely and successfully to evaluate the mode I interlaminar fracture toughness of fiber reinforced composites. However, interlaminar performance is characterized by pronounced weakness under both shear and tensile stresses. In many laminates, the strength reduction has been observed due to delamination between plies. Delamination induced failure is normally a result of a combination of compressive and bending stresses caused by the delaminated plies as they buckle out of plane. Fiber breakage and matrix cracking also have an effect on the strength. Interlaminar shear, tension and the matrix cracking largely cause internal delamination which in turn gives rise to residual stresses that further reduces the strength. The End-notched flexure (ENF) test is one of the methods designed to measure the interlaminar fracture toughness under in-plane shear deformation mode, commonly known as Mode II. The measured $G_{IIc}$ is believed to represent the critical strain energy release rate for crack growth from the insertion film. In Mode II test, the load is introduced by flexural forces to produce a crack from the insert. The crack then extended as a result of shear forces at the crack tip as shown in Fig.4.7 [78-79]. An ENF or 4ENF test involves performing a three-point or four-point bending test on a specimen with initial delamination at one end. While applying a load onto the specimen the initial delamination will grow towards the center under sliding shear conditions.

One of the methods most often used for the experimental evaluation of shear behaviour is the ENF test, which calculates the value of the fracture energy required for the inter-laminar crack propagation by shear strength. The ENF test consists of a three-point or four-point bending test in which the pre-existing interlaminar crack is forced to propagate by shear stresses. These shears are generated when the sample is flexurally loaded at three points or four points and a relative movement between both surfaces of the crack occurs, causing its mode II propagation. Experimental results show that the ENF test gives reliable initiation value of fracture toughness. Specifically, the effect of friction in the 4ENF test is much lower than other methods such as the over notch flexural (ONF) test. Hence, in this thesis the four-point bend end notched flexural (4ENF) test has been conducted to evaluate the fracture toughness of nano reinforced CFRP composite specimens [78-79].

In the 4ENF test, conventional compliance method is used to determine the critical energy release rates as follows:
where $C$ is the compliance expressed by

$$C = C_0 a + C_1$$

(4.8)

where $C_0$ and $C_1$ are constants which can be determined from experimental compliance-crack curve. The compliance is determined from the slope of the loading line. According to LEFM theory and neglecting the thermal energy loss due to friction the energy release rate can be expressed as follows:

$$G_{II} = \frac{1}{B} \frac{dU}{da}$$

(4.9)

where $U$ is the strain energy and $a$ is the crack length. Considering the point-friction model as described in [79] the Mode II interlaminar fracture toughness can be calculated as follows:

$$G_{II} = \frac{9P^2 s^2}{16E_L b^2 h^3} \left(1 - \frac{4\mu h}{3s} + \frac{4\mu^2 h^2}{9s^2}\right)$$

(4.10)

where $P$ is the load in N, $\delta$ is the loading-line displacement (the deflection of the center of the inner span in mm), $s$ is the distance from the supporting point to load point in mm i.e., half of the difference between support distance and load pint distance, $h$ is half of the thickness of the specimen in mm, $\mu$ is the friction coefficient, $b$ the specimen width in mm and $a$ is the delamination length in mm [78-79].

Fig.4.7. Schematic of ENF specimen and load
5. Materials and Experimental Methods

5.1 Materials

The materials used in this study include Bisphenol-A-epichlorohydrin epoxy resin, mainly consisting of Bisphenol-A-diglycidyl ether (BADGE) obtained from Sika (Biresin CR170), a mixture of cis- and trans-1,2-Diaminocyclohexane (Biresin CH170-3) hardener, multi-walled carbon nanotubes (MWCNT) and vapor-grown carbon nanofibers (VGCNF) and a plain weave and high tenacity (HT) carbon fibers obtained from SGL Group.

![Chemical structures of the main component of the resin and hardener.](image)

Fig. 5.1: Chemical structures of the main component of the resin (left) and hardener (right).

The CNTs used in this study were multi-walled carbon nanotubes (MWCNT) from the company Nanocyl, a standard grade of neat MWCNT (NC7000) and carboxyl-functionalized COOH-MWCNT [79]. Whereas, the CNFs used were vapor-grown carbon nanofibers (VGCNF) produced by Pyrograf (PR-25-XT-HHT), obtained from Sigma-Aldrich [79]. To produce CFRP, a plain weave with an aerial weight of 245 g/m² and a yarn fineness of 200 tex (3k) warp/weft from high tenacity (HT) carbon fibers obtained from SGL Group was used. According to the supplier, the received CNFs (VGCNF) had a diameter of approximately 125-150 nm and length of 20-200 μm whereas the CNT has a diameter of approximately 9.5 μm and length of 1.5 μm.

5.2 Dispersion of CNTs and CNFs in epoxy resin

As discussed in the previous sections, appropriate dispersion of CNTs/CNFs is challenging due to the very high agglomeration tendency of both filler types especially CNTs. Hence, dispersion is a critical processing step in the production of CNT or CNF enhanced polymer composites. Dispersion of CNTs in thermosets such as epoxy usually achieved using the TRM (also known as calender), ball milling or ultrasonication [a]. Depending on the type and quantity of processed polymer certain dispersion techniques are preferred. Only extrusion and calendering
are reported as non-destructive methods relating to the structure of dispersed CNTs and additionally both techniques can be used in industrial scale.

5.2.1 Three-roll-mill (TRM)

A three-roll-mill (TRM) or calendering is one of the most effective methods for the dispersion of CNT in viscous media like resins. In calendering, a CNT/resin mixture passes through thin gaps between rollers, rotating in the opposite direction as shown in Fig. 5.3. In this method, nano filler such as CNT can be individualized without being shortened due to locally high acting shear forces, in contrast to ultrasonication or high-speed mixing in which fiber shortening occurs.

Fig.5.3. Schematic showing the working mechanism of a Three Roll Mill (TRM) machine that is used for dispersion of CNTs/CNFs into a polymer matrix [76]

In this study, the nano fillers (the neat MWCNT, COOH-MWCNT or CNF) were dispersed in the viscous epoxy resin using a three-roll-mill (TRM) from Exakt (80E) with SiC-coated rollers. In order to obtain a high quality of dispersion of the respective filler material the gap size was precisely controlled starting from 120 μm in the very first step, down to 5 μm in the final processing steps. The maximum speed of the roller was maintained at 300 rpm and four passes through the rollers were conducted with gap of 120 μm (first pass), 30 μm (second pass), 10 μm (third pass) and 5 μm (final pass) for feeding roller and a gap of 40 μm (first pass), 10 μm (second pass), 5 μm (third pass) and 0 μm (final pass) for apron roller. To facilitate the dispersion and minimize the agglomeration, pre-dispersions of 0.7 wt% MWCNT/CNF, based on the amount of epoxy resin, were first mixed with a mechanical stirrer, before processing on
the TRM. To see dispersion quality, thin layers of the dispersions were prepared on a glass slide and then using optical light microscope the images were taken in transmission light mode. All parameters for the creation of MWCNT/CNF epoxy dispersions are listed in Table 5.1.

Table 5.1: Processing parameters of CNT, COOH-MWCNT & CNF in epoxy on the TRM

<table>
<thead>
<tr>
<th>Set up</th>
<th>Gap 1 (μm)</th>
<th>Gap 2 (μm)</th>
<th>Line pressure (N/mm)</th>
<th>Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>COOH-MWCNT</td>
<td>CNF</td>
</tr>
<tr>
<td></td>
<td>Gap 1</td>
<td>Gap 2</td>
<td>Gap 1</td>
<td>Gap 2</td>
</tr>
<tr>
<td>1</td>
<td>120</td>
<td>40</td>
<td>3.87</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>10</td>
<td>5.63</td>
<td>3.97</td>
</tr>
<tr>
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<td>15</td>
<td>5</td>
<td>5.4</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>0</td>
<td>6.33</td>
<td>10</td>
</tr>
</tbody>
</table>

5.3 Production of CFRP

Once the MWCNTs/CNFs functionalized with hydrogen peroxide and dispersed in epoxy resin using TRM, the COOH-MWCNT/CNF epoxy dispersions were mixed with the hardener in a stoichiometric weight ratio of 100:16 and stirred for 7 min at 300 rpm under vacuum conditions to avoid the formation of bubbles. Then, CFRP laminates consisting of 20 layers 3k plain weave (245 g/m²) from high tenacity carbon fibers supplied by SGL Group were produced in a hand lay-up. The 3k plain weave carbon fiber is highly formable and wets out easily. It provides excellent longitudinal strength while adding minimal weight and thickness to the piece being reinforced. It is recommended for wet layups, vacuum bag molding or infusion and used in aviation, industrial field, architecture, sporting and recreational goods.

Using hydraulic hot press machine, plates with a dimension of 55 x 20 (cm²) and 4 mm thickness were produced in a hot press at 140°C at 30 bar hydraulic pressure and cured for 1 hour at a company SECAR. Specimens for the DCB tests with a dimension of L=125 mm, b=11 mm and h=4 mm were cut out of the cured plates using water-jet cutting according to ASME standard D 5528. The fiber volume ratio \( V_f \) of the tested specimens was calculated from a measured areal weight of the plain weave (229 g/m²), its density (1.8 g/cm³) and the thickness of the CFRP specimens for 20 ply layers. Relatively high values were obtained due to the compression of the CFRP plates in a hydraulic press. The fiber volume content of the test specimen can be calculated as ration of the fiber volume over specimen volume which is equal to 20 times areal wt. of CF mat over density of fiber times the thickness.
5.4 Orientation of CNTs/CNFs

For the in-situ orientation of the MWCNT/CNF in epoxy during the curing process of the CFRP, two electrode plates with a Cu-coating, wrapped with PTFE-foil for electrical isolation, were placed on both sides of the CFRP laminate inside the press. The electrodes were connected to an AC voltage source (signal generator and amplifier), providing an electrical field strength of $E=100 \text{ V/mm}$ at a frequency of 1 kHz (Fig.5.4). Once the laminate was placed inside the press, the electrical field was applied from the beginning of the curing reaction to achieve a maximal orientation of the MWCNT/CNF.

5.5 DCB and 4ENF tests

The DCB test were conducted according to ASME standard D 5528 [77]. A schematic of the DCB test is shown in Fig.5.5, where the specimen thickness is represented by $h$, the crack length is given by $a_0$, and the applied load is given by $P$. A non-adhesive Teflon film was
inserted in the mid-plane of the laminate during fabrication which acted as delamination initiator. Loading blocks are attached to the test specimen using a mixture of epoxy and hardener and stayed for 4 hr and then cured in an oven for one hour at 60°C. The delaminated end of the DCB specimen was opened by quasi-static loading at a displacement control mode with a constant crosshead speed of 4mm/min on a universal testing machine (Zwick/Roell, 10 kN) with a spindle-driven frame. For each testing series at least three specimens were tested.

Fig. 5.5: Schematic of DCB specimen (top) and the specimen under DCB test (bottom)

The Mode II 4ENF test were conducted according to the recommendation of [79]. For the Mode II 4ENF test, a computer-operated, a universal testing machine (Zwick/Roell, 10 kN) with a spindle-driven frame was used by setting the displacement speed at 1mm/min. During the 4ENF test, a high-speed video camera recorded the shear slippage of the crack tip. For each material at least three tests were performed. The initial crack was first produced using Teflon film during curing process. Then before testing the specimen the Teflon is removed using razor blade and extended ahead of the crack tip were produced. In the 4ENF
test, the initial crack length \(a\), which was defined as the distance from the support of the cracked portion to the crack tip, was 23 mm. The specimen was supported by 66 mm spans. A load was applied as shown in the Fig. 5.5 and the crosshead speed was set to be 1 mm/min. The total testing time was about 10 min.

![Schematic diagram of the four-point bend end-notched flexure (4ENF) test.](image)

Fig. 5.6. Schematic diagram of the four-point bend end-notched flexure (4ENF) test.

![Specimen under four-point bend end-notched flexure (4ENF) test.](image)

Fig. 5.7. The specimen under four-point bend end-notched flexure (4ENF) test.
6. Results and Discussions

6.1 Dispersion results

After processing on the three-roll mill (TRM), the dispersion quality of the CNT/CNF dispersions in epoxy was controlled by optical light microscopy. As can be seen in Fig.6.1, a homogenous distribution of COOH-MWCNT in epoxy resin with agglomerate size of approximately around 5 μm has been observed from light microscope images in case of COOH-MWCNT. Light microscope also shows homogenous distribution of CNF in the resin with some large agglomerations were visible, as well.

Fig.6.1: Light microscopy images of dispersions of 0.7 wt% COOH-MWCNT (top) and CNF (bottom) in epoxy for different magnification

The shape and size of the agglomerates of the COOH-MWCNT and CNF slightly differs from each other which indicates to which extent the fillers interact with the matrix. Larger and spherical shaped agglomerates have been observed in case of COOH-MWCNT which influence the alignment and hence the electrical conductivity and mechanical properties such as fracture toughness of CFRP. As can be seen in Fig.6.1, the dispersion of pristine CNT has been found to have more and larger agglomerates compared to COOH-CNT which indicates that functionalizing CNT helps to facilitate the dispersion and minimize the agglomeration.
The dispersion of nano fillers (the COOH-MWCNT or CNF) in the viscous epoxy resin using a three-roll-mill (TRM) is reported as effective method because nano fillers can be individualized without being shortened due to locally high acting shear forces, in contrast to other methods. The high shear stress applied by rollers helps to disentangle CNT bundles and distribute the dispersed CNT into polymer matrix, while a short residence time will likely limit the breakage of individual nanotubes [60-63]. The effectiveness of the three-roll mill (TRM) method has been also demonstrated by SEM images, which clearly indicate individualized CNT in the fracture surface of the DCB specimen. However, even after TRM dispersion, there are still agglomerates remaining of around 5 μm in size and in some images taken agglomerates with size of even more than 5 μm were observed due to re-settling of MWCNT. This will influence the final mechanical properties by hindering the alignment of filler in the CFRP.

6.2 Alignment and electrical conductivity of MWCNT/CNF reinforced CFRP

The limitation for some potential applications of CNTs come from the fact that randomly oriented nanotubes embedded in polymer matrices have exhibited substantially lower mechanical, electrical and thermal conductivities than expected [66]. Therefore, different in-situ and ex-situ methods by which the arrangement of CNTs can be controlled and adjusted are of great importance. The factors that affect the quality of alignment include availability of individualized MWCNT/CNF in the epoxy matrix, the electric field strength and its frequency. In this thesis, the alignment of nano fillers has been done using dielectrophoresis (DEP) technique where the MWCNT/CNF are aligned by applying AC field to MWCNT/CNF suspension on substrate placed between electrodes.

Most MWCNT and CNF show high electrical conductivity and hence the electrical conductivity of CFRP composites are also improved by the addition of nano fillers [69-70]. In this thesis, the electrical conductivity of MWCNT/CFRP, COOH-MWCNT/CFRP and CNF/CFRP were measured using digital ohmmeters. The sample with a known thickness (t in m) and a constant cross section (A in m$^2$) together with measured resistance (R in ohm) are used to calculate the conductivity ($\sigma = t/R A$) of the nano reinforced CFRP composites in the aligned direction. As can be seen in Fig.6.2, due to alignment, improved conductivity was recorded with maximum value for COOH-MWCNT followed by the aligned CNF and neat MWCNT compared to the reference i.e.; the conventional CFRP without nano-filler enhancement.
Fig. 6.2: Electrical conductivity of CFRP reinforced with 0.7 wt.% COOH-MWCNT (with and without alignment), 0.7 wt.% CNF (with alignment) and the reference

Quantifying the alignment of nano fillers (MWCNT and CNF) is much more difficult, since light microscopy is not suitable for resolving individual MWCNT/CNF and other methods such as Raman spectroscopy and X-ray scattering suffer from signal overload from the carbon fiber layup as compared to the weak signal from MWCNT/CNF. It is very important to well disperse and align the nano fillers because, after all the full potential of reinforcement is obtained only from individualized and aligned MWCNT/CNF, providing their whole surface as interaction interface to the matrix. In this thesis, the alignment of the MWCNT and CNF is characterized by measuring the electrical conductivity of MWCNT/CNF enhanced CFRP in the direction normal to the specimen surface i.e.; through the thickness.

6.3 Mode I inter-laminar fracture toughness properties of CFRP

Once DCB test is done, the collected testing data was analysed in Microsoft Excel and Python. Among the results that were obtained, the first was load versus crack opening distance for aligned COOH-MWCNT and non-aligned COOH-MWCNT which was averaged from at least three tested specimens for each case. In Fig 6.3, the load versus crack opening displacement curves from the mode I interlaminar fracture toughness testing of the reference and COOH-MWCNT modified CFRP with and without alignment are compared. For all material types, a linear increase in the load is initially observed, followed by a notable load...
drop after the crack initiation caused by an increasing lever of the test machine. For the aligned COOH-MWCNT, after the maximum load which corresponds to the onset of the crack growth, the load remains relatively high during the propagation of the crack as compared to the load of the other specimens.

![load vs. crack mouth displacement curve from a DCT test](image)

**Fig. 6.3** load vs. crack mouth displacement curve from a DCT test.

Generally, one can observe from the graph that before the onset of crack propagation, the slope of the curves is linear. However, after onset of crack propagation, the load versus crack opening displacement profile was not very smooth for all samples indicating a series of unstable stick-slip crack growth steps occurred. Each stick-slip point in the load versus crack opening displacement curve was accompanied by increment in crack growth which resulted in delamination of the DCB. In each stick-slip process, the peak loads of these curves corresponded to the onset of crack growth, while the lower values of load corresponded to the arrest of the fast propagating crack. The unstable zigzag crack propagation is consequence of regions with different toughness. When the crack reaches the tougher region, it slows down until the rate of release of elastic stored energy is sufficient to propagate the crack through the tougher region. The release rate of stored energy is then higher than that required for stable
growth. The crack then accelerates, and unstable fracture occurs [70, 80]. The average maximum peak load which represents the largest amount of force that the specimen could withstand, or the ultimate strength of the material were also calculated. The result showed 23 % and 15 % increment in peak load has been observed for CFRP with aligned COOH-MWCNT compared to the nonaligned COOH-MWCNT and the reference respectively.

Another key DCB test result that was analysed was the fracture energy ($G_f$). The fracture energy is the area under load versus crack opening displacement curve and it is calculated through integration of area under the load versus crack opening displacement curve. Fracture energy is a parameter that measures how much energy is required to completely fracture the specimen. In the plot of fracture energy versus crack opening distance (Fig. 6.4), the result shows high fracture energy in the case of CFRP with aligned COOH-CNT compared to the nonaligned and the reference. Comparing the failure mechanism of the nano composites i.e., the aligned and randomly distributed nano fillers, a fracture nature which is characterized by lower energy absorption prior to the specimen fracture has been observed for randomly distributed nano-filler whereas for the aligned nano-filler, the crack propagates slowly when the stress (load) is increased and the material absorbs significant energy before fracture.

![Fracture energy versus crack opening displacement curve from a DCT test.](image)

**Fig. 6.4** Fracture energy versus crack opening displacement curve from a DCT test.
As can be seen from Fig. 6.3 and Fig. 6.4, after the onset of crack growth (in the whole post peak part of the load and fracture energy versus crack opening distance curves), the value of the aligned COOH-MWCNT is higher which indicates higher total fracture energy (work done) compared the non-aligned COOH-MWCNT and reference. In the crack initiation phase, an initial steeper rise in toughness has been observed in the case of random COOH-MWCNT and also the reference, however, this initial part of the load-crack opening displacement curves shows only the early part of the load-crack opening displacement curve i.e.; before the onset of crack propagation and cannot be used to determine the post peak value. Generally, the increase of the total fracture energy of the interface in the case of aligned COOH-MWCNT is due to the toughed nature of the nanocomposite through stitching and/or bridging mechanism because of the alignment of the nano-filler and matrix fragments. As can be seen in Fig. 6.5, the aligned COOH-MWCNT has improved the fracture energy by 21% and 32% compared to the reference and non-aligned COOH-MWCNT respectively. Fig. 6.6 also show that the aligned COOH-MWCNT have improved the fracture toughness by 20% compared to the reference material.

![Graph showing Mode I Fracture energy values from a DCT test.](image)

Note that only the aligned COOH-MWCNT have improved the fracture energy and fracture toughness of the reference material by 20% and 21% respectively. The value of fracture toughens of COOH-MWCNT and the reference was statistically indifferent. However, the decreasing effect caused by the non-aligned MWCNT compared to the reference, maybe due to the availability of agglomerates greater than 5µm which may act as defects and formed stress...
concentration. Failure initiates at a surface defect that is larger than the nanoparticles or small CNT agglomerates. Due to the nature of loading condition defects have more serious impact in decreasing the fracture toughness in mode I test.

![Mode I fracture toughness, $G_{Ic}$ obtained from DCB test](image)

Mode I delamination samples are subjected to an open loading condition, and agglomerated CNTs might have acted as defects and formed stress concentration. Besides the availability of agglomerates, if the well dispersed part of the MWCNT are not aligned it may result in less toughened nature of nanocomposite due to lack of stitching and/or bridging mechanisms [81-82]. In addition, air-bubble that occur during fabrication due to non-vacuum pressing technique maybe also be the reason behind the decrease in fracture toughness in case of the random distributed nanofillers.
6.4. Fracture surface morphology

The improvement of delamination performance achieved by adding aligned nano-fillers to CFRP laminates was supported by examinations of the fracture surfaces of the Mode I fracture testing of specimens. Fig. 6.7 shows SEM observations of the fracture surfaces for the laminates of CFRP composites with a 0.7 wt% of aligned and nonaligned CNT. As can be seen from the fracture surfaces, in case of the aligned carbon nanotubes several CNT/epoxy matrix fracture surfaces were clearly observed. The existence of more fracture surface and/or more complex surfaces implicate that more energy is needed during the crack propagation, and consequently, the fracture energy increased.

In order to see the nano fillers, the fracture surface of CFRP specimens with aligned and nonaligned COOH-CNT were also examined at a higher resolution using SEM. As can be seen in Fig. 6.8, the presence of the MWCNTs at the fracture surface is clear. Even though not very well refined, the aligned arrangement of MWCNT in the hierarchically structured carbon fiber composite can be seen in Fig. 6.8. Noting that the orientation direction (the electrical field direction) is pointing out-of-plane, the aligned MWCNTs are clearly visible in contrast to randomly distributed MWCNT. Many MWCNTs are aligned perpendicularly to the fracture surface, which may have played a “bridging” role to resist the delamination propagation.

The fracture surface observations support the fact of higher experimental fracture toughness for the aligned COOH-MWCNT laminates compared to the non-aligned COOH-MWCNT and reference CFRP laminates. Hence, from these SEM pictures, we may conclude that the improved fracture toughness is related to the ability of the nano-reinforcement to spread the damage through crack bridging. As can be seen in Fig. 6.7, SEM observations of the fracture surface of nano filler modified laminates showed that CFRP laminates modified with aligned COOH-MWCNT had several or scraps of matrix materials and several fracture surfaces compared to the nonaligned COOH-MWCNT reinforced laminates. The occurrence of these several stepwise scraps and/or fracture surfaces implicated crack deflection and creation of new fracture surface, and consequently, more energy was required to fracture [73, 81].

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Fig. 6.7. SEM images of the fracture surfaces of CFRP composites with a 0.6 wt% of aligned CNT (top), nonaligned CNT (middle) and CNF (bottom) under Mode I open loading.

Ideally, the high aspect ratio, elasticity, strong interfacial bonding (due to functionalization) should result in higher absorption of energy through effective crack bridging (including mechanical interlocking with the matrix material), momentary crack arrest and/or deflection and strong absorption of fracture energy when pulled out from the matrix. However, the non-aligned COOH-MWCNT was not able enhance the toughness of the reference material. This may be due to the combined effect of the availability of agglomerates greater than 5µm and the non-alignment of well dispersed parts MWCNT. The MWCNT agglomerates act as defects and formed stress concentration. Failure initiates at a surface defect that is larger than the nanoparticles or small CNT agglomerates [81-82].
Fig. 6.8. SEM images of CFRP fracture surfaces with aligned MWCNT (first row), random MWCNT (second row), random & aligned CNF (third row) and agglomerates of CNF (last row), with alignment direction pointing out of plane.
6.5. Surface roughness Analysis

In this thesis, the quantitative micro-measurements of fractured surfaces were conducted to further understand the surface roughness of the fractured specimens. The roughness measurements were performed using VHX 5000 digital microscope which is a noncontact optical profilometer that has the capability to capture high quality multiple images focused on different heights and composes a single 3D image by stitching them. By selecting a line along the plane of the fractured surface of the specimen, the digital profilometer of VHX 5000 digital microscope computes the small surface variations in the vertical direction as a function of position. From this result the surface roughness parameters such as the arithmetic mean roughness (Ra), the maximum height of the profile (Ry) or the ten-point mean roughness (Rz) can be calculated [83-84].

As can be seen in Fig. 6.9, the fractured surfaces of the delaminated DCB specimens were not perfectly flat but exhibited some waviness. The formation of more local and global wave-like fracture surface is a toughness enhancing mechanism as it promotes slip-stick fracture processes. The fracture surface for the aligned COOH-MWCNT is more rough and rugged compared to that of the nonaligned and the reference, which indicates a potential for fracture toughness increase. The maximum height of the surface roughness profile was also higher in case of the aligned nano filler [80-83]. These optical micrographs can be viewed as a global representation of surface features as the images were captured at low magnification in order to cover maximum region of fractured surfaces.

Fig. 6.9. shows fractured surface profiles for aligned, non-aligned and reference cases with horizontal axis representing scanning length and vertical axis denoting the asperity height. A scanning length of 11 mm was chosen in the stable crack growth region. The roughness profile data was recorded at 3 different scan lines at different locations on the surface of the specimen along the delamination direction within the regions of interest. The scanned data obtained from the surface profiler was also automatically plotted over the image of fractured specimen surface. From the plotted profile one can easily compare the different surface roughness values for the aligned, non-aligned and reference cases. The surface profile of the aligned COOH-MWCNT shows more local and global waviness coupled with larger amplitudes (up to 120 µm) compared to the others. On the other hand, the non-aligned COOH-MWCNT and reference fracture profile show less local waviness, less amplitude (around 60 µm) and less roughness demonstrating its brittle nature with less energy expenditure. Thus, the qualitative
as well as quantitative investigations showed higher surface roughness for the aligned COOH-MWCNT compared to other cases which suggest higher fracture performance in case of the aligned nano filler composite.

Fig.6.9. Surface roughness profiles for aligned, random and reference specimens with horizontal axis represents scanning length and vertical axis denoting the asperity height.
Fig. 6.10. Surface roughness profiles (top) and images of fracture surfaces with colour code representation for lower and upper limit of the fracture surface (bottom) of aligned MWCNT
Fig. 6.11. Surface roughness profiles (top) and images of fracture surfaces with colour code representation for lower and upper limit of the fracture surface (bottom) of random MWCNT
Fig. 6.12. Surface roughness profiles (top) and images of fracture surfaces with colour code representation for lower and upper limit of the fracture surface (bottom) for the reference case.
6.6. Investigation and quantification of air bubbles

In this thesis, to avoid air bubbles, the COOH-MWCNT/CNF epoxy dispersions were mixed with the hardener in a stoichiometric weight ratio of 100:16 and stirred for 7 min at 300 rpm under vacuum conditions. Then, after a few minutes, the mixture was applied to each layer of the substrate followed by hot pressing technique. However, this procedure (vacuum stirring of the hardener and CNT/epoxy mixture before the hand lay-up of the laminates during manufacturing process) doesn’t prevent the air bubbles from occurring in the fabricated specimens. Characterization of voids can be done either by simple density determination methods (which calculates the void content value, i.e. the void volume fraction by the relative difference between theoretical and measured composite density) or by means of optical and electron microscopic techniques such as SEM via optical counting and area fraction. It has been suggested that a statistical analysis of 20-25 images can determine the void content with an acceptable accuracy. Even though, the microscopy technique allows characterization of the void size, shape, and distribution, it is the density determination technique which is suitable for quality control purposes since it is applicable to large samples and is relatively fast [85-88].

In this study, with the motivation to find out the reason behind the decreasing effect in toughness value by non-aligned nano filler, investigation of air bubbles on the fracture surface of tested specimens has be done using SEM and VHX 5000 digital light microscope followed by quantitative analysis of the average number of bubbles in the fractured surface area. Interestingly, closer average number of air bubbles have been found in both the fracture surface of the non-aligned and the reference composite material with a little bit more in number and size of voids in case of randomly nanofillers enhanced CFRP. However, in case of the aligned nano filler enhanced composite material the average number of air bubbles were relatively fewer. In a single fractured surface area of a specimen the average area of voids was 58.5 mm² (5.3 %), 38.7 mm² (3.5 %) and 8.5 mm² (1 %) for the random, reference and aligned MWCNT material respectively. However, it should be noted that these void are only the 2D intra-laminar voids that have been investigated using microscopy by approximating each void as square and circular shaped, other irregular shaped inter-laminar voids maybe also present throughout the specimen volume.

It has been observed that voids in fiber reinforced composites, even in small amounts influence the mechanical behavior, in particular matrix-dominated properties such as inter-laminar shear strength, inter-laminar fracture toughness, longitudinal compressive strength and transverse
tensile strength. It has been reported that, a decrease of 22% in Mode I inter-laminar fracture
toughness were observed with 5% increase in void content. This because the voids provide
readily available free surfaces for the crack with not much energy being dissipated by the voids
[85]. Hence, in this study, the decreasing in fracture toughness of the random distributed nano
filler reinforced CFRP composites compared to reference material maybe due to the increased
number of voids present as a result of the availability of agglomerates which in turn arises from
the failure of the epoxy resin to penetrate the wet MWCNT resulting in large void formation
and hence creating a weak interlaminar region [88-90].

The reason behind observing relatively fewer number of air bubble in case of aligned
nanofillers may be attributed to the effect of heating process during curing of specimens
covered from up and bottom by plate electrodes and insulation material. To avoid air bubbles,
some researchers used relatively longer curing time with elevated temperature whereas, others
use vacuum assisted pressing method. Even though, voids are the most studied type of
manufacturing defects in processing of fiber-reinforced composites, the investigation is still an
active research field in composites community because of remaining unknowns and
uncertainties about voids as well as difficulties in their suppression in modern manufacturing
techniques. Formation and evolution of voids during processing of carbon fiber reinforced
composites are not the same for all manufacturing techniques due to the difference in
thermodynamic and rheological phenomena happening in these processes.

The main sources of intra and inter voids in prepreg composites are air entrapment either during
impregnation or during laying up, volatiles arising from resin during its cure, and moisture
dissolved in the resin. Moreover, increase in gel temperature was found to increase the void
content, at a given pressure and moisture content attributed to higher void growth at higher
temperatures. However, modern prepregs have very small volatile and moisture contents,
which makes mechanical air entrapment the chief mechanism. In out of autoclave
manufacturing techniques such as hot press, alleviation of voids maybe done by means of high
pressure and also appropriate processing conditions, especially sophisticated thermal cycles,
are essential to achieve a high consolidation and low void contents. Most out of autoclave
manufacturing techniques applies vacuum along with high-temperature initial- and post-cure
to consolidate laminates. Resin outflow has been also indicated as the dominant mechanism for
evacuation of voids during curing [85-88].
Fig. 6.13. SEM images showing the air bubbles in fractured surface for reference material (CFRP without nano filler)
Fig. 6.14. SEM images showing the air bubbles in fractured surface for the random nano filler (COOH-MWCNT/CFRP)
Fig. 6.15. SEM images showing the air bubbles in fractured surface for the aligned nano filler (COOH-MWCNT/CFRP)
Fig. 6.16. Air bubble distribution in fractured surface area of a tested specimen for the reference, the random and aligned nano fillers.

Fig. 6.17. Air bubble distribution in fracture surface area of a tested specimen in case of the random nano filler.
Fig. 6.18. Air bubble distribution in fracture surface area of a tested specimen in case of the reference material.

Fig. 6.19. Air bubble distribution in fracture surface area of a tested specimen in case of the aligned nanofillers.
6.7 The Mode II inter-laminar fracture toughness properties of CFRP

Once 4ENF test is conducted, among the results that were obtained and analysed, the first was the load versus displacement curve which was averaged from at least three tested specimens for each case. In Fig. 6.20, the load versus displacement curves from the mode II fracture toughness testing of the reference, CNF or COOH-MWCNT modified CFRP with and without alignment are compared. As can be seen in the Fig 6.20, the load-displacement curves can be subdivided into four parts i.e., first phase ($\delta \approx$ ca. 0 to 1.4 mm), second phase ($\delta \approx$ ca. 1.4 to 1.7 mm), third phase ($\delta \approx$ ca.1.7 to 2.25 mm), and fourth phase ($\delta \approx$ ca. 2.5 to 3.5 mm). In the first part, for all material types, a linear increase in the load is initially observed, followed by a notable first load drop ($\delta \approx$ ca. 1.4 mm). This first part illustrates the linear load-displacement relationship between the beginning of the investigation and the point indicating the position of the non-linear point, $\delta \approx$ ca. 1.4 mm [91-93].

![Fig. 6.20. The force-displacement curves recorded from the 4ENF test.](image)

The second phase of the load-displacement curve corresponds to crack initiation phase and storage of energy by plastic deformation. Energy release, a sudden reduction in force and unstable crack growth are observed in third phase where propagation of the crack starts at the
first point of the second load drop ($\delta \approx \text{ca. 1.7 mm}$) which is also the point of maximum force $F_c$. After the end of the third phase, fracture in the fourth phase is not anymore a result of interlaminar delamination rather it is a result of the independent loading of the upper and lower laminates. Once the adhesive rupture is produced, both upper and lower laminates continue to work independently until the rupture of the composite occurs at the second peak [91-93]. The initiation fracture energy corresponding to the initiation of growth, at the onset of non-linearity ($\delta \approx \text{ca. 1.4 mm}$) of the load-displacement curve. Starting of propagation of the crack and unstable crack growth is noticeable at the point of maximum force $F_c$ ($\delta \approx \text{ca. 1.4 mm}$). When stable crack growth is observed during experimental testing the load-displacement curve has a continuous shape similar to the curve of the random nanotubes in Fig.6.20.

![Fig.6.21. The shear force-displacement curves calculated from the 4ENF test result.](image)

The shear force of the interlaminar adhesive calculated by dividing the critical force ($F_c$, the first peak in the load displacement curve) to the delaminated area is depicted in Fig.6.21. As can be seen in the figure, the result indicates that the aligned COOH-MWCNT and aligned CNF produced higher average rapture stress which are 37% and 17% higher compared to the reference respectively. As discussed in the force versus displacement curves, the first peak with a threshold ($\delta = \text{ca. 1.3 mm}$), corresponds to the onset of failure so that up to this point the
force/deflection curve is (quasi) linear and no crack propagation can be observed. Following first peak, the decrease of load corresponds to stable crack propagation. The ‘end’ of the propagation period is marked by a change of apparent crack growth rate. The transition between crack growth and crack ‘arrest’ (or, at least, exceedingly slow growth rate) periods is smooth, suggesting that when the crack front approaches the second loading point after mid-span position, increased compressive stress modifies the propagation, i.e., the punch (load line) hinders crack propagation and the load increases again. When the sample approach to its ultimate strength (the last peak in the load versus displacement curve), it absorbs the excess energy in the form of plastic deformation and damaging mechanism. Since the nanocomposites are brittle in nature, at the ultimate strength, no necking ductile fracture takes place; the excess energy is utilized to damage the composites [91-96]. Fig.6.22 and Fig.6.23 show the maximum average interlaminar shear stress and the longitudinal Young’s modulus i.e., the adherends’ Young’s modulus along the specimens’ length of the composite laminates for the reference and carbon nanotube/fiber modified laminates. As can be seen in the results, the mode II interlaminar shear stress, the Young’s modulus values of the aligned CNT/CNF modified composite laminates are higher than those of the reference and randomly distributed nanofillers reinforced composite laminates.

![Graph showing shear force in MPa](image)

**Fig.6.22.** The maximum average interlaminar shear force calculated from 4ENF test results
Fig. 6.23. The longitudinal Young’s modulus of the nano composites

The calculated mode II fracture toughness values of the reference and carbon nano tube/fiber modified composite laminates were depicted in Fig. 6.24. The result shows that the fracture toughness values of the aligned CNT/CNF modified composite laminates are 31% and 22% higher than that of the reference composite laminates. Since fiber bridging does not occur under mode II loading, two other important mechanisms such as friction and hackles are responsible for the energy absorption. Unlike DCB specimens that exhibit continuous crack growth along the fiber/matrix interface, ENF specimens show discontinuous crack growth by micro-crack coalescence which leads to many hackles to occur at the fracture surface. It seems that nanotube bundles act as rigid fillers which arrest the crack, preventing or delaying the expansion of micro-cracking within the matrix rich interface area. So, it is realistic to anticipate a higher amount of hackles present at the fracture surface of the CNT modified composite laminates as compared to that of the reference composite laminates. This leads to a relatively high energy absorption by friction in nanotubes modified composite laminates. In other words, nanotubes may improve the adhesion between the interlayer and the adjacent composite layers at the same time [93-96].
6.8. Discussion and comparison of results

As presented in the previous results section, in this study, the fracture toughness properties of the aligned and random -COOH functionalized MWCNT and neat CNF reinforced CFPC have been investigated by conducting both Mode I and Mode II test. It has been found that only the aligned COOH-MWCNT led to considerable improvement of the fracture toughness of CFRP in both Mode I and Mode II cases. Noting that only the aligned COOH-CNT have enhanced the interlaminar fracture toughness of CFRP as compared to the others, implicates that for toughening of a nanocomposite, the nano fillers should be aligned and/or hierarchically arranged besides its homogenous dispersion in the polymer matrix. Likewise, the biological nanocomposite structural materials such as cuticle of the crab exoskeleton developed their toughening mechanism from hierarchical assembly of their nano elements, here in this work, it was also demonstrated that the aligned and/or hierarchically organized bioinspired synthetic nanocomposites have enhanced the toughness value of the conventional CFRP nanocomposites. This indicates that besides homogenous dispersion of nano-fillers more focus has to be given in the hierarchical assembly of the whole nanocomposite in order to exploit more effectively the potential of those nano-fillers.

In case of Mode I test, the surface roughness profile of the fractured specimens also showed that the aligned COOH-MWCNT shows more local and global waviness coupled with larger amplitudes (up to 120 μm) compared to the others. On the other hand, the non-aligned COOH-
MWCNT and reference material fracture surface profile showed less roughness (less local and global waviness and less amplitude around 60 µm) demonstrating their brittle nature with less energy expenditure. Thus, the qualitative as well as quantitative investigations show higher surface roughness for the aligned COOH-MWCNT compared to other cases which suggest higher fracture performance in case of the aligned nano filler composite [80-83].

The fracture surface observations using SEM also supported the fact that higher experimental fracture toughness for the aligned COOH-MWCNT laminates compared to the non-aligned COOH-MWCNT and reference CFRP laminates by displaying several scraps of matrix materials and more complex fracture surfaces in case of aligned COOH-MWCNT compared to the nonaligned COOH-MWCNT reinforced laminates. The occurrence of these several stepwise scraps and/or fracture surfaces implicated crack deflection and creation of new fracture surface, and consequently, more energy was required to fracture [73, 81]. In addition, many MWCNTs are aligned perpendicularly to the fracture surface, which may have played a stitching and/or bridging role to resist the delamination propagation [81-82].

In principle, with the high aspect ratio, elasticity, strong interfacial bonding (due to functionalization) both the randomly and aligned nano fillers should result in higher absorption of energy through effective crack bridging (including mechanical interlocking with the matrix material), momentary crack arrest and/or deflection and strong absorption of fracture energy when pulled out from the matrix. However, in this study the non-aligned COOH-MWCNT was not able enhance the toughness of the reference material. This may be due to the effect of the availability of agglomerates which may act as defects and formed stress concentration [81-82]. Since the size of air bubbles were also larger in case of the randomly distributed COOH-MWCNT compared to the reference, this may also the reason behind the decreasing in fracture toughness of the random distributed nano filler reinforced CFRP composites compared to reference material as a result of the availability of agglomerates which in turn arises from the failure of the dispersion technique or the resin to penetrate the MWCNT bundles resulting in large void formation and hence creating a weak interlaminar region [88-90].

In case of Mode II investigation, the maximum force, the longitudinal Young’s modulus, fracture toughness values and the maximum average interlaminar shear force were calculated for the reference and carbon nanotube/fiber modified laminates in 4ENF test. The results showed that the aligned nanofillers have enhanced mechanical properties of the composite. The fracture toughness values of the aligned COOH-MWCNT/CNF modified composite laminates
are 31 % and 22 % higher than that of the reference composite laminates. The aligned COOH-MWCNT and CNF nanofillers have also enhanced the interlaminar shear force by 35 % and 17 % and Young’s modulus by 28 % and 15 % respectively compared to the reference material. Since fiber bridging does not occur under mode II loading, other important mechanisms such as friction and hackles are responsible for the energy absorption [93-96]. For the purpose of comparison examples of improvements in the fracture toughness of mode I (G_{IC}) and mode II (G_{IIC}) of the nano filler reinforced composites are presented in the Table 6.1.

Table 6.1: A summary of the techniques of dispersion, production and improvements in the fracture toughness of nano filler reinforced hierarchical composites.

<table>
<thead>
<tr>
<th>Fiber type and content</th>
<th>Matrix material, curing agent</th>
<th>Filler type /content</th>
<th>Dispersion technique</th>
<th>Production mechanism</th>
<th>G_{IC} / G_{IIC} improvement</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Plain weave Glass fiber with 39-44 vol%</td>
<td>Epoxy (liquid blend of bisphenol A and bisphenol F) and a slow-curing hardener</td>
<td>VGCNFs (0.70 vol.%)</td>
<td>Three-roll milling process followed by mixing of curing agent at a weight ratio of 5:1</td>
<td>Hand lay-up, vacuuming the prepreg for 30 min, curing for 24 hr at 25 °C, AC electric field of 30 V/mm at 10 kHz for alignment of the filler</td>
<td>G_{IC} increase by 25% (random) and 80% (aligned)</td>
<td>[69]</td>
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<td>Unidirectional Carbon fibre with 48 to 54 vol.%</td>
<td>Epoxy FM-20 epoxy with T-16 and curing agent</td>
<td>MWCNT (0.1 to 1 wt.%)</td>
<td>three roll milling (four passes) followed by mixing of curing agent at a weight ratio of 100:20</td>
<td>The hand lay-up, rolling the laminate after every two plies to avoid air bubbles, pressing for 12 hours under 30 kN at 25 °C</td>
<td>G_{IC} increase up to 33%</td>
<td>[99]</td>
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<tr>
<td>Unidirectional carbon-fibre</td>
<td>Epoxy and amine-based curing agent</td>
<td>CNFs (up to 1.6 wt%) at the middle interface</td>
<td>First CNF were hand mixed with surfactants Disperbyk-191 and -192 in 1:1:1 ratio, the mixture was then added to the epoxy resin and hand mixed for 5 min before the three roll mill dispersion</td>
<td>After amine-based curing agent was hand mixed with the CNF/epoxy resin, the mixture is then poured between the substrate and cured at room temperature for 48 h, AC electric field of 30 V/mm at 10 kHz was applied for alignment</td>
<td>Up to sixteen fold &amp; 25% increase in G_{I} compared to the reference and random</td>
<td>[70]</td>
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<tr>
<td>Carbon fiber</td>
<td>Epoxy - diglycidyl ether of bisphenol A and cyclo aliphatic amine</td>
<td>0.3 wt. % COOH-MWCNTs</td>
<td>Mechanical stir, ultrasonication (for 30 min at 40 °C) and then three roll milling at 150 rpm</td>
<td>Hand lay-up process, compression molding at a pressure of 130 KN and temperature of 120 °C for 4hr</td>
<td>20% and 15% increase in flexural strength</td>
<td>[67]</td>
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<td><strong>Unidirectional carbon fibre with 60 vol.%</strong></td>
<td>Epoxy - bisphenol-A based, dicyandiamide curing agent</td>
<td>hardener in 10:3 ratio</td>
<td>with a roller gap of 20, 10 and 5 µm,</td>
<td>Mechanical stir using planetary mixer and wet mill for 45 min</td>
<td>laminates fabricated using an autoclave, a pressure of 490 kPa at of 130 °C for 2 h.</td>
<td>97 and 29 % increase in $G_{IC}$ and $G_{IIC}$</td>
</tr>
<tr>
<td><strong>Carbon fiber</strong></td>
<td>diglycidyl ether of bisphenol-F epoxy resin, polyaminoamide hardener in 100:62 weight ratio</td>
<td>5 wt. % COOH-MWCNTs</td>
<td></td>
<td>First heating the epoxy resin at 60 °C for 5 min, then dispersing using a planetary mixer at 2000 rpm for 10 min, and finally adding the hardener into the mixture &amp; agitating for another 10 min at 1000 rpm</td>
<td>Pouring the dispersed mixture into the mould and pre-curing it for 12 h at room temperature and then further placing them into the oven for post-curing at 80 °C for 6 hr.</td>
<td>85.5% increases in $G_{IC}$ for MWCNT with 2 wt.% and a decrease in $G_{K}$ value has been seen in case of VGCF</td>
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<tr>
<td><strong>Unidirectional carbon fibre with 49 vol.%</strong></td>
<td>epoxy mixture consisted of a 635 thin epoxy resin mixed with a 2:1 ratio slow epoxy hardener</td>
<td>COOH-MWCNTs with 0.5% to 1.5 wt.%</td>
<td>Hand stirred, then the mixture was degassed for 5 min, Sonicated for 1 hr at 40 °C, magnetic stir for 2 hr at a 80 °C and 700 rpm. Then, cooling mixture for 1 hr, the hardener was added and hand stirred for 15 min</td>
<td>Laminate fabrication was completed using vacuum infusion with constant vacuum pressure of 3.07 Pa for the next 24 h. Then each plate was left to cure at room temperature for six weeks before testing</td>
<td>17 to 25% increase in $G_{IC}$</td>
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<tr>
<td><strong>Unidirectional glass fibre</strong></td>
<td>Epoxy bisphenol-A based and curing agent of polyether Amine mixed with a ratio of 100:40. 0.5 wt.% air release additive BYKA 501 was also added</td>
<td>COOH-MWCNT, OH-MWCNT, VGCFNT, CNF with 0.5 wt.% to 1 wt.%</td>
<td>Magnetic stir at 160-240 rpm for 15 min, sonication for 2-8 h, magnetic stir at 120 -200 rpm. During sonication, at one-hour interval, the resin mixture was removed from the bath and magnetically stirred on a hot plate for 5 min</td>
<td>Layer by layer process, and applying for mode I hot press with a pressure of 240 KN and 80 °C for 2hr and then 125 °C for 3hr.</td>
<td>79% and 91% [98]</td>
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</table>

As discussed in Table 6.1, many scholars investigated mode I and II interlaminar fracture toughness of CFRP laminates incorporating aligned and non-aligned carbon nanotubes/ fibers.
They found an increase in average crack propagation, $G_{IC}$ and $G_{IIC}$, especially in specimens containing functionalized and aligned nanofillers. In this study, the mechanical properties such as, fracture energy and fracture toughness of COOH-MWCNT/CNF modified epoxy based carbon fiber reinforced polymer composite laminates have been investigated under mode I and mode II tests. The result showed that, both the Mode I and Mode II fracture energy, fracture toughness value of the aligned COOH-MWCNT and aligned CNF was found to be significantly higher compared to the reference and the non-aligned nano fillers. The Mode I fracture toughness and fracture energy has been increased by 20 and 21% compared to the reference material. In Mode II 4ENF test, it was also observed that the interlaminar shear strengths of the aligned COOH-MWCNT and aligned CNF reinforced composite laminates were 28% and 15% higher than the reference composite material. However, in both the mode I and Mode II cases the randomly distributed nanofillers did not enhance the interlaminar mechanical properties such as fracture toughness value of the reference material. Only the aligned nanofillers have significantly improved the mechanical properties of carbon fiber reinforced polymer composites. As the SEM micrograph investigation showed, the aligned COOH-CNT/CNF enhanced composites fracture surface have less air bubbles and also more complex fracture surfaces which maybe the reason behind the increased fracture toughness value of those composites. Nanofillers play a toughening mechanisms by roughening the matrix fracture surface and increasing matrix fracture surface area of the composites. Among the four types of materials investigated, COOH-MWCNT have showed the highest fracture toughness in both Mode I and II cases. In case of aligned COOH-MWCNT, in addition to van der Waals binding, chemical bonding and the presence of less voids, it seems that aligning nanofillers helps to individualize the functionalized nanofillers and hence increases the opportunities to provide mechanical interlocking between the matrix and the fibers, increased interfacial friction, and local strengthening of the matrix at the interface [94-96]. As a general statement, despite reports of a pronounced increase in the matrix toughness, it seems that it is still a big challenge to transfer the improved nanotube modified matrix properties such as fracture toughness or shear strength into conventional long fiber composites due to some difficulties with composite processing particularly for randomly distributed nanofillers. Overall, a stronger interfacial bonding, uniform dispersion and orientation nanofillers coupled with proper manufacturing method to avoid formation of bubbles are key to accomplish the desired properties in their resultant composite materials [96-98].
7. Conclusion and recommendations

In this thesis, after highlighting the hierarchical organization nature of structural biological materials such as cuticle of the crab exoskeleton to illustrate the inherent interconnection between design of the structure, a bioinspired synthetic aligned and non-aligned COOH-MWCNT/CNF enhanced CFRP have been developed by copying the laminate and tubular structural design elements of biological composite material. To examine the degree of alignment, the electrical conductivity of the nanocomposite has been also measured. The result showed that the addition of nano fillers and alignment improved the conductivity of the composite. The aligned COOH-MWCNT, aligned CNF and randomly distributed COOH-MWCNT improved the conductivity by 355 %, 307 % and 222% respectively compared to the reference. Then, the Mode I fracture toughness of the aligned and non-aligned COOH-MWCNT enhanced epoxy matrix of CFRP composites have been investigated in DCB test. In mode II, the 4ENF test has been conducted to investigate the shear fracture toughness value of both the reference, the aligned and non-aligned COOH-MWCNT/CNF enhanced CFRP. Clear differences between randomly and aligned COOH-MWCNT/CNF were obtained for the fracture toughness of the tested CFRP specimens. In Mode I DCB test, the aligned COOH-MWCNT have improved the fracture toughness by 20 % compared to the reference. The aligned COOH-MWCNT have also improved the fracture energy by 21 and 32 % compared to the reference and the nonaligned COOH-MWCNT respectively. The Mode II 4ENF test result also showed that aligned COOH-MWCNT and aligned CNF provide 31 % and 22 % increased fracture toughness value compared to the reference. In the 4ENF test, the interlaminar shear stress and Young’s modulus of aligned COOH-MWCNT and aligned CNF were significantly higher compared to the reverence.

However, it was interesting that even though the dispersion was same, the randomly distributed COOH-MWCNT/CNF did not enhance the fracture toughness of the CFRP in both Mode I and Mode II tests. Only the aligned COOH-MWCNT/CNF improved the toughness of the reference material. This may implicate that for toughening of a nanocomposite, the nano fillers should be aligned and/or hierarchically arranged besides its homogenous dispersion in the polymer matrix. Likewise, the biological nanocomposite structural materials such as cuticle of the crab exoskeleton developed their toughening mechanism from hierarchical assembly of their nano elements, here in this work, it was also demonstrated that the aligned and/or hierarchically organized bioinspired synthetic nanocomposites enhanced the toughness value of the
conventional CFRP nanocomposites. This indicates that besides homogenous dispersion of nano-fillers more focus has to be given in the hierarchical assembly of the whole nanocomposite in order to exploit more effectively the potential of those nano-fillers. As material selection reaches its limitations, looking toward nature’s example of structural optimization for the next generation of technology is recommended. Overall, creating stronger interfacial bonding through functionalization, uniform dispersion and orientation nanofillers coupled with proper manufacturing method to avoid formation of bubbles are key to accomplish the desired properties in their resultant composite materials.
8. References


75. Wenming Zhao, W., (2011). Mode I Delamination Fracture Characterization of Polymeric Composites under Elevated Temperature. Syracuse University, surface