CHAPTER 1
INTRODUCTION

1.1 Introduction

The discovery of nanofillers may be considered as a paradigm shift in the field of conventional composites. Due to these fillers tremendous changes were noticed in overall properties of the composites. As of now several nanofillers have been synthesized by various groups of researchers. Amongst the available nanofillers carbon nanotube (CNT) and graphene have attracted more as compare to other fillers. This may be due to the extraordinary mechanical, electrical, chemical, physical and thermal properties possesses by them.

CNTs have already proved themselves as a promising candidate for the betterment of carbon fiber reinforced polymer (CFRP). Their elastic modulus which even exceeds 1 TPa and tensile strength in the range of 140–160 GPa, make CNT polymer two phase nanocomposites much stiffer and stronger than conventional material such as steel, while being three to five times lighter. However, there are several challenges that need to be addressed when it comes to using CNTs as an effective reinforcement in polymer nanocomposites. The various defects in CNTs and their dispersion in polymers are most widely acknowledged difficulties. Agglomeration due to van der Waal (vdW) interaction between CNTs and the poor load transfer through the CNT matrix interface are some of the other unsolved problems as explored by (Breuer and Sundararaj 2004; Hussain et al. 2006)\(^1\).

Though CNT reinforcement in the pool of matrix produces better properties as compare to the basic composites but from last decade (Geim and Novoselov 2004)\(^2\) graphene becomes the center of attraction amongst the scientists doing research on
nanocomposites. Graphene may be defined as a single layer arrangement of carbon atoms, covalently bonded to other tightly packed two-dimensional (2D) atoms crafted in hexagonal crystalline honeycomb lattice structure. Amine Functionalized Multiple Graphene Layer (AFMGLs) based polymer matrix nanocomposites materials possess high specific tensile strength and modulus. AFMGL based nanocomposites significantly reduce weight of the structure with near similar or even better performance than that of conventional metallic materials. Owing to this excellent weight reduction and high strength property of epoxy (LY 556, CY212 etc.) composites they continue to be one of the primary constituents in many structural applications, such as military, automotive, space vehicles, commercial aircrafts and marine. The properties of epoxy based composites can be further enhanced by incorporating high-potential nanofiller, such as Graphene, resulting in a material popularly known as two phase nanocomposites. Two phase nanocomposites are particularly useful for imparting multi-functionality to structures including in-situ damage-sensing, blast and impact resistance and flame retardancy. The coming section encompasses the brief introduction about the different above mentioned constituents.

1.2 Nanofillers

Discovery and research of carbon nanofillers has been attract more researchers from the field of composites. The critical aspects for the progress and commercialization of nanocomposite technology are closely related to the properties and processing of the reinforcing element. Carbon nanofillers are a leading material in the field of nanotechnology. The discovery and research of these nanofillers has contributed a major role in the production of nanocomposites. The researchers have tried to categories
materials on the basis of their dimensions. After the discovery of fullerene and CNT, which is zero and one-dimensional carbon nanofillers respectively, the researchers have focused to make 1D nanoribbon from 2D crystals.

Nanofillers are doping agents which are always expected to evenly distribute in the composite matrix. The particle size of nanofiller is below 100 nm. Nanofillers are available in abundant amount in nature because they are produced by nature by different processes like photochemical reaction, simple soil erosion and by forest fires as well by plants and animals. They contain hundreds of atoms which has different types of shape, size and also with materials having different chemical and physical properties. Nanofillers can be classified on the basis of morphology, composition, uniformity, and agglomeration.

1.2.1 Classification of Nanofillers

Nano-structured (NS) materials are defined as solids having micro-structural features in the range of 1-100 nm in at least in 1D. These materials have extraordinary thermal, electrical and mechanical properties due to their fine particle size and high grain boundary volume fraction. NS materials demonstrate properties which are quite different from their bulk properties. These materials contain a controlled morphology with at least one nano scale dimension. NS materials can be nano-sized along only one, two and all the three dimensions (Pokropivny and Skorokhod 2007)\(^3\), in the form of a film, rod, or a dot (Gleiter 2000)\(^4\), gave the first classification scheme of NS materials on the basis of crystallinity and chemical composition. However, this classification was not fully described because of low dimensional structures such as nanoflakes, nanotube and
nanowires, which were not taken into consideration. The general classifications of nanofillers on the basis of their dimensions are listed in Table 1-1.

Figure 1-1 Graphene is a 2D material for all the carbon structure of all other dimensionalities (a) wrapped up into 0D buckyballs (b) rolled into 1D nanotubes (c) stacked into 3D graphite [Rao et al. (2009), Gupta et al. (2015)]\textsuperscript{5}.

Table 1-1 Classification of nanostructured materials on the basis of their dimensions

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D</td>
<td>Nanoparticles binary arrays, Quantum dots, Hollow MoS\textsubscript{2}nanospheres, Hollow core–shell nanoparticles.</td>
</tr>
<tr>
<td>1D</td>
<td>Nanotubes, Nanoribbons, Nanobelts, Nanowires, Nanorods</td>
</tr>
<tr>
<td>2D</td>
<td>Nanodisks, Nanoplates, Nanowalls, Nanosheets</td>
</tr>
<tr>
<td>3D</td>
<td>Nanoflowers, Nanoballs, Nanocoils, Nanocones</td>
</tr>
</tbody>
</table>
Materials are available on earth surface from decades in various forms (liquid and solid state). These materials are used for different type of engineering works and according to this work they are divided into three different categories like metals, ceramics and polymers.

1.2.2 Carbon Nanotubes (CNTs)

CNTs are the allotropes of carbon with a nano level dimension cylindrical structure. The structure of a single walled carbon nanotube (SWCNT) can be conceptualized by wrapping a one atom thick layer of graphite called graphene into a seamless cylinder. The structure of MWCNT consists of multiple rolled layers (concentric tubes of graphene). The various forms of nanofillers have been shown in Figure 1-1.

1.2.3 Graphene

![Graphene Diagram](image)

**Figure 1-2** Different types of nanofillers (Georgakilas et al 2015).

Graphene is a crystalline allotrope of carbon with a tightly packed layer of carbon atoms exfoliated from graphite. It has a hexagonal honeycomb tightly packed lattice with a molecular bond length of 0.142 nm. It is only form of carbon in which every atom is available for chemical reaction due to its 2D structure. Graphene exists in the form of sheets but when it is rolled in the form of cylinder it is treated as CNT and when it is
rolled in circular form it behave as fullerene/ bucky-ball as shown in Figure 1-2. The graphene can be subdivided into two categories; (a) armchair, and (b) zigzag.

1.2.4 Properties of Nanofillers

Several researches have been published with regards to characterization for different properties of nanofillers especially CNT and graphene; few of them were discussed in this section:

Experimental methods for measuring the mechanical properties are based mainly on the techniques of transmission electron microscopy (TEM) and atomic force microscopy (AFM). The first experimental measurement of the elastic modulus of CNTs has given a value $1.8 \pm 0.9$ TPa obtained by measuring thermal vibration method (Treacy et al. 1996)$^7$. Later, a slightly lower value of $1.28 \pm 0.59$ TPa has been obtained by using the tip of AFM to bend anchored CNTs (Wong et al. 1997)$^8$.

Graphene progressively proved themselves as a capable candidate to take over the position of CNTs as filler in polymers for the overall improvement in mechanical, electrical (Phiri et al. 2017)$^9$ and thermal properties of nanocomposites [Phiri et al. (2017), Geim (2011)]$^{9-10}$. Graphene is an atomically 2-D (dimension) hexagonal shape network of sp$^2$ hybridized carbon atoms. The exceptional properties (Zhang et al. 2010)$^{11}$ and anisotropic [Zhang et al. (2010), Young et al. (2012)]$^{11-12}$ behavior of graphene (experimentally calculated and predicted) can be summarized as follows:

(Dikin et al. 2007)$^{13}$ prepared graphene oxide (GO) and found elastic modulus and fracture strength to be around 32 and 120 MPa respectively. (Lee et al. 2008)$^{14}$ found graphene to be the strongest material with a tensile strength of 130 GPa by using AFM. They also reported the strength of single layer exfoliated graphene, more than 200 times
that of steel, and stiffness as 1 TPa. (Frank et al. 2007) experimentally calculated the stiffness about 0.5. In the next section nanofillers reinforced nanocomposites has been briefly introduced.

1.3 Composite Materials

A composite material is one which made of two or more distinct phases with different chemical and physical properties. The fabrication of composite material generally depends upon the fundamental of placing a hard material as reinforcing phase while ductile material is expected to place with matrix. Therefore, nanocomposites material generally constitutes two phases i.e. nanofillers and epoxy matrix. Composites are becoming popular day by day because of its superior properties like strength, lighter in weight and less expansive when compared to individual material. The particles of composites were closely combined together to form a nanocomposites phase and the particles of composites are so small that they are not visible with naked eyes. Composites are designed to offer low weight, stiffness, strength, lower coefficient of expansion, and ease in manufacturing complex shapes. Classification of different phases composites have been detailed in Table 1-2.

Table 1-2 Classification of Composites on the basis of phase composition criteria

<table>
<thead>
<tr>
<th>Phases Composition</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-phase solids</td>
<td>Crystalline polymers, amorphous particles and layers</td>
</tr>
<tr>
<td>Multi-phase solids</td>
<td>Matrix composites, coated particles</td>
</tr>
<tr>
<td>Multi-phase system</td>
<td>Colloids, aero gels, ferro fluids</td>
</tr>
</tbody>
</table>
1.3.1 Classification of Composite Materials

Composite material can be developed by combining two or more materials which may differ in their physical and chemical properties. These properties generally depend on the weight percent of nanofillers and matrix phase which finally constitute two phase composites. Classification of different phase composites has been illustrated in Figure 1-3.

![Classification of composite based on the type of reinforcement](image)

**Figure 1-3** Classification of composite based on the type of reinforcement (Otani et al. 2014)\(^6\).

1.3.1.1 Classification based on Reinforcement Materials

1. Particle Reinforced Composites

2. Fiber Reinforce Composites

3. Structural Composites
1.3.1.1.1 Particle Reinforced Composites

Particle reinforced composites consist of particles of one material which are evenly dispersed in the matrix of second material. The size of particles is very small (< 0.25 micron). Particles are used to increase the strength or different physical and mechanical properties of economical cheaper materials by addition of other materials. Generally polyhedral, spherical, ellipsoidal and irregular shapes of particles are used for the reinforcement of the composites. Particle composites are divided as follows:

- **Large Particle Composite**

  Mechanical behaviour of composite material where depend on the bonding of filler material between the matrix particle and matrix interfaces. Particles can have variety of geometries but they should be approximately the same dimension in all direction. The particle should be small and evenly distributed throughout the matrix for effective reinforcement. Mechanical properties of the component where increased by increasing the particulate content e.g. concrete etc.

- **Dispersion Strengthened Composites**

  Dispersion-strengthened means of strengthening materials. In this type of composites the particle which are used for strengthen have very small diameter generally between 0.01 & 0.1 µm. These particles where uniformly distributed with in a load bearing matrix phase. The dispersed phase may be metallic or non-metallic, oxide materials are often used.

1.3.1.1.2 Fiber Reinforced Composites

Fiber reinforced composites are those composites in which fibers are embedded in the matrix material. The main objective of these types of composites is to provide high specific strength and high specific modulus to the material. Fiber reinforce composites
are classified on the basis of orientation of fibers which are as follows (a) Continues and aligned fibers, (b) Discontinuous and aligned fibers, and (c) Discontinuous and randomly oriented fibers as demonstrated in Figure 1-4.

![Fiber Orientations in Fiber Reinforced Composites](image)

**Figure 1-4** Various fiber orientations (Mallikarjuna et al. 2018)\(^7\).

### 1.3.1.1.3 Structural Composites

A structural composite is a different type of composites in which two thin sheets are assembled together to a lightweight thick core. Core is a low strength material with low density. This is a well known fact about wood that is natural occurring structural composite and some other examples of structural composites are plywood, wood fiber board, plastic composites and many more comes under this category. Structural composites are further divided into two types:
• **Sandwich Structures**

A sandwich structure is a special class of composite material which are fabricated by attaching two relatively thin, stiff and strong sheets which are separated by light weight but thick core. Different type of materials can be used for the thin faces and for thick core. An adhesive is used in this process for the proper bonding between the faces and core for sandwich structure. Core material used in sandwich process have following properties like stiffness, Lighter in weight, Strength, Thermal insulation, provide high damping resistance for vibration and noise, and water ingress prevention. Some important characteristics of sandwich structures are: (a) Lighter in weight as compared to metallic, (b) High stiffness, and (c) Less cost as compare to other composite material and structures as shown in Figure 1-5.

![Sandwich Structure Diagram](image)

**Figure 1-5** General arrangement of fabricated sandwich panel (Park and Seo 2015).

• **Laminated Structures**

Laminated structure are the structure which are manufactured by using lamination technique, in lamination technique in which material is produced in multiple layers to
improve different parameters such as strength, stability, sound insulation, and other properties by the use of different materials. A lamina itself is a fiber matrix configuration. Laminates are permanently assembled by using welding, adhesives, heat or pressure. When layers of different materials are used in laminated structure to form a laminate, hence these types of laminates are called hybrid laminate structure, as shown below (Figure 1-6).

**Figure 1-6** Laminated Structures (Koide et al. 2013)\(^1\).

### 1.3.1.2 Classification based on Matrix Phase

Composites based on matrix phase, as shown in Figure 1-7, can be classified as follows:

1. Metal Matrix Composites (MMC)
2. Ceramic Matrix Composites (CMC)
3. Polymer Matrix Composites (PMC)
Metal Matrix Composites

MMC’s can be the combination of two constituents such as metal and ceramic or any organic compound. The expected properties of matrix to be used in MMC must be continuous in structure and light in weight. In MMC, reinforcing surface should be coated to prevent it from chemical reaction in matrix. MMCs are usually low density metals, such as aluminium or magnesium which are reinforced with fibers of ceramic material like silicon carbide or graphite.

Ceramic Matrix Composites

CMC’s are those materials which are form by reinforcing the two distinct ceramic phases, to increase the properties of monolithic ceramic materials. CMCs are also known as ceramic fiber reinforced ceramic (CFRC). Compared to conventional technical ceramics, which fracture easily under loads, moreover CMCs have greater crack resistance. CMCs are fabricated using vapour phase infiltration or deposition techniques. Typical fibrous materials which commonly used are carbon, silicon carbide and alumina fibers. CMCs are used at a place where require high strength, high temperature resistance, armour or...
ballistic properties and erosion or wear resistance. CMCs are best replacement of super alloys.

1.3.1.2.3 Polymer Matrix Composites

PMC’s is a composite material which composed of different types of short or continuous fibers, bonded through an organic polymer matrix (OPM). PMCs are used for the improvement of fracture toughness of the material. PMCs are light in weight and highly stiff, corrosion and fatigue resistance.

1.4 Summary

This chapter witnessed the brief introduction about the properties of naofillers especially CNT and graphene. Classification of composites materials on the basis of two major factors such as filler material and matrix has also been briefly discussed. The next chapter contains the deep literature review which certainly helps to the researchers for bridging up the existing gaps.