Chapter-1

Introduction: Composites & A Selective History of CNT Reinforced Composites
1.1. Composites

There is never ending search for improved materials. Materials with unusual combination of properties generally cannot be met by conventional metals, alloys, ceramics, and polymeric materials. This is especially true for materials that are needed for aerospace, underwater, transportation and other strategic high performance applications. For example, aircraft engineers are increasingly searching for structural materials that have low densities, possesses high specific strength/stiffness high abrasion and impact resistant, and are not easily corroded. This is a rather formidable combination of characteristics. Many of these improved materials are composite materials. Composites by simplest definition are the materials made from two or more components that are constructed to take advantage of the combination of properties offered by the components. The idea is to take best advantage of the strength of each component material while minimizing their weakness. Composite may be engineered with unique physical properties to suit very distinct applications.

The different materials work together to give the composite unique properties, but within the composite one can easily distinguish the different materials apart – they do not dissolve or blend into each other. There are a lot of composites around us. A piece of wood is a natural composite, with long fibres of cellulose (a very complex form of starch) held together by a much weaker substance called lignin. Cellulose is also found in cotton and linen, but it is the binding power of the lignin that makes a piece of timber much stronger than a bundle of cotton fibres. An important historical example is the mixture of clay and straw used to build adobe structures. The clay provides a high-volume solid matrix, whereas the straw reinforces the brick against fracture. Concrete is also a composite made up of cement, gravel, and sand, and often has steel rods inside to
reinforce it. The piece of plywood, used commonly in daily life is also a composite as shown in figure 1.1.

Composites are composed of mainly two phases; one is termed as the matrix, which surrounds the other phase, often called the filler or dispersed phase. In addition, the constituent phases must be chemically dissimilar and separated by a distinct interface. Usually, the matrix is continuous and completely surrounds the dispersed phase to bind it together somewhat like an adhesive and serves several functions. First, it acts as a medium by which externally applied stress is transmitted and distributed to the dispersed phase. Only a very small proportion of applied load is sustained by matrix phase. The second function of the matrix is to protect the dispersed phase from surface damage as a result of mechanical abrasion or chemical reaction with the environment. Such interactions may introduce surface flaws capable of forming cracks, which may lead to failure at low tensile stress levels. The matrix also transfers the load placed on a composite from one filler bundle to the next. In other words, the matrix phase serves as a barrier to crack propagation [1]. Fillers are employed in polymer to play a number of roles in encapsulated matrix. It not only reduces the cost of composites, but also frequently imparts performance improvements that might not otherwise be achieved by the reinforcement and resin ingredients alone. It not only serves the purpose of making the matrix stronger and stiffer but also helps it to resist cracks and fractures. Fillers can improve fire and smoke performance by reducing organic content in composite laminates. Also, resins filled with filler shrinks less than unfilled resins, thereby improving the dimensional control of composites. Important properties, including water resistance, weathering, surface smoothness, stiffness, dimensional stability and temperature resistance, can all be improved through the proper use of fillers.
Unlike many natural and artificial materials, which find applications by chance only after they have been discovered or invented, composites are often carefully designed with a particular application in mind. Originally developed as light and strong materials for the aerospace industry in the mid-20th century, they have now found their way into a wide range of products. The strength and lightness of composites has made them particularly attractive for transportation. From the high cost stealth bomber to low-cost home-build glider kits, composites have made airplanes lighter, more economical, and more affordable and solved problems such as cracking and metal fatigue. Composites have also made possible new craft called tilt rotors—airplanes with a swiveling propeller at the end of each wing that can hover or take off vertically like a helicopter. Made from traditional materials such as aluminum, craft of this sort would have been simply too heavy to carry their cargo. Space rockets and satellites are also benefiting from composites, and in some unusual ways. Composites are not just useful in making things fly. Cars of the future must be safer, more economical, and more environmentally friendly, and composites could help achieve all three. Engineers believe carefully designed composites could cut the weight of a typical steel car by as much as 40 percent, increasing fuel economy by as much as a quarter, yet maintaining body strength and crash-resistance. High-temperature ceramic-matrix composites are also making possible cleaner-burning, more fuel-efficient engines for both cars and trucks. The strength and lightness of composites has made them equally popular in the design of sports equipment. The composite fibres used in tennis racquets are angled specifically to reduce bending and twisting and to improve stability. The latest composite hockey sticks made from aerospace-grade carbon fibres in a nylon polymer matrix are as twice and tough as and six times stronger than ordinary hockey sticks. The same material is used to make wheels for mountain bicycles, but more advanced Kevlar composites are used to make the light, super-strong, solid wheels used in Olympic-style cycles. Composites are so versatile that they are now being used even to build large-scale structures like bridges and oil rigs. NASA scientists and industry engineers are currently developing composites that could be used in place of metals to construct offshore oil platforms and the pipelines that carry
their oil to shore. Once developed, the technology is expected to yield extra-durable pipes that could be used for everyday applications such as sewage disposal.

1.1.1. Types of Composites

Fillers and matrix are usually (but not always) made from different types of materials. The fillers are mainly some fibrous material made from glass, carbon, silicon carbide, or asbestos, while the matrix is usually plastic, metal, or a ceramic material. Depending on the matrix used in the composite, composites can be broadly classified as:

- Ceramic-Matrix Composites
- Metal-Matrix Composites
- Polymer-Matrix Composites

All these categories of composites are useful in different areas depending on the applications.

1.1.1.1. Ceramic-Matrix Composites

Ceramic-Matrix Composites (CMCs) consist of a ceramic material as a matrix, with particulates, fibres or whiskers as the reinforcement medium. Ceramic materials are inherently resilient to oxidation and deterioration at elevated temperatures. Some of these materials would be ideal candidates for use in high temperature and severe-stress applications, specifically for components in automobile and aircraft gas turbine engines. The fracture toughness of ceramics has been improved significantly by the development of a new generation of ceramic-matrix composites. This improvement in the fracture properties result from the interaction between advancing cracks and dispersed phase particles [1, 2]. Crack initiation normally occurs within the matrix phase, whereas crack propagation is impeded or hindered by the particles, fibres, or whiskers. In general, increasing the fibre content improves strength and fracture toughness. In addition, these CMCs exhibit improved high-temperature creep behavior and resistance to thermal shock (i.e., failure resulting from sudden change in temperature). These are generally used in lightweight, high-temperature components, such as parts for airplane jet engines.
1.1.1.2. Metal-Matrix Composites

Metal-Matrix Composites (MMCs) are defined as materials consisting of a combination of fibres, whiskers, and particulates embedded in a metallic matrix which could be Al, Mg, Cu, Fe, etc [2]. The development of metal matrix composites has been driven primarily by the need for structural materials with better specific strength and modulus than monolithic metals, especially at high temperature. These materials demonstrate one of the most intriguing characteristics of composites, which is, the ability to tailor mechanical and physical properties over much greater ranges that can be obtained with monolithic materials. As the name implies, in the MMCs, the matrix is a ductile material and reinforcement is a brittle ceramic. The matrix material lends good toughness and high thermal conducting properties to the MMC. Some of the advantages of these materials over the polymer matrix composites include higher operating temperatures, non-flammability, and greater resistance to degradation. MMCs are much more expensive than polymer-matrix composites and therefore, their use is somewhere restricted.

1.1.1.3. Polymer-Matrix Composites

Polymer-Matrix Composites (PMCs) as suggested by name consists of a polymer resin as the matrix [1]. These materials are used in greatest diversity of composite applications, as well as in largest quantities, in light of their room-temperature properties, ease of fabrication, and cost. Some of these commonly used reinforcement used in PMCs includes; glass fibres, either, continuous or discontinuous, contained within a polymer matrix. Filler-reinforced polymer composites are currently being utilized extensively in sports and recreational equipment (fishing rods, golf clubs), pressure vessels, and aircraft structural components – both military and commercial. Polymer composites emerged as a distinct technology in an era when improved performance for advanced systems provided a primary motivation for materials development.

As the matrices, modern composites use thermosetting or thermo softening polymers. Thermosetting plastics are usually low viscosity liquids or low
molecular weight solids when prepared but harden and become rigid when heated, or cured with some suitable additives known as cross-linking agent or curing agent or under pressure. The setting process is irreversible, so that these materials do not become soft under high temperatures. These plastics are more chemical or corrosion-resistant, fire retardant, shrink-resistant and thermally stable and resist wear and attack by chemicals making them very durable, even when exposed to extreme environments. The common examples are epoxy which cures using curing agent, phenolic resins which cures on heating under pressure, polyesters, amino resins, urea/ formaldehyde resins etc. Thermo softening plastics, as the name implies, are hard at low temperatures but soften when they are heated. Although they are less commonly used than thermosetting plastics they do have some advantages, such as greater fracture toughness, long shelf life of the raw material, capacity for recycling and a cleaner, safer workplace because organic solvents are not needed for the hardening process. Some common examples are polycarbonate (PC), polymethyl methacrylate (PMMA), Polyurethane (PU), Polyethylene (PE), Polypropylene (PP) etc.

1.2. Fillers

The term filler is very broad and encompasses a very wide range of materials. There is a significant diversity in shapes, sizes, chemical structure and inherent properties of fillers and hence can be classified in a variety of ways depending on

(1) Particle size - Most filler are grouped and ranked by their particle size. Fillers can be of macro, micro or nano size. There are a number of different ways to measure and report particle size. Actually the term “particle size” is in itself misleading. Even a small sample of filler will contain many particles of different sizes. What we are actually dealing with is a particle size distribution. Most data sheets give the average size or the midpoint (median) value in their product’s size distribution.

(2) Chemical family-In terms of chemical family fillers can be divided as organic or inorganic. Some commonly used inorganic filler are glass (fibre, sphere), calcite (cube, block) etc. and the examples of organic filler are carbon black, carbon nanotubes (fibre), carbon fibre, aramid fibre, etc.
(3) Shape of filler - Shape plays an important role in defining filler’s reinforcing characteristics. Filler particles come in a variety of shapes like spherical, fibrous, thin sheet, cubical and irregular. The only and important characteristic of shape is aspect ratio.

### 1.2.1. Aspect Ratio

The aspect ratio of a filler particle is the ratio between the particle’s largest dimension (L) and its smallest (t). In the case of a rod it would be the length divided by the diameter. A sphere would have an aspect ratio of 1 while a fibre can be vary from few tens to several thousands. Fig. 1.2 shows the different shaped fillers with their aspect ratios.

![Aspect ratio measurement of different shape fillers](image)

**Fig. 1.2 Aspect ratio measurement of different shape fillers**

Aspect ratio is one of the important parameter, which plays an important role in filler and has significant effect on mechanical, electrical, electromagnetic interference (EMI) shielding and other properties of composites. Higher aspect ratio of fillers provide virtually more load-carrying characteristics to the composite by transferring more load from matrix and hence results in their higher mechanical properties. A lot of studies have been carried out in this regard [3-5]. Higher aspect ratio fillers achieved the same properties at low loading as achieved by low aspect ratio fillers at higher loading [6-7]. In case of conductive filler electrical properties of composites is enhanced with higher aspect ratio filler. The results of Jou et al [8] demonstrate that the high aspect ratio of raw material or reinforced fillers for composites would assist in the construction of a
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c conducive network in the composites and hence important factor in describing the percolation threshold. Also with increase in aspect ratio of fillers in composites the dielectric constant and the dielectric loss also increases due to greater instances of interparticle conduction. Also a lot of studies are available in open literature that shows the effect of aspect ratio of conductive fillers on mechanical properties as well as EMI shielding effectiveness (SE) of composites.

A more convenient scheme proposed by Mascia [9] for classification of fillers according to specific functions, such as their ability to modify mechanical, electrical or thermal properties, flame retardancy, processing characteristics, solvent permeability or simply formation costs. Fillers however are multifunctional and may be characterized by a primary function and a plethora of additional functions. The classification of fillers according to five primary functions are as follows.

1. Mechanical property modifier
2. Fire retardancy
3. Electric and magnetic property modifiers
4. Surface property modifier
5. Processing aids

Most of the composites have used fibres as the filler phase. Because of its high aspect ratio, tremendous stiffness and weight to strength ratio these carry the load imposed on the composite that in the industrial arena translates to high performance. Also the ability to tailor composites by changing the orientation of the fibre allows the user to strengthen a structure in preferential direction to meet performance requirements. They also provide good design flexibility and usually require lower tooling costs. Because of these advantages, fibre reinforced composites are ideal in structural components for industrial applications. A wide variety of properties can be achieved by selecting the proper glass type, filament diameter, sizing chemistry and fibre forms.

1.3. Carbon as Filler

Carbon, which is a high performance material, is the most commonly, used as reinforcement in advanced polymer-matrix composites. As carbon-carbon (C-C) bond is
one of the strongest bonds, this provides the carbon reinforced polymer composites high mechanical properties. Also because of the flexibility of its bonding, carbon-based filler system shows an unlimited number of different structures with an equally large variety of physical properties. Carbon fillers are available in a wide range of sizes. Carbon black has the shape spherical or ellipsoidal, fullerenes have spherical or rugby shape, graphene has a planar structure whereas carbon fibre and carbon nanotubes have fibrous structure. The distribution of carbon materials with respect to their size is shown in Fig. 1.3. In recent years a long list of other promising applications was produced by proponents of the novel forms of carbon.

![Fig. 1.3 Distribution of Carbon Fillers w.r.t their size](image)


Carbon is without doubt one of the most versatile elements known to man, as can be seen by the fact that it is the basis of life on this planet. Carbon, which is a high performance material, is the most commonly, used as reinforcement in advanced polymer-matrix composites. The reasons why carbon is such a diverse element is that it can form bonds to a huge range of other compounds, such as N, S, O, Cl, Br and P which crucially, are all thermodynamically stable. In addition to this, carbon can form single, double or triple bonds to other atoms and crucially, can also form these bonds to other carbon atoms. These carbon-carbon bonds have a very high intrinsic strength compared to similar bonds between other elements, for example, the bond strength of a C-C single
bond has a value of 356 kJmol$^{-1}$ compared to a value of 226 kJmol$^{-1}$ for the equivalent Si-Si bond. As a result of this, it is possible to form carbon chains of phenomenal lengths, which is a property that allows materials such as carbon fibres to be produced.

Carbon-based materials, clusters, and molecules are unique in many ways. One distinction relates to the many possible configurations of the electronic states of a carbon atom, which is known as the hybridization of atomic orbitals and relates to the bonding of a carbon atom to its nearest neighbors. Carbon is the sixth element of the periodic table and has the lowest atomic number of any element in column IV of the periodic table. Each carbon atom has six electrons that occupy 1$s^2$, 2$s^2$, and 2$p^2$ atomic orbitals. The 1$s^2$ orbital contains two strongly bound core electrons. Four more weakly bound electrons occupy the 2$s^2$2$p^2$ valence orbitals. In the crystalline phase, the valence electrons give rise to 2$s$, 2$p_x$, 2$p_y$, and 2$p_z$ orbitals which are important in forming covalent bonds in carbon materials. Since the energy difference between the upper 2$p$ energy levels and the lower 2$s$ level in carbon is small compared with the binding energy of the chemical bonds, the electronic wave functions for these four electrons can readily mix with each other, thereby changing the occupation of the 2$s$ and three 2$p$ atomic orbitals so as to enhance the binding energy of the C atom with its neighboring atoms. The general mixing of 2$s$ and 2$p$ atomic orbitals is called hybridization, whereas the mixing of a single 2$s$ electron with one, two, or three 2$p$ electrons is called sp$^n$ hybridization with $n = 1, 2, 3$.

1.3.1. Different forms of Carbon

From the above discussion it is clear that three possible hybridizations occur in carbon: sp, sp$^2$ and sp$^3$, while other group IV elements such as Si and Ge exhibit primarily sp$^3$ hybridization. The various bonding states are connected with certain structural arrangements, so that sp bonding gives rise to chain structures, sp$^2$ bonding to planar structures and sp$^3$ bonding to tetrahedral structures.
1.3.1.1. **Diamond**

The $sp^3$ hybridization of carbon is found in diamond. As we all know that diamond is very hard and strong substance which is a direct consequence of its microscopic tetragonal structure comprises of each carbon atom being covalently bonded to three other carbon atoms via C-C single bond in giant lattice structure. The 3D picture of diamond structure is shown in Fig. 1.4(a).

![Fig. 1.4(a) Structure of Diamond](image1)

1.3.1.2. **Graphite**

Graphite, a three dimensional (3D) allotrope of carbon shown in Fig. 1.4(b) is $sp^2$ hybridized, became widely known after the invention of the pencil in 1564 and its usefulness as an instrument for writing comes from the fact that graphite is made out of stacks of graphene layers that are weakly coupled by van der Waals forces. Each individual carbon atom is $sp^2$ hybridized (opposed to $sp^3$ in diamond) and is bonded to 3 other carbon atoms via C-C bonds, each in a trigonal planar geometry, giving an overall hexagonal, "honeycomb" structure, like the one shown above. The $sp^2$ hybridization between one s orbital and two p orbitals leads to a trigonal planar structure with a formation of an $\sigma$ bond between carbon atoms that are separated by 1.42Å. The $\sigma$ band is responsible for the robustness of the lattice structure in all allotropes. Due to the Pauli principle, these bands have a filled shell and, hence, form a deep valence band. The unaffected p orbital, which is perpendicular to the planar structure, can bind covalently with neighboring carbon atoms, leading to the formation of a $\pi$ band. Since each p orbital has one extra electron, the $\pi$ band is half filled. Half-filled bands in transition elements
have played an important role in the physics of strongly correlated systems hence, due to their strong tight-binding character; the Coulomb energies are large, leading to strong collective effects.

Also since the in-plane C-C bond is very strong and the nearest-neighbor spacing between carbon atoms in graphite is very small, the in-plane lattice constant is quite stable against external perturbations. The complete structure of graphite consists of many of these "sheets" lying one on top of the other, with weak inter-layer forces of attraction between each layer. The nearest neighbor interplanar spacing between two layers in graphite is ~3.4Å. The consequence of the small value of a_{c-c} in graphite is that impurity species are unlikely to enter the covalently bonded in-plane lattice sites substitutionally (except for boron), but rather occupy some interstitial position between the graphene layer planes which are bonded by a weak van der Waals force. The weak interplanar bonding of graphite allows entire planes of dopant atoms or molecules to be intercalated between the carbon layers to form intercalation compounds.

The structural flexibility of graphite is reflected in its electronic properties. Due to sp^{2} hybridization of carbon in graphene three out of four electrons participate in bonding. The remaining electron from each carbon atom is then delocalized within this structure. These free electrons explain why graphite is one of the few non-metallic structures that conduct electricity.

1.3.1.3. Fullerenes

The fullerenes are the third major allotrope of carbon. Fullerenes (also known as "buckyballs") are large molecules, where carbon atoms are arranged spherically, and hence, from the physical point of view, are zero-dimensional objects with discrete energy states with a general formula of C_{n}; where n is generally greater than or equal to 60. Fullerenes can be obtained from graphene with the introduction of pentagons and heptagons that create positive curvature defects, and hence, fullerenes can be thought as wrapped-up graphene. The van der Waals diameter of a C_{60} molecule is about 1.1 nanometers (nm). The nucleus-to-nucleus diameter of a C_{60} molecule is about
0.71 nm and composed of 20 hexagonal faces and 12 pentagonal ones and resembles a football. The other less recognized fullerenes are $C_{70}$, $C_{78}$ and $C_{84}$.

There has recently been a major research interest in the fullerenes and the possibility of using them in the treatment of a wide variety of diseases and other futuristic applications as energy materials, high-performance/high temperature wear-resistance materials, and superconductive materials. Fullerenes are stable, but not totally unreactive. Carbon is present in both sp$^2$ and sp$^3$ hybridization state in fullerenes. The $C_{60}$ and $C_{70}$ fullerenes are shown in Fig. 1.5(a & b) and how the curvature takes place in fullerenes is shown in Fig. 1.5(c).

1.3.1.4. Graphene

Among systems with only carbon atoms, graphene is a two-dimensional (2D) allotrope of carbon. Graphene is made out of carbon atoms arranged on a honeycomb structure made out of hexagons and can be thought of as composed of benzene rings stripped out from their hydrogen atoms. It can also suppose as a single planar layer of graphite. Like graphite, all carbon atoms in graphene are sp$^2$ hybridized. More precisely, graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, and is a basic building block for graphitic materials of all other dimensionalities. It can be wrapped up into 0D fullerenes, rolled into 1D nanotube or stacked into 3D graphite. It can also be considered as an indefinitely large aromatic molecule. The largest known isolated molecule of this type consists of 222 atoms and has 10 benzene rings across. The structure of graphene is shown in Fig. 1.6.
Graphene is one of the strongest, lightest and most conductive materials known to humankind. It is also 97.3 percent transparent. Intrinsic graphene is a semi-metal or zero-gap semiconductor. This strictly two-dimensional material exhibits exceptionally high crystal and electronic quality, and, despite its short history, has already revealed a cornucopia of new physics and potential applications. Their thermal conductivity and mechanical stiffness may rival the remarkable in-plane values for graphite (approx 3,000 W m\(^{-1}\) K\(^{-1}\) and 1,060 GPa, respectively); their fracture strength is higher than steel and recent studies have shown that individual graphene sheets have extraordinary electronic transport properties. Graphene has also high intrinsic electron mobility [10] due to its lack of lattice defects as compared to most other semiconductor materials and its unique linear dispersion relation. One possible route to harnessing these properties for applications would be to incorporate graphene sheets in a composite material. Usually graphene sheets are extracted from graphite by exfoliation process. Other method of graphene synthesis is CVD technique.
1.3.1.5. Carbon nanotubes

The flat graphene sheet is also known to be unstable with respect to scrolling i.e. curling up, which is its lower energy state. The unique novel nanostructure formed after their rolling is carbon nanotube (CNT). The physical reason why these nanostructures form is that a graphene layer of finite size has many edge atoms with dangling bonds, index dangling bonds and these dangling bonds correspond to high energy states. Therefore the total energy of a small number of carbon atoms is reduced by eliminating dangling bonds, even at the expense of increasing the strain energy, thereby promoting the formation of closed cage clusters such as fullerenes and carbon nanotubes. Therefore we can expect the planar sp\(^2\) bonding that is characteristic of graphite to play a significant role in carbon nanotubes. The curvature of the nanotubes admixes a small amount of sp\(^3\) bonding so that the force constants (bonding) in the circumferential direction are slightly weaker than along the nanotube axis. Fig. 1.7 shows the rolling up of graphene to form a single walled carbon nanotube.

![Fig. 1.7 Rolling up of Graphene into SWCNT](image)

Carbon Nanotubes were discovered in 1991 by the Japanese Electron Microscopist, Sumio Iijima, at NEC Laboratory, Japan who was studying the material deposited on the cathode during the arc-evaporation synthesis of Fullerenes and examines the samples by using High Resolution Transmission Electron Microscope (HRTEM) and he saw needle like tubes in the soot which was known as carbon nanotubes. Iijima's discovery of carbon nanotubes in the insoluble material of arc burned graphite rods created the buzz that is now associated with carbon nano tubes. These nanotubes are
concentric graphitic cylinders closed at either end due to the presence of five-membered rings.

1.4. Structure and Properties of CNTs
1.4.1. Structure of CNTs

Carbon nanotubes structurally are of two types depending on the number of graphene layers rolled up. If only a single one atomic thick layer of graphene rolled up to form tubular seamless structure it is single walled carbon nanotube (SWCNT) and if more than one layers of graphene rolled up to form a number of concentric cylinders it is Multiwalled carbon nanotube (MWCNT). Fig. 1.8(a&b) shows a SWCNT and MWCNT respectively. The first nanotube discovered by Iijima was MWCNTs and the single-walled carbon nanotubes SWCNTs was discovered in 1993 by his group. SWCNTs are used to define the properties of carbon nanotubes. A carbon nanotube consists of two separate regions with different physical and chemical Properties. The first is the sidewall of the tube derived from rolling of graphene layer and the second is the end cap structure of the tube and is similar to or derived from a smaller fullerene shown in Fig. 1.9.
Since the SWCNT is only one atom thick and has a small number of atoms around its circumference, only a few wave vectors are needed to describe the periodicity of the nanotubes. These constraints lead to quantum confinement of the wave functions in the radial and circumferential directions, with plane wave motion occurring only along the nanotube axis corresponding to a large number or closely spaced allowed wave vectors. Thus, although carbon nanotubes are closely related to a 2D graphene sheet, the tube curvature and the quantum confinement in the circumferential direction lead to a host of properties that are different from those of a graphene sheet.

The way the graphene sheet is wrapped is represented by a pair of indices \((n, m)\) called the chiral (Fig. 1.10). The integers \(n\) and \(m\) denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If \(m = 0\), the nanotubes are zigzag, if \(n = m\), the nanotubes are armchair, otherwise, they are chiral as shown in Fig. 1.11(a). The structure of these three types of CNTs is shown in Fig. 1.11(b).
It has been predicted that pure armchair, zigzag and chiral SWCNTs should have densities of 1.33, 1.34 and 1.40 g cm$^{-3}$[11]. The structure of nanotube influences its properties, including conductance, density and lattice structure. It is known that electronic structures of SWCNTs determine their electrical properties. Depending on their chiral vector, SWCNTs with small diameter are either metallic or semiconducting. The differences in conducting properties are caused by the molecular structure that results in a different band structure and thus a different band gap. The (n, m) can determine their conducting properties. As a result if n-m is divisible by 3 then the carbon nanotube is a metal otherwise it is a semiconductor.

1.4.2. Properties of CNTs

Carbon nanotubes are endowed with exceptionally high material properties, very close to their theoretical limits, such as electrical and thermal conductivity, strength, stiffness, and toughness and having low density of 1.3 to 1.4 g cm$^{-3}$.

1.4.2.1. Mechanical Properties of CNTs

The strength of C-C bond gives rise to a large interest in mechanical properties of nanotubes. Theoretically, these should be stiffer than any other known substance. Theoretically the Young's modulus of the SWCNTs can be as high as 2.8-3.6 TPa and 1.7-2.4 TPa for MWCNTs [12] which is approximately 10 times higher than steel, the
The strongest metallic alloy known. Experimental values of Young’s modulus for SWCNTs and MWCNTs are as high as 1470 GPa and 950 GPa respectively [13, 14], nearly 5 times of steel. MWCNTs appear to fall victim to their own in-plane structural perfection which minimizes load transfer to the inner shells when the outermost shell is strained in tension. Also the tensile strength or breaking strain of nanotubes can be up to 63 GPa, around 50 times higher than steel. Tension and compression are mostly governed by the in-plane σ-bonds, while pure bending is affected by the out-of-plane π-bonds. SWCNTs are quite hard and can withstand a pressure up to 24GPa without deformation. Hence the simulations and experiments demonstrate a remarkable “bend, don’t break” response of the CNTs as shown in figure given by the Yakobson’s simulation [15]. Also these get twisted a lot without damaging as shown in Fig. 1.12(a). The HRTEM images of bent CNTs are shown in Fig. 1.12 (b). There are no direct mechanical testing experiments that can be done on individual nanotubes (nanoscopic specimens) to determine directly their axial strength. However, the indirect experiments like AFM provide a brief view of the mechanical properties as

![Bended & Twisted structure of CNT](image1)

**Fig. 1.12(a) Bended & Twisted structure of CNT**

![HRTEM images of bended MWCNT & SWCNT](image2)

**Fig. 1.12(b) HRTEM images of bended MWCNT & SWCNT**
well as Scanning Probe techniques that can manipulate individual nanotubes, have provide some basic answers to the mechanical behavior of the nanotubes [16]. The analysis performed on several MWCNTs gave average Young’s modulus values of 1.8 TPa, which is higher than the in–plane modulus for single crystal graphite. So the high stiffness and strength combined with low density implies that nanotubes could serve as ideal reinforcement in composite materials. These properties, coupled with the lightness of carbon nanotubes, give them great potential in applications such as aerospace and other military applications.

1.4.2.2. Electrical Properties of CNTs

The nanometer dimensions of the CNTs, together with the unique electronic structure of a graphene sheet, makes the electronic properties of these one-dimensional (1D) structures extraordinary. The one dimensional structure of CNTs helps them in making a good electric conductor. As in a 3D conductor the possibility of scattering of electrons is large as these can scatter at any angle. Especially notable is the fact that SWCNTs can be metallic or semiconducting depending on their structure and their band gap can vary from zero to about 2 eV, whereas MWCNTs are zero-gap metals. Thus, some nanotubes have conductivities higher than that of copper, while others behave more like silicon. Theoretically, metallic nanotubes can carry an electric current density of $4 \times 10^9$ A/cm$^2$ which is nearly 1,000 times greater than metal copper and hence can be used as fine electron gun for low weight displays. The room temperature conductivity of SWCNTs was about $6 \times 10^7$ S/m for the metallic nanotubes and about 10 S/m for semiconducting tubes. Since MWCNTs have larger diameters, confinement effects disappear, and the transport properties approach those of turbostratic graphite [17]. Theoretically study also shows that in case of MWCNTs the overall behavior is determined by the electronic properties of the external shell [18, 19]. Conductivities of individual MWCNTs have been reported to range between 20 and $2 \times 10^7$ S/m [20], depending on the helicities of the outermost shells or the presence of defects [21]. The electronic property of larger diameter MWCNTs approaches those of graphite. Nanotubes have been shown to be superconducting at low temperatures. As probably CNTs are not
perfect at ends and end defects like pentagons or heptagons are found to modify the electronic properties of these nanosystems drastically. There is great interest in the possibility of constructing nanoscale electronic devices from nanotubes, and some progress is being made in this area. SWCNTs have been recently used to form all conducting and semiconducting layers (source, drain and gate electrodes) in thin films transistors. So the high electrical conductivity of CNTs makes them an excellent additive to impart electrical conductivity in otherwise insulating polymers. Also their high aspect ratio means that a very low loading is needed to form a connecting network in a polymer compared to make them conducting.

1.4.2.3. Thermal Properties of CNTs

CNTs are expected to be very good thermal conductors along the tube, but good insulators laterally to the tube axis. Experiments on individual tubes are extremely difficult but measurements show that a SWCNT has a room-temperature thermal conductivity along its axis of about 3500 W·m⁻¹·K⁻¹ and MWCNTs have a peak value of ~ 3000 W·m⁻¹·K⁻¹ at 320 K; compare this to copper, a metal well-known for its good thermal conductivity, which transmits 385 W·m⁻¹·K⁻¹ [22]. Although for bulk MWCNTs foils, thermal conductivity limits to 20 W·m⁻¹·K⁻¹ suggesting that thermally opaque junctions between tubes severely limit the large scale diffusion of phonons. The thermal conductivity of CNTs across axis (in the radial direction) is about 1.52 W·m⁻¹·K⁻¹, which is as thermally conductive as soil. Both SWCNT and MWCNT materials and composites are being actively studied for thermal management applications, either as “heat pipes” or as an alternative to metallic addition to low thermal conductive materials. In case of composites, the important limiting factors are quality of dispersion and interphase thermal barriers.

1.4.2.4. Chemical Reactivity of CNTs

As a result of the curvature of the CNT surface it is also chemically reactive. Carbon nanotube reactivity is directly related to the pi-orbital mismatch caused by an increased curvature. Therefore, a distinction must be made between the sidewall and the
end caps of a nanotube. For the same reason, a smaller nanotube diameter results in increased reactivity. Covalent chemical modification of either sidewalls or end caps has shown to be possible. For example, the solubility of CNTs in different solvents can be controlled this way. Though, direct investigation of chemical modifications on nanotube behavior is difficult as the crude nanotube samples are still not pure enough.

1.5. Multiwalled Carbon Nanotubes (MWCNTs)

SWCNTs have better properties than MWCNTs but latter have a few advantages. One of them is large scale synthesis by Chemical Vapor Deposition (CVD) and other is their stiffness, especially in compression. Although these are weaker in tension due to “pullout” of the individual tubes. The large scale production of MWCNTs by CVD technique cut their cost to large extent and paves their way to be used in other applications where large amount of CNTs are required. The structure or multiple layers of MWCNTs is especially important when functionalization is required (grafting of chemical functions at the surface of the nanotubes and discussed later in this chapter) to add new properties to the CNT. In the case of SWCNT, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties. In the case of MWCNT, only the outer wall is modified. Moreover, MWCNTs are polymers of pure carbon and can be reacted and manipulated using the rich chemistry of carbon. This provides opportunity to modify the structure and to optimize solubility and dispersion, allowing innovative applications in materials, electronics, chemical processing and energy management, to name just a few.

The structure of MWCNTs are intrinsically uncertain since it is impossible to satisfy epitaxy simultaneously, or compatibility of wrapping indices (n, m) on adjacent shells, with very strong tendency to maintain the intershell spacing close to that of the graphite intershell spacing of 3.35 Å. Experimentally the intershell correlations in MWCNTs are characteristic of turbostratic graphite in which the ABAB stacking order is severely disrupted. MWCNTs are the most reasonable ones for commercialization as a composite additive or coating element.
MWCNT consist of multiple rolled layers (concentric tubes) of graphite. There are two models which can be used to describe the structures of multi-walled nanotubes [23]. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders, e.g. a (0, 8) single-walled nanotube (SWCNT) within a larger (0, 10) single-walled nanotube (SWCNT). In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper. In MWCNTs there is no three-dimensional ordering between the individual graphite layers, suggesting that the internal layer structure is rotationally disordered. The aspect ratios of MWCNTs are usually smaller than that from SWCNTs because diameter is of MWCNTs are greater than SWCNTs.

1.6. Synthesis of CNTs

CNTs are attracting must interest for their potential applications, which largely derives from their unusual structure and electronic properties. Since all these properties are concerned directly to the atomic structure of nanotubes, it is quite necessary a thorough understanding of the phenomenon to control nanotube size, the number of shells (walls), the helicities and the structure during growth. The full potential of nanotubes for applications will be realized until the growth of nanotubes can be optimized and well controlled. For utilization of CNTs properties in real world applications, like composite preparation and hydrogen storage, it is desired to obtain high quality CNTs in bulk quantity using growth methods that are simple, efficient and inexpensive. Significant work has been carried out in this field and various methods have been studied to synthesize CNTs.

A variety of synthesis methods now exist to produce carbon nanotubes. However, these carbon nanostructures differ greatly with regard to their diameter, aspect ratio, crystallinity, crystalline orientation, purity, entanglement, surface chemistry, and straightness. These structural variations dramatically affect intrinsic properties, processing, and behavior in composite systems. However, it is not yet clear which type of nanotube material is most suitable for composite applications, nor is there much theoretical basis for rational design. Ultimately, the selection will depend on the matrix
material, processing technology, and the property enhancement required. Thus, in order
to interpret the data obtained for nanotube composites, and to develop the required
understanding, it is essential to appreciate the range of nanotube materials available.

The three main production methods used for synthesization of CNTs are chemical
cvapor deposition (CVD), arc discharge and laser ablation methods [24-27]. In addition
CNTs have been prepared electrochemically and under hydrothermal conditions [28].
Several other methods have also been developed for the synthesis of CNTs; these include
the pyrolysis of the hydrocarbons over the small metal nanoparticles. In each synthesis
method, the selective formation of CNT is triggered by enriching the graphite source
material with a single species or a mixture of transition metal catalyst. Pyrolysis of
organometallic precursors such as metallocenes (e.g. ferrocene) in a two stage furnace
provides a straight forward procedure to prepare CNTs. These methods by and large,
yielded MWCNTs. Aligned CNTs bundles, metal filled MWCNTs, Y junction MWCNTs
and SWCNTs are under various experimental conditions. But up to now it is not possible
to selectively grow one certain kind of CNT.

MWCNTs can be produced from the evaporation of pure carbon with high-
temperature methods, but the synthesis of SWCNTs additionally requires the presence
of a metallic catalyst. The catalytic vapor phase deposition of carbon was first reported in
1959 [29] but until 1993 [30] this process was not used to form carbon nanotubes. During
CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly
nickel, cobalt, [31], iron, or a combination [32]. The metal nanoparticles can also be
produced by other ways, including reduction of oxides or oxides solid solutions. The
diameters of the nanotubes that are to be grown are related to the size of the metal
particles. This can be controlled by patterned (or masked) deposition of the metal,
annealing, or by plasma etching of a metal layer. The substrate is heated to approximately
700°C. To initiate the growth of nanotubes, two gases are bled into the reactor: a process
gas (such as argon, ammonia, nitrogen or hydrogen) and a carbon-containing gas (such
as toluene, acetylene, ethylene, ethanol or methane). Nanotubes grow at the sites of the
metal catalyst; the carbon-containing gas is broken apart at the surface of the catalyst

[24]
particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. This mechanism is still being studied. The catalyst particles can stay at the tips of the growing nanotube during the growth process, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate. With the catalytic chemical vapor deposition (CCVD) method CNTs can be grown directly on substrates and their quality is governed by the catalyst used in process. In general transition metals can be used to catalytically activate CNT growth where the metal nanoparticles serve as nucleation sites and follow a reshaping during the chemical process. The CVD products tend to be highly entangled; however, aligned nanotube arrays can be obtained under conditions that lead to rapid and dense nucleation on flat substrates [16, 33-35]. The quality and yield of carbon nanotubes depend on the synthesis technique and the specific growth conditions used. Compared to other methods for CNTs synthesization, more parameters, including temperature, feeding gases, flow rate, catalyst components and heating rate are accessible to control the growth process in CVD. By changing the growth conditions, we can control the properties of the produced carbon nanotubes such as length, orientation and diameter to some extent. The CVD approach requires a catalyst for both types of CNTs.

Electric arc discharge and laser ablation leads to very similar materials, a single mechanism is sufficient which should not sharply depends on the details of the experimental conditions but more on the kinetics of carbon condensation in a non equilibrium situation.

The electric arc method is based on the generation of a DC arc plasma between two carbon electrodes in an inert (usually helium) atmosphere. While the anode is consumed, a soft, dark black, fibrous deposit forms on the cathode which consists of about 50 vol% straight MWCNTs, often arranged in a fractal structure. Addition of a suitable catalyst such as NiCo, Co-Y or Ni-Y leads to the formation of interconnected web-like SWCNT bundles on the walls of the reaction chamber [36-39]. Macroscopically long ropes of well-aligned SWCNTs can be synthesized by the arc-discharge method using hydrogen [40]. Laser ablation is a similar process, using a different technique to
generate the carbon vapor; although the method can generate MWCNTs, it is usually used for the production of SWCNTs at yields higher than 70%. A graphite target, containing a 1–2% metal catalyst, is held in a furnace at 1200°C in an inert atmosphere and is evaporated using a high power laser [41-42]. The resulting products are swept from the high-temperature zone by the flowing inert gas and are deposited on a conical water-cooled copper collector. The products of both high-temperature routes tend to be highly crystalline, with low defect concentrations, but are relatively impure, containing other, unwanted carbonaceous impurities. These methods usually work on the gram scale and are, therefore, relatively expensive. For the use of nanotubes in composites, large quantities of nanotubes are required at low cost, ideally without the requirement for complicated purification. At present, only CVD-grown nanotubes satisfy these requirements and, as such, tend to be the materials of choice for composite work, both in academia and in industry.

Experimental results show that the width and diameter distribution depends on the composition of the catalyst, the growth temperature and the various other growth conditions.

During CNTs synthesis impurities in the form of catalyst particles, amorphous carbon and non tubular fullerenes are also produced. It was observed that the gas phase processes produces CNTs with fewer impurities and are most amenable to large scale processing. So the gas phase techniques such as CVD, for nanotube growth offer the greatest potential for scaling up nanotube production for processing of composites. Also as most of the production methods involve the use of catalysts which are normally transition metals (Fe, Co, Ni or Y) which would remains in the resulting nanotubes as spherical or cylindrical particles after experiments. Through careful control of process parameters one can minimize the formation of amorphous carbon particles, so that the main impurities in CNTs are the remaining catalyst particles. However as the most of these catalytic particles may either hide in internal cavity or stick firmly to the walls of CNTs, it is almost impossible to get rid of these effectively without damaging the order of nanotubes.
1.7. Carbon Based fillers

Carbon based fillers serve as one of the best options used for reinforcements and attracted considerable attention as a means to enhance the properties and overcome the limitations of matrix resins. One additional advantage of using carbon materials as filler over other fillers is that it also enhances the electrical and thermal conductivity because of the sp$^2$ hybridization of its orbitals.

1.7.1. Carbon Nanotubes

The unique properties of carbon nanotubes will undoubtedly lead to many applications. These outstanding properties of nanotubes have given cause for the development of composite materials and currently there is great interest in exploiting these properties by incorporating these into some form of polymer matrix. Filler-based applications of nanotubes for polymer composites are another area being hotly researched and a wide range of polymer matrices have been employed. The other notable members of the carbon family used in composite are carbon black and carbon fibres.

1.7.2. Carbon Black

Carbon black (CB) is a form of amorphous carbon having high surface area to volume ratio and is produced by incomplete combustion of heavy petroleum products such as coal tar and vegetable oil etc. It contains greater than 97% elemental carbon arranged as aciniform (grape like cluster) particulate and distinct from black carbon and root carbon that contains 60% carbon. CB possessed well-developed porosity and predominantly made up of nanopores. Because of its ready availability and compatibility with organic materials CB is used as pigment and reinforcing phase in polymers especially in rubbers [43–44]. These are chemically inert and easy to prepare in the fine sizes and shapes required. Most importantly they naturally possess a surface that is able to form acceptably strong attachments to elastomeric molecules, without the need for expensive coupling agents. The SEM and TEM image of CB is shown in Fig. 1.13.
Fig. 1.13 SEM & TEM of Carbon Black

One major application of CB is as reinforcement in automobile tyres where it helps conduct heat away from the tread and belt area of the tyre, reducing thermal damage and increasing its life. While a pure gum vulcanization of styrene-butadiene has a tensile strength of no more than 2.5 MPa and almost nonexistent abrasion resistance, compounding it with different weight fraction of CB improves its tensile strength, wear resistance and flex fatigue. It also increases tractum and durability. Also some CB particles are employed in some radar absorbent materials.

1.7.3. Carbon Fibre

Carbon fibre is a long, thin strand of material about 7.0 µm in diameter and composed mostly of carbon atoms. Carbon fibre is although not pure carbon it is formed from another polymer mainly polyacrylonitrole (PAN) (Fig. 1.14) or petroleum pitch and having 90-95 % carbon. The expected structure of carbon fibre made from PAN is shown in Fig. 1.15(a). The carbon atoms are bonded together in microscopic crystals that are more or less aligned parallel to the long axis of the fibre. The crystal alignment makes the fibre incredibly strong for its size. Several thousand carbon fibres are twisted together to form a yarn, which may be used by it or woven into a fabric shown in Fig. 1.15(b).

Carbon fibres with density ~ 1.8 g/cc have exceptionally good mechanical properties and fantastic weight-to-strength ratio. They have tensile strength of 7 GPa and
modulus of elasticity (> 450 GPa) greater than steel and highly chemically inert. These properties of carbon fibre are pretty much useless unless embedded in polymer. Carbon fibres have found wide application in commercial and civilian aircraft, recreational, industrial, and transportation markets. Carbon fibres are used in composites with a lightweight matrix. Carbon fibre composites are ideally suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. Carbon Fibre Reinforced Polymers (CFRP) are used for manufacturing: automotive marine and aerospace parts, sport goods (golf clubs, skis, tennis racquets, fishing rods), bicycle frames [45-46].

1.8. Nanocomposites

The behavior of composite depends entirely on the size of the fillers added. With the advancement in today’s era, technologies that allow a reduction in size, weight, and cost while improving functionality and performance are highly desired for military and commercial applications, including telecommunications, network systems, automotive, and computer electronic devices. In recent years, nanocomposites in which one of the phases has dimensions less than 100 nanometers or structures having nano-scale repeat distances between the different phases have attracted both scientific and technological interest to meet the growing demand for material with improved properties and challenging applications. Although the terms nanomaterial and nanocomposites represent new and exciting fields in materials science, such materials have actually been used for centuries and have always existed in nature. However, it is only recently that the means
to characterize and control structure at the nanoscale have stimulated rational investigation and exploitation.

So nanocomposites are a subset of composites that take advantage of unique materials properties on the small scale. The nanocomposites have revealed clearly the property advantages that nanomaterial additives can provide in comparison to both their conventional filler counterparts and base polymer. These properties include improvement in mechanical properties, electrical conductivity, thermal stability, flame retardancy, chemical resistance and decrease in permeability. Nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. Due to the exceptionally high surface area of the nanofillers, the interphase region between the matrix and the filler comprises a considerable portion of the composite. Nanocomposites don’t lose transparency as the nano-reinforcements not significantly scatters light. Also nano-reinforcements, as opposed to traditional reinforcements, have been shown to improve the properties at much lower filler-loading levels that results in significant weight reductions and of obvious importance in various military and aerospace applications. The small size of nanoscale reinforcements also overcomes a common problem found in conventional composites where microscale elements lead to an increase in strength and stiffness but result in a decrease in toughness because of large local stress concentrations. The small size of nano-reinforcements can also facilitate composite processing, making it possible, e.g., to mold polymer nanocomposites into complex shapes because nano-reinforcements can be processed with the polymer using normal methods such as injection molding or extrusion.

1.8.1. MWCNT Nanocomposites

The nanoscopic fibre, CNT molecules are a new form of elemental carbon with intriguing properties. For example, as discussed above the strongest tubes exhibit roughly eighty times the strength, six times the toughness, or Young’s Modulus, and one-sixth the density of high carbon steel. Utilizing the carbon nanotube as a molecular “fibre” in a carbon nanotube reinforced polymer provides a potentially favorable material for
aerospace applications. Carbon nanotubes are often seen as the intersection of traditional carbon fibres with the fullerene family [28]. This ambiguity is characteristic of nanomaterials, and it is not yet clear to what extent conventional fibre composite understanding can be extended to CNT composites. As carbon fibre composites tend to be less dense than metals, and often provide improved strength and corrosion protection, CNT composites will likely provide a low density, corrosion resistant composite that can be used in lower volumes. Incorporating CNT reinforced composites in an airframe potentially offers each of these advantages to the aircraft.

1.8.1.1. Mechanical properties of MWCNT polymer nanocomposites

Different thermoplastic and thermoset polymer matrices have been tried to realize the superior mechanical properties of CNTs for development of light weight super strong material and have obvious applications in several fields including aerospace, sports, automotive, infrastructure and defense. NASA scientists are considering CNT-polymer composite for space elevator. To date, a volume of literature is available on the improvement of mechanical performance of polymers with addition of CNTs. The first study for formation of CNT-polymer composites was carried out by Ajayan [28]. CNTs were aligned within the epoxy matrix by the shear forces induced by cutting with a diamond knife, however no quantitative mechanical measurements were made. The first true study for tensile and compression properties of CNT polymer composites was carried by Schadler [47] with epoxy. On addition of 5 wt% MWCNTs the tensile modulus increased from 3.1 GPa to 3.71 GPa. And compression modulus increased from 3.63 to 4.5 GPa. However no significant increases in toughness values were observed. Bai et al [48] observed a doubling of Young’s modulus from 1.2 to 2.4 GPa and significant increase in strength from 30 to 41 MPa on addition of 1 wt.% MWCNTs. Also excellent matrix–nanotube adhesion was confirmed by the observation of nanotube breakage during fracture surface studies. Zhou [49] reported steady increase of flexural modulus in CNT-epoxy composite with higher CNT weight percentage and found an improvement of 11.7% in modulus with 0.4 wt% loading of CNTs and 28% enhancement in flexural strength with 0.3 wt% loading. Garg et al [50] reported 155 % increment in flexural
strength of epoxy with addition of merely 0.3% amine functionalized MWCNTs. Also an increment of 38% in flexural modulus was reported. Colemann et al [51] reviewed the mechanical properties of a large number of CNT reinforced polymer (thermoplastic and thermosetting) composites fabricated by various methods and reported enhancement in mechanical properties. Also Du et al [52] studied the experimental results for mechanical performance of CNTs nanocomposites carried out by different research groups and observed that the gains are modest and far below the simplest theoretical estimates.

Haggenmueller [53] applied the Halpen Tsai composite theory to CNT nanocomposites and observed that the experimental elastic modulus is smaller than predicted by more than one order. It is attributed to the lack of perfect load transfer from nanotubes to matrix due to non uniform dispersion and small interfacial interaction. Although chemical fictionalization of CNTs has sorted out those problems to an extent, yet the best results have to be achieved. Also aspect ratio is other source of uncertainty in mechanical properties. Defects on the CNT surface are also expected to influence the mechanical properties significantly. Also methods of handling nanotubes, including acid treatments and sonication for long time are known to shorten nanotubes results in decreasing aspect ratio and are detrimental to mechanical properties. The mechanical properties of CNT based composites have increased upto a certain loading of CNTs and beyond which it starts decreasing. This may be because of excess CNTs increase the viscosity of polymers and also causes the surface of CNTs not be completely covered by polymers matrix due to the large specific surface area of CNTs.

Many research groups have investigated the interaction and load transfer between nanotubes and polymer matrices in nanocomposites. Lourie et al [12] collected TEM images showing good epoxy- CNT wetting and significant adhesion and hence concluded CNT epoxy interfacial affinity. Lordi and coworkers [54] also concluded that the strength of interface results from the molecular level entanglement of pristine nanotubes and polymer chains. Haggenmueller et al [53] investigated the effect of both CNTs loading and alignment on the elastic modulus of CNT–PMMA composites. CNT could effectively enhance the friction reduction and antiwear capacity of the nanocomposites.
because it increased the load capacity and mechanical strength of the composites. The complexity of the CNT, the range of chemical and physical processing methods and the breadth of polymer matrices being explored, variability in the mechanical properties of CNT nanocomposites will persist.

### 1.8.1.2. Electrical Properties of MWCNT polymer nanocomposites

CNTs because of their extraordinary electrical conductivity are also excellent additive to impart electrical conductivity to polymer. Many experimental results shows that the conductive CNT composites can be constructed at low loading of CNTs due to low percolation threshold originated from the high aspect ratio and conductivity of CNTs [52, 55]. Colemann et al [51] showed that the electric conductivity of CNT-PMPV polymer could be increased upto ten orders of magnitude on adding 8 % CNTs.

![Fig. 1.16 General Trend of Electrical Conductivity of CNT composites](image)

**Fig. 1.16 General Trend of Electrical Conductivity of CNT composites**

Fig. 1.16 shows the general trend of electrical conductivity of CNT- polymer nanocomposites. It can be found from almost all the experimental results and also obvious from figure that CNT nanocomposites exhibit a typical percolation behavior and CNT reinforcement to polymers can increase the conductivity of resulting composites to several order of magnitude or even some times higher than ten orders of magnitude.

According to percolation theory the conductance should follow the following power law close to threshold percolation

\[
\sigma = \sigma_0 (p - p_o)^f \quad \text{for } p > p_o \tag{1}
\]
where \( \sigma \) is the composite conductivity, \( \sigma_0 \) is a constant, \( p \) the weight fraction of nanotubes, \( p_o \) is the percolation threshold, and \( t \) the critical exponent [21]. Theoretical and experimental results have shown that percolation laws are applicable to CNT based composites and that the enhanced maximum conductivity and percolation can be achieved with significantly lower filler concentrations than with carbon and other conductive fillers. Depending on the polymer matrix, the processing technology, and the type of nanotubes used, recent experimental studies have achieved percolation thresholds between 0.0021 to 9.5% by weight and critical exponents varying from 0.9 to 7.6 [52].

Sandler et al [56] observed the percolation threshold of CNTs/epoxy nanocomposites between 0.0225 and 0.04 wt %. They further observed very low percolation threshold at 0.0025 wt% for aligned CNT-epoxy composites [57]. The current voltage behavior measurements exhibited non-ohmic behavior, which is most likely due to tunneling conduction mechanism. The main mechanism of conduction between adjacent nanotubes is probably electron hopping when their separation distance is small. At concentration greater than percolation threshold, conducting paths are formed through the whole nanocomposites, because the distance between the conductive CNT filler (individual or bundles) is small enough to allow efficient electron hopping.

The electrical conductivity of CNT/polymer composites is also affected by dispersion and aspect ratio of CNTs and is studied by Barrau et al [58]. They used palmitic acid as surfactant to improve the nanotube dispersion and reduced the threshold concentration from 0.18 to 0.08 wt%. To study the effect of aspect ratio on electrical conductivity of CNT nanocomposites Bai et al [59] pretreated MWCNTs to alter their aspect ratios before preparing epoxy/MWCNTs composites and found that the threshold concentration varied from 0.5 to > 4 wt % with decreasing aspect ratio. The effect of alignment of CNTs in polymer composites was also studied. Du et al [60] found some contradictory results with respect to alignment of rod like fillers and observed the lowest percolation threshold and maximum conductivity with their random orientation. They found that the electrical conductivity of 2 wt% CNT/PMMA nanocomposites decrease significantly (from \( \sim 10^{-4} \) to \( \sim 10^{10} \) S/cm) when CNTs were highly aligned. In contrast
Choi et al [61] observed that the nanotube alignment increased the conductivity of a 3 wt% CNT/epoxy composites from ~10-7 to ~10-6 S/cm. In most of the cases the CNT nanocomposites with isotropic nanotubes orientation have greater electrical conductivity than the nanocomposites with highly aligned CNTs especially at lower CNT loadings. By alignment of CNTs in polymers, the percolation pathway is destroyed as aligned CNTs seldomly intersects each other. At higher CNTs loading the conductivity is more in case of aligned CNTs as compare to randomly oriented CNTs.

The study carried out by different researchers also revealed that the composites with thermoplastic polymers have higher conductivity as compared to that of thermosetting polymers above percolation threshold. Transport properties in CNT-PMMA composites have been reported by Stephan et al [62] and Benoit et al [63] where low percolation threshold of 0.5 wt% and 0.33 wt% respectively were obtained. Singjai et al [64] found that increase in number of defects lead to a decrease in conductivity. However Lau et al [65] concluded that functionalization of CNTs by a variety of methods can enhance the electrical conductivity of MWCNTs. The reason attributed to this phenomenon is electron transfer from the carbon atoms on MWCNTs to functionalized groups attached to the surface favorably promoting conductivity. The study carried out by Grimes et al [66] revealed that the electrical response of as fabricated MWCNTs is

![Fig. 1.17 Different molecules of catalyst Fe entrapped in CNT](image1)

![Fig. 1.18 TEM image showing entrapped catalyst](image2)
significantly influenced by the residual catalyst metal particles present. Certainly the core of tubes shown in Fig. 1.17 and TEM image (Fig. 1.18) appears filled with Fe, which acts in some measures to increase the tube conductivity.

1.8.1.3. EMI Shielding properties of MWCNT polymer nanocomposites

The electric conductivity of CNT reinforced polymer composites makes them a very suitable candidate to be employed for electromagnetic interference (EMI) shielding. EMI is the process by which disruptive electromagnetic energy is transmitted from one electronic device to another via radiation or conduction. As we all know that the electromagnetic waves produced from some electronic instrument have an adverse effect on the performance of the other equipments present nearby causing data loss, introduction of noise, degradation of picture quality etc. The common example is the appearance of noise in television signal when a telephone or mobile rings. Also recent reports of deteriorous effects of electromagnetic radiations on electro medical devices have caused concern among health care providers. The overlapping of signals transmitted in air traffic system with signals from other electronic equipments became cause of several accidents in past. Also mobile phones and passing taxi radios have been known to interfere with anti-skid braking system (ABS), airbags and other electronic equipments causing drivers to lose control. In today’s scenario where rapid communication is required, there is an increase in electromagnetic radiations within the spectrum in which the wireless, cordless and satellite system operates. So it a strong desire to shield electronics equipments from the undesired signals. Problems with EMI can be minimized or sometime eliminated by ensuring that all electronic equipments are operated with a good housing to keep away unwanted radio frequency from entering or leaving. The shielding effectiveness (SE) of the shielding material is its ability to attenuate the propagation of electromagnetic waves through it and measured in decibels (dB) given by

\[ SE(\text{dB}) = -10 \log \left( \frac{P_t}{P_0} \right), \]

where \( P_t \) and \( P_0 \) are, respectively, the transmitted and incident electromagnetic power. A SE of 10 dB means 90% of signal is blocked and 20 dB means 99% of signal is blocked.
The main requisition for a material to be used for EMI shielding material is that it should be conducting. Because of their high electrical conductivity metals have been used for past several years as EMI shielding materials. But the shortcomings of metals like heavy weight, physical rigidity and corrosion restricts their use. The most notable substance that could overcome these shortcomings is the CNT-polymer composites. As discussed in previous sections these are electrically conductive, have low density, corrosion resistant and can be molded in any form. Due to easy processing and good flexibility, CNT–polymer composites have been employed for application as promising EMI shielding materials. The SE of the CNT-polymer composites depends on various factors like thickness and electrical conductivity of the sample used, aspect ratio of CNTs. Several studies have been reported on EMI shielding properties of randomly oriented CNT based polymer composites. Mathur and co-workers [38] have prepared MWCNT-PMMA and MWCNT-PS composites and observed 18dB and 17dB SE respectively with 10 wt % MWCNT loading. Park et al [20] reported a SE of 20 to 26 dB in frequency range of 0.3 – 1 GHz for 5 wt% of MWCNTs composites with epoxy/ glass fabric composites with 10 mm thickness. The effect of the length (aspect ratio) of CNTs on EMI SE of composites was also studied by few researchers. Huang [67] reported EMI SE of 18 dB with 15 wt% small CNTs and 23-28 dB with 15 wt% long CNTs in X band (8-12.4 GHz). Li [68] also observed that SE with long length CNTs is more as compared to small length CNTs at the same 15wt % loading composites. The residual catalyst metal particle in the cavity of CNTs also effects the SE of the composites.

There are few additional advantages of using MWCNTs as EMI shielding material. The EMI SE also depends on the source of origin of electromagnetic waves. Electrically conducting material can effectively shield the electromagnetic waves generated from an electric source, whereas magnetic materials effectively shield the electromagnetic waves generated from a magnetic source [69]. The MWCNTs exhibits electrical properties because of presence of pi electrons and magnetic properties because of the presence of catalytic iron particles in tubes. Also one common problem experienced with commonly used composite materials for EMI shielding is build up of
heat in the substance being shielded. The possible solution for this is to add thermal conducting material. Composites with MWCNTs can easily overcome this problem as it has high thermal conductivity.

1.8.1.4. Thermal properties of MWCNT polymer nanocomposites

As discussed above that the CNTs have thermal conductivity as high as 6600W/mK predicted for SWCNTs [70] at room temperature and have experimental value 3000W/mK for isolated MWCNT. So it is quite expected that the reinforcement of CNTs can significantly enhance the thermal properties of CNT-polymer nanocomposites. The improvement in thermal transport properties of CNT polymer composites leads their applications for usage as printed circuit boards, connectors, thermal interface materials, heat sinks and high performance thermal management from satellite structures to electronic device packaging.

Engineers at the Massachusetts Institute of Technology (MIT) are using carbon nanotubes to stitch together plies of carbon fibre materials that could make aircraft skins and other products perhaps 10 times stronger at a nominal increase in cost. ‘Nanostitching’ aligns billions of carbon nanotubes perpendicular to each carbon fibre layer and uses a thermal process to melt a polymer ‘glue’ between the layers. The nanotubes are sucked up into the polymer as it melts, filling the spaces around the carbon fibres and ‘stitching’ the layers together. Since the nanotubes are 1000 times smaller than carbon fibres, they cause no damage to them. Dramatic improvements can be achieved with nanotubes comprising less than 1% of the mass of the overall composites, while adding only a few percent to the cost of the composite. CNTs are also used in organic photovoltaic devices. Also it is expected that well aligned CNT compounded polymer films or coatings should have wide applications including super hydrophobic surface to textile, coatings, gene delivery, microfluid channels, non wetting liquid transfer and many more [71].
1.9. Fabrication of MWCNT polymer nanocomposites

A large number of techniques have been used for the fabrication of CNT-polymer nanocomposites based on the type of polymer used. Solvent casting and melt mixing are the two common and most used techniques.

1.9.1. Solvent Casting Method

The solvent casting is most valuable technique to form nanocomposites of CNTs/polymer however its use is restricted to polymers that are soluble. Solvent casting facilitates nanotube dispersion and involves preparing a suspension of CNTs in the desirable polymer solution via energetic agitation (magnetic or mechanic stirring, reflux or sonication) and then allowing the solvent to evaporate to produce CNT-polymer nanocomposites. A lot of study is available in open literature for the formation of CNT nanocomposites by this method [72-73]. Mathur et al [39] cast the solutions of the MWCNT/polystyrene (PS)/toluene and MWCNT/ polymethyl methacrylate (PMMA)/toluene suspensions after sonication into a dish to produce nanotubes composites with enhanced electrical and mechanical properties. Benoit et al [63] obtained electrically conductive nanocomposites by dispersing CNT and PMMA in toluene, followed by the drop casting on substrate. The choice of solvent is generally based on the solubility of the polymer. Not only has the selection of solvent for nanotube, dispersion also had a significant influence on the flexural strength of the nanocomposites. The solvent effects are in the order of DMF > ethanol > acetone as studied by Lau and co-workers [74]. Their results demonstrates that, contrary to the general belief that small traces of CNTs alone will serve to strengthen the epoxy composites, the choice of the solvent used in the dispersion of the CNTs also can have a significant impact. The changed trend of the mechanical properties was found to be related to the boiling point of respective solvent used. In the samples observed in their study, only acetone-dispersed nanocomposites displayed improvements in flexural strength over the pure epoxy, while ethanol and DMF used in the CNTs dispersion actually countered the benefits of CNTs in the resulting nanocomposites. It is reasonable that the easier the solvent can evaporate, the less the solvent will remain to affect the curing reaction. Their results of
thermogravimetric analysis (TGA) proved the existence of the residual solvent in the resulting nanocomposites. Further evidence of the solvent influence was obtained by Fourier transform infrared (FTIR) spectra, which displayed the difference in the molecular structure of the final nanocomposites depending on the solvent used. The solvent influence is attributed to the different amount of unreacted epoxide groups and the extent of cure reaction in the manufacturing process. So here in our studies we used acetone as dispersion medium for MWCNTs.

The presence of the residual solvent may alter the reaction mechanism by restricting the nucleophile–electrophile interaction between the hardener and epoxy, henceforth, affect the cross-linking density and thus degrade the transport properties [75] and mechanical properties of the cured structures; second, the residual solvent may absorb some heat energy from the composites system in the pre-cured process, causing a change in local temperature. Islam et al [69] dispersed CNTs in water with the use of surfactant NaDDBS followed by sonication to form composites. Nanocomposites with other thermoplastic materials with enhanced properties have been fabricated by solvent casting [72-73]. The limitation of this method is that during slow process of solvent evaporation, nanotubes may tend to agglomerate, that leads to inhomogeneous nanotube distribution in polymer matrix. The evaporation time can be decreased by dropping the nanotube/polymer suspension on a hot substrate (drop casting) [63] or by putting suspension on a rotating substrate (spin-casting) [76]. Du et al. [60] developed a versatile coagulation method to avoid agglomeration of CNTs in PMMA-CNT nanocomposites that involves pouring a nanotube/polymer suspension into an excess of nonsolvent. The precipitating polymer chains entrap the CNT, thereby preventing the CNT from bundling.

1.9.2. Melt Mixing Method

The alternative and second most commonly used method is melt mixing, which is mostly used for thermoplastics and most compatible with current industrial practices. Unlike solvent casting method, in which nanotubes are typically dispersed by sonication, this range of techniques makes use of the fact that thermoplastic polymers soften when heated. Melt mixing uses elevated temperatures to make substrate less viscous and high
shear forces to disrupt the nanotubes bundle. Bulk samples can then be fabricated by techniques such as compression molding, injection molding or extrusion. Andrews and co-workers [33] formed composites of commercial polymers such as high impact polystyrene, polypropylene and acrylonitrile–butadiene–styrene (ABS) with MWCNT by melt processing. Initially these polymers were blended in a high shear mixer with nanotubes at high loading level to form master batches that were thereafter diluted with pure polymer to form lower mass fraction samples. Compression molding was used to form composite films. A similar combination of shear mixing and compression molding is studied by many other groups discussed elsewhere [72]. Also Meincke et al. [16] mixed polyamide-6, ABS and CVD-MWCNT in a twin screw extruder at 260°C and use injection molding to form nanocomposites. Tang et al [34] used both compression and twin-screw extrusion to form CNT/polyethylene composites. Although melt-processing technique has advantages of speed and simplicity, it is not much effective in breaking of agglomeration of CNTs and their dispersion. Bhattacharyya et al [77] made 1 wt% CNT/polypropylene (PP) nanocomposites by melt mixing, but found that melt mixing alone did not provide uniform nanotube dispersion. Niu et al [41] studied both methods to prepare polyvinylidene fluoride (PVDF)-CNT nanocomposites to study electrical properties and found it better in composites formed by solution casting. Garg et al [50] compared the mechanical properties of MWCNT/epoxy nanocomposites fabricated by solvent casting using acetone as solvent and melt mixing with high speed stirring to disperse CNTs. The results show that the solvent casting method is more efficient to enhance mechanical properties. Detailed discussion is given in chapter 3.

Some studies have been also carried out using combined methods, such as solvent casting in conjunction with sonication, followed by melt mixing. Haggenmueller et al [78] observed considerable nanotube dispersion in CNT-polymer nanocomposites using combination of solvent casting and melt mixing. Shailaja et al [38] also prepared MWCNT bulk composites with PMMA and PS using a two-step method of solvent casting followed by compression molding and obtained better electrical and mechanical properties.
In addition to solvent casting and melt mixing the other common method which combines nanotubes with high molecular weight polymers is in situ polymerization starting with CNTs and monomers. In situ polymerization methods enable C-C covalent bonding between nanotubes and the polymer matrix using various condensation reactions. The most common in situ polymerization methods involve epoxy in which the monomer resins and hardeners are combined with CNTs prior to polymerizing [79]. Mathur and coworkers [39] performed the in situ polymerization of MWCNT/ PMMA composites for the enhancement in flexural strength and modulus of composites. Li et al [35] reported the fabrication and characterization of CNT/Polyaniline (PANI) composites. Xiao [80] deposited polypyrrole (PP) and poly(3-methylthiophene) (PMet) on the surface of MWCNTs by in situ polymerization. Moniruzzaman [73] reported many other studies of in-situ polymerization of CNTs with different polymers. Generally, in situ polymerization can be used for the fabrication of almost any polymer composites containing carbon nanotubes that can be non-covalently or covalently bound to polymer matrix. This technique enables the grafting of large polymer molecules onto the walls of carbon nanotubes. The additional advantage of this method is that it is effective and convenient for preparation of high loading CNTs composites with almost any polymer type. This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which cannot be processed by solution or melt processing. The other less commonly known methods for CNT-polymer nanocomposites formation are twin screw pulverization [81], latex fabrication [82], and coagulation spinning [83].

1.10. Challenges in MWCNT polymer composites fabrication and possible solutions

Although these fabrication methods helped to enhance the properties of CNT reinforced composites over neat polymer but there are several key challenges that hinders the excellent CNT properties to be fruitful in polymer composite formation. Primarily, one needs to ensure that the properties of the composite are homogeneous throughout.
1.10.1. Dispersion

The difficulty in achieving it is non-dispersion of the nanoscale filler in a composite, independent of their shape and aspect ratio. Dispersion involves separation and then stabilization of CNTs in a medium. The methods described above for the nanocomposites fabrication require CNTs to be well dispersed either in solvent or in polymer for maximizing their contact surface area with polymer matrix. As CNTs have diameters on nanoscale the entanglement during growth and the substantial van der Waals interaction between them forces them to agglomerates into bundles. The ability of bundle formation of CNTs with its inert chemical structure makes these high aspect ratio fibres dissolving in common solvents to form solution quite impossible. The scanning electron micrographs of the MWCNTs synthesized in our lab by CVD technique seems to be highly entangled and the dimension of nanotube bundles is tens of micrometers, indication of hundreds of MWCNTs in one bundle as shown in Fig. 1.19. These bundles exhibits inferior mechanical and electrical properties as compare to individual nanotube because of slippage of nanotubes inside bundles and lower aspect ratio as compare to individual nanotube. The aggregated bundles tend to act as defect sites which not only adversely affect mechanical and electrical properties of nanocomposites but also influence optical transmissivity. Moreover, these entangled bundles of CNTs making handling and processing during composite formation a formidable hurdle. Effective separation requires the overcoming of the inter-tube van der Waal attraction, which is anomalously strong in CNT case. To achieve large fractions of individual CNT several methods have been employed. The most effective methods are by attaching several functional sites on the surface and sidewall of CNTs through some chemical treatment or by surrounding the nanotubes with dispersing agents such as
surfactant. Thereafter the difficulty of dispersion can be overcome by mechanical/physical means such as ultrasonication, high shear mixing or melt blending.

Another obstacle in dispersing the carbon nanotubes is the presence of various impurities including amorphous carbon, spherical fullerenes and other metal catalyst particles. These impurities are responsible for the poor properties of CNTs reinforced composites [84]. So the purification of CNTs is needed. The common and most commonly used method for purification is based on oxidation which includes burning away of these impurities at temperature > 400°C in air or oxygen.

1.10.2. Adhesion between CNT and polymer

The second key challenge is in creating a good interface between nanotubes and the polymer matrix. From the research on microfibre based polymer composites over the past few decades, it is well established that the structure and properties of filler-matrix interface plays a major role in determining the structural integrity and mechanical performance of composite materials. CNTs have atomically smooth non-reactive surfaces and as such there is a lack of interfacial bonding between the CNT and the polymer chains that limits load transfer and hence the benefits of the high mechanical strength of CNTs seems to be lost. The first experimental study focusing on interfacial interaction between MWCNT and polymer was carried out by Cooper et al [85]. They investigated the detachment of MWCNTs from an epoxy matrix using a pullout test for individual MWCNT and observed the interfacial shear stress varied from 35-376 MPa. This variability is attributed to difference in structure, morphology and structure properties of the CNTs.

There are three main mechanisms for load transfer from matrix to filler. The first is weak van der Waal or electrostatic interaction between filler and polymer. Using small size filler and close contact at the interface can increase it. The large specific surface area of CNTs is advantageous for bonding with matrix in a composite, but is a major cause for agglomeration of CNTs. So also from this point of view individual nanotubes dispersed in matrix is helpful. The second mechanism of load transfer is micromechanical interlocking which is difficult in CNTs nanocomposites due to their atomically smooth
surface. Although local non uniformity along length of CNTs i.e. varying diameter and bends or kicks due to non hexagonal defects contributes to this micromechanical interlocking. This interlocking can increase by using long CNTs to block the movement of polymer chains. The contribution of this mechanism may reach saturation at low CNT content. The third and best mechanism for better adhesion and hence load transfer between CNTs and polymer is covalent or ionic bonding between them. The chemical bonding between CNTs and polymer can be created and enhanced by the surface treatment such as oxidation of CNTs with acids or other chemicals. This mode of mechanism have much importance as it provides strong interaction between polymer and CNT and hence efficiently transfers the load from polymer matrix to nanotubes necessary for enhanced mechanical response in high-performance polymers.

1.10.3. Chemical Functionalization of CNTs

The best route to achieve individual CNT to ensure better dispersion is chemical modifications of CNT surface that makes it more amendable to predictable manipulation. The chemical functionalization involves the attachment of chemical bonds to CNT surface or sidewall. Nanotube functionalization typically starts with oxidative conditions, commonly by refluxing in nitric or sulfuric acid or combination of both to attach carboxylic acid moieties to the defect sites. The end caps of nanotubes have extra strain energy because of their high degree of curvature with pentagons and heptagonal carbon atoms are most vulnerable to reaction with acid. The side walls also contain defects like pentagon-heptagon pairs, sp$^3$ hybridized defects and vacancies in nanotube lattice and are easily supplemented by oxidative damage and can be stabilized by formation of functional groups mainly carboxylic acid and hydroxide group. These acid moieties and hydroxide groups can be further replaced with more reactive groups like $-\text{COCl}$ or $-\text{CONH}_2$. The addition of these functional groups on CNTs possesses intermolecular repulsion between functional groups on surface that overcomes the otherwise weak van der Waal attraction between CNTs. Also it is vital to stabilize the dispersion to prevent reagglomeration of the CNTs. Chemical functionalization can prevent reagglomeration of CNTs also. Sen et al [86] carried out chemical functionalization to form ester
functionalized CNTs and found that it is an effective approach to exfoliate the CNTs bundles and improve their processibility with polymer matrix. Georgakilas et al [87] observed that CNT covalently functionalized with pyrrolidine by the 1,3-dipolar cycloaddition of azomethine shows a solubility of 50 mg/mL in chloroform, even without sonication whereas the pristine CNT is completely insoluble in this solvent. Also Liang et al [88] performed reductive alkylation of CNTs using lithium and alkyl halides in liquid ammonia for sidewall functionalization of CNTs and observed their extensive debundling by inspection of the HRTEM images. Kinloch et al [89] studied the rheological behavior of oxidized CNTs and found that the composites filled with functionalized CNTs had better dispersion.

Also the adhesion between the polymer and CNTs can be enhanced by chemical modification of CNTs. Gojny et al [90] achieved surface modified MWCNTs by refluxing of oxidized MWCNTs with multifunctional amines and observed from TEM images that these were completely covered by epoxy matrix that confirmed the bonding between them. Sinnott [91] has provided an in depth review of chemical functionalization of CNTs where the chemical bonds are used to tailor the interactions between nanotubes and polymers or solvent. The chemical functionalization of CNTs has also been accomplished through irradiation with electrons or ions [91, 92]. In this manner one may hope to improve the binding of CNTs by interdigitation of active sites on its sides into polymer matrix.

Fig. 1.20 Different Functional Groups attached on CNT Surface
Covalent bond also benefits phonon transferring between nanotubes and polymer matrix, which is a key factor for improving thermal conductivity of the nanocomposites. To ensure the adhesion between polymer and nanotubes various surfactant and chemical modification procedures have been adopted to modify the surface of otherwise inert surface of CNTs that provides bonding sites to the polymer matrix. The Fig. 1.20 shows the attachment of some active sites after chemical treatment of CNTs.

So the surface modification of CNTs is the crucial factor that decides the effective dispersion and improves the interactions between CNTs and matrix. However there are certain drawbacks of using chemically functionalized CNTs. Chemical functionalization normally employs harsh techniques resulting in tube fragmentation and also disrupts the bonding between graphene sheets and thereby reduces the properties of CNTs. Studies revealed that different chemical treatments may decrease the maximum buckling force of nanotubes by 15% [72]. Also the chemically functionalized CNTs significantly decrease the electrical conductivity of CNTs nanocomposites due to unbalance polarization effect, shortening of length and physical structure defects during acidic treatment [93]. But it is still necessary to increase dispersion and strengthens the interfacial bonding of CNTs with polymer matrix that is more important in structural applications.

The challenges faced in the modification of MWCNTs are related to poor reactivity of sidewalls caused by high stability of graphene polyaromatic structure, with lower curvature (only on caps) and growing strain in the tubular frame with the number and size of the functional group attached on the graphene wall. Also it is required to non-destructive attachments of functional groups to the graphene walls in order to the preserve the tubular structure.

The solubility or dispersion of CNTs in certain specified solvents or polymers can also be increased by non covalent association which is more fragile. The non-ionic surfactant such as sodium dodecylbenzene sulfonate (SDS) or polyoxyethylene-8-lauryl (PoEL) has two segments. The hydrophobic segment of surfactant shows strong interactions with carbon of CNTs via van der Waal force and the hydrophilic segment shows hydrogen bonding with solvent or polymer used for dispersion. Islam et al [69]
reported that ~ 65% CNT bundles exfoliated into individual nanotubes even with a very low of 20 mg (CNT)/ml of water containing SDS as surfactant. Barrau et al [94] used palmitic acid as surfactant to disperse CNTs into epoxy resin and observed that electrical percolation threshold decreases indicating better CNT dispersion. Gong et al [95] added PoEL as surfactant in CNT/Epoxy composite to assist the dispersion of CNTs. The improvement in dispersion in chitosan with nitric acid treated CNTs was also reported by Ozarkar et al [96] and the stability of the dispersion prepared by using functionalized carbon nanotubes was observed to be better. However, CNTs treated with different surfactants are wrapped in it and hence contacts between CNTs decreases thereby the transport properties (electrical and thermal conductivities) of CNTs/polymer nanocomposites are adversely affected.

1.10.4. Alignment of CNT in Polymer Matrix

The other key challenge is to understand the effect of nanotube alignment on nanocomposites properties because the nanotubes have asymmetric structure and properties. Like other one-dimensional fibre fillers CNTs displays highest properties in the oriented reinforced direction and the mechanical, electrical, magnetic and optical performance of its composites are linked directly to their alignment in the matrix. So to take the full advantage of excellent properties of CNTs these should be aligned in a particular direction. For example, the alignment of CNT increases the elastic modulus and electrical conductivity of nanocomposites along the nanotube alignment direction. Andrews et al [97] prepared aligned CNT/pitch composites and found that the tensile strength and electrical conductivity is enhanced by 90% and 340% respectively due to orientation of CNTs. Du et al [52] compared the mechanical performance of randomly oriented and aligned CNTs polymer composites. Their study revealed that in aligned CNT polymer nanocomposites tensile strength and modulus even reached to 3600 MPa and 80 GPA respectively which is much higher than the general value of 100 MPa and 6 GPa in case of randomly oriented CNT polymer nanocomposites. Also they observed that the mechanical properties are always higher for aligned CNTs composites with higher loading while the case is different for isotropic CNT polymer composites. Several
methods like application of electric field during composite formation and carbon arc discharge \cite{98}, composite slicing \cite{28}, film rubbing \cite{55}, chemical vapor deposition \cite{36-37}, mechanical stretching of CNT-polymer composites \cite{42} and magnetic orientation \cite{99} have been reported for aligning nanotubes in composites. Electrospinning is also an effective method for the alignment of CNTs in polymer matrix.

1.1. Objective of the thesis

Carbon nanotubes have been recognized as one of the mechanically strong, highly electric conducting material with good electromagnetic interference shielding properties. Significant efforts have been made by various researchers to reap out these extraordinary properties in polymers with their reinforcement. Though the results observed an enhancement in properties of polymers but experimental values are far lower than the theoretically predicted values. For further improvement in properties of composites, the thorough understanding of discrepancies and practical problems should have been known. The major problems faced are the dispersion and the interaction of CNTs with polymer. Some of the examples of heavily studied CNT reinforced composites are epoxy-CNT composites and have been used for many structural applications. The objective of this thesis is to focus on epoxy resin based CNT composites and to understand various mechanisms of dispersion, surface modification and composite fabrication. This has helped to explore further the mechanical, electrical and EMI shielding properties of CNT reinforced epoxy and other thermosetting and thermoplastic materials. A newer scheme for curing of epoxy resin is discussed which makes use of a thermosetting polymer as a replacement of hazardous amine based hardener.

In this thesis the main emphasis has been given to the different techniques for composite fabrication and the study of their mechanical, electrical and EMI shielding properties. The novel research results explored their applications in various structural applications. Along with experimental investigations various models have been presented to interpret the experimental observations. The thesis tries to correlate the experimental and theoretical results.
Also the thesis aims to develop new approaches for composite formation to achieve high electrical conductivity of composites and hence pave their way for use in absorption dominant high EMI shielding applications. As dispersion is a big concern with increase in loading of CNTs the thesis discovers a new method to prepare composites with very high loading (upto 50 wt%) of CNTs with uniform dispersion.

Optimization of dispersion of CNTs in polymer and solvent is a tedious process and SEM and TEM observations have been discussed in literature for qualitative measurements of dispersion. The objective of this thesis is also to discover some newer and less tedious method to observe qualitative as well as quantitative dispersion of CNTs in polymers and solvents. The thesis also discovers a newer approach to measure the aspect ratio of CNTs used in formation of composites.

The thesis explains how the functionalization of CNTs helps in achieving their better dispersion in polymer and shows how the interaction takes place in functional group on CNT surface and reactive site of polymer. Our experimental data provides a relevant proof to explain which type of treatment to CNTs gives best results for mechanical and electrical properties of composites. Emphasis has also been given to make composites of aligned CNTs and their application as highly conducting and shielding material. So we concluded that this research is unique in its attempt to develop new MWCNT-based material that utilizes all of the MWCNTs characteristics.

1.12. Organization of the thesis
1.12.1. Chapter 1

Chapter 1 contains the introduction of CNTs with their reinforcement in polymers for composite formation and their applications. A brief introduction of different forms of composites with distribution of fillers according to shape, size and chemical family has been discussed. A brief introduction of various fillers of carbon family along with detailed study of carbon nanotubes including their structure, novel properties and synthesization has been discussed. A section of this chapter deals with the study of enhancement in mechanical, electrical, thermal, EMI shielding and other properties with reinforcement of CNTs with literature survey. This chapter also deals with different
formation methods of CNT-polymer nanocomposites. It also deals with key problems faced during their formation. Dispersion and interactions between CNTs and polymers and alignment of CNTs in polymers is an important issue and have been discussed in details in one section. In the last it contains methods to improve dispersion and interaction of CNTs with polymers.

1.12.2. Chapter 2
Chapter 2 deals with the details of experimental techniques used in our study. The methods of formation of CNT used in our study have been discussed. A brief introduction has been given to the various characterization tools used in our studies to investigate CNTs and composites viz scanning electron microscopy (SEM), tunneling electron microscopy (TEM), X-ray diffraction (XRD), Ultraviolet-visible (UV-vis) spectroscopy, Infra red (IR) spectroscopy and thermal analysis (DSC, TGA, DTA). A brief introduction of the instruments used for these characterizations have also been given. A section of this chapter deals with the methods adopted for formation of CNT polymer composites. A precise description is made for determining the properties of the resulting polymer composites viz flexural and tensile properties, electrical and shielding properties. A brief description of the instrumentation used to measure these is also contained in this chapter.

1.12.3. Chapter 3
Chapter 3 contains the results of investigations carried out on the effect on mechanical properties of epoxy with the reinforcement of MWCNT. MWCNTs produced by CVD method are treated with different chemicals to attach various functional groups on its surface. IR spectroscopy and TGA studies has been carried out to confirm the attachment of functional groups. Two different methods direct and solvent casting have been used to disperse same amount of as produced and different types of functionalized MWCNTs in epoxy. UV-vis spectroscopy has been used to optimize the dispersion of MWCNTs in epoxy by both methods. A comparative study has been carried out for the mechanical properties of composites formed by these methods. Also the results obtained
are compared with the results obtained by previous studies. The effect of using two different types of hardeners, amine based and phenol (novalac) based are also discussed.

1.12.4. Chapter 4

Chapter 4 is devoted to the investigations on the electrical and EMI shielding properties of MWCNT reinforced epoxy composites. The effect of aspect ratio of MWCNTs on electrical conductivity and EMI SE of composites has been discussed by using two different aspect ratios of MWCNTs for comparison. A section of this chapter includes a novel way of the calculation of aspect ratio of MWCNTs from the experimental measurements of the electrical conductivity of the composites. The results are also verified experimentally using SEM and TEM studies. A correlation between the electrical conductivity with reflection or absorption components of SE of composites has been drawn and experimentally verified.

1.12.5. Chapter 5

Under normal circumstances it is impossible to properly disperse more than 2-3 % MWCNT in the polymer matrix. A new technique is reported in Chapter 5 where stacking a number of bucky paper laminates of MWCNTs are used for the fabrication of composites with very high loading of MWCNTs upto (50 wt%). SEM and optical microscopy has been carried out to study the morphology of the bucky paper surface. The EMI shielding of 100 dB of such composites, measured in X and Ku band (8-18 GHz), is the highest reported in open literature so far. The reasons are adequately discussed in the chapter.

1.12.6. Chapter 6

Chapter 6 deals with the study of the LDPE-MWCNT composites prepared by using a combination of solvent casting and compression molding scheme. A thorough characterization using TGA, XRD and DSC reveals improved crystallinity and thermal stability of these composites. The electrical and EMI shielding properties of the
composites was also evaluated and a correlation between the electrical conductivity and reflection/absorption components of SE of composites has been verified experimentally.

1.12.7. Chapter 7

Chapter 7 summaries the present work and brings forth the salient features of improved performance of the CNT polymer composites obtained by following these studies. A future course of research work is also projected to carry forward the excitement that CNT reinforced polymer composites has to offer for potential applications.