

A Major Project
on
Studies on Carbon fiber Multiwalled Nanotube Epoxy Hybrid
Composites

*A dissertation Submitted In Partial Fulfillment of the requirements for the award
of degree of*

MASTER OF ENGINEERING
IN
POLYMER TECHNOLOGY

By

Varun Katyal

Under the supervision of

Dr. A.P. Gupta

Professor

Department of Applied Chemistry
Delhi College of Engineering,
University of Delhi



DEPARTMENT OF APPLIED CHEMISTRY

**Delhi College of Engineering New Campus , Bawana Road New Delhi ,
University of Delhi 110042**

CERTIFICATE

It is certified that the work embodied in the thesis entitled “**Studies on Carbon fiber Multiwalled Nanotube Epoxy Hybrid Composites**” is original and has been carried out under my guidance by *Mr. Varun Katyal* at *National Physical Laboratory, New Delhi* in *Carbon Technology Unit*, for the award of the degree of Master of Engineering (Polymer Technology) from **Delhi College of Engineering, University of Delhi**, and has not been submitted, in part or full, for the award of any other degree/diploma to this or any other University. The project work has been carried out during the academic year 2010-2011

Dr A.P .Gupta
Supervisor
Professor
Deptt. of Applied Chemistry
Delhi College of Engineering
University of Delhi
Delhi

Dr R.B. Mathur
Co-supervisor
Scientist G
Carbon Technology Unit
National Physical Laboratory
New Delhi

Dr G.L..Verma
Professor & Head
Deptt of Applied Chemistry
Delhi College of Engineering
University of Delhi
Delhi

ACKNOWLEDGEMENTS

I am especially grateful to my research advisor, Dr. R.B.Mathur, Scientist-G, Carbon Technology Unit, National Physical Laboratory, for the rewarding experience of working with him and for his continuous guidance through my research work. I am thankful to Mr. B.P. Singh, Scientist 'C' for his valuable and continuous guidance during the course of the entire project.

I am sincerely grateful to my internal supervisor Dr A.P. Gupta in the Department of Applied Chemistry, Delhi College of Engineering, University of Delhi for guiding me and helping me in all the related problems before and during the project period from such a long apart.

I pay my sincere thanks to Dr.G.L.Verma Professor and Head Deptt of applied Chemistry , for their kind help .I express appreciation to the faculty members of the Department of Applied Chemistry, Delhi College of Engineering, University of Delhi.

I would like to convey my heartiest thanks to Dr. Shailaja Pande Women Scientist-PI and Dr. S. R. Dhakhate, Scientist E-2, Carbon Technology Unit for their constant support and encouragement.

I gratefully acknowledge Prof. R.C. Budhani, Director NPL and Dr. Rajeev Chopra, Head Division, and Mr. Dharamvir Singh Saini (Tech. Officer) for providing me the opportunity to work in an esteemed organization like Nation Physical Laboratory.

I would like to convey my heartiest and warmth gratitude to Mr. Jagdish, V.K. Chaddah and N.K. Sharma for their valuable help and support throughout my work.

I am sincerely thankful to all the members of my research group Mr. Indresh Pandey Mr. T.K Gupta, Mr. Parveen Garg, and Mr. Gaurav Kumar, for their continuous support, helpful discussions and assistance.

I am thankful to my friends Mr. Parth, Deepak and Ms.Parsanta for their valuable support and encouragement.

My special thanks to Mr. R.K Seth for TGA analysis.

Lastly, I would like to thank the people that made my stay here in N.P.L. an exciting and memorable experience, extending helping hands in all the concerned matters.

Finally, this work is dedicated to my parents. I owe everything of this research work sincerely to their care and affection, without which all this would just have been a dream.

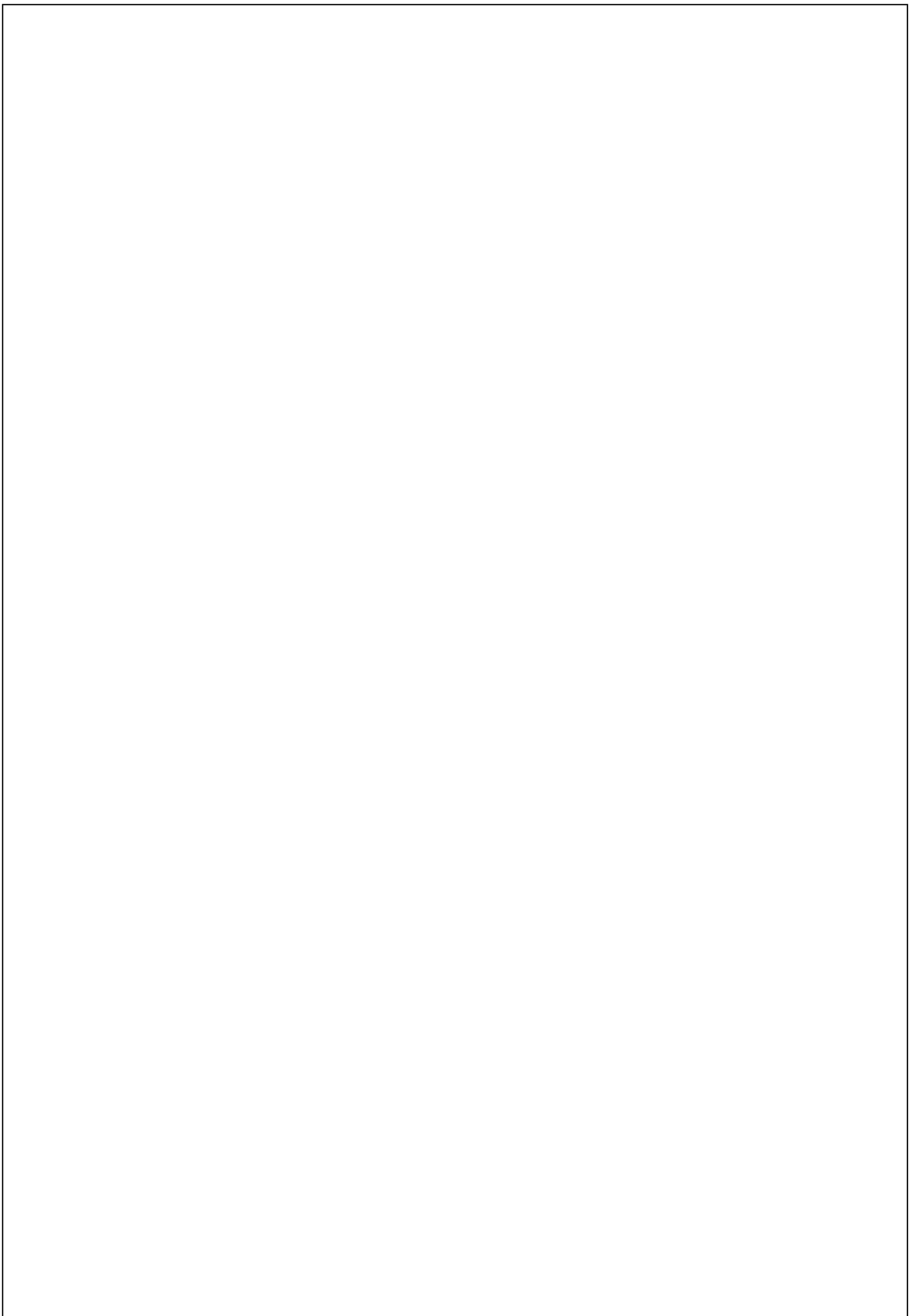
Varun Katyal

CONTENTS

| | |
|--|-------------|
| Abstract | 1 |
| List of figures & Tables | 2 |
| | |
| CHAPTER 1 | 4-50 |
| INTRODUCTION OF CARBON AND ITS ALLOTROPES | |
| | |
| 1.1 Carbon | 4 |
| 1.2 Allotropes of Carbon | 5 |
| 1.3 Fullerene | 8 |
| 1.4 Carbon Nanotubes | 9 |
| 1.4.1 Classification of Carbon Nanotubes | 11 |
| 1.4.1.1. Single Walled Carbon Nanotubes | 11 |
| 1.4.1.2. Multi-walled carbon nanotubes | 12 |
| 1.4.2 Synthesis Techniques of carbon nanotube | 15 |
| 1.4.2.1. Arc discharge | 15 |
| 1.4.2.2. Laser ablation | 15 |
| 1.4.2.3. Chemical vapor deposition (CVD) | 18 |
| 1.4.3. Functionalization and dispersion of carbon nanotubes | 22 |
| 1.4.4. Special properties of carbon nanotubes | 22 |
| 1.4.4.1 Chemical reactivity | 23 |
| 1.4.4.2 Electrical conductivity | 23 |
| 1.4.4.3 Optical activity | 24 |
| 1.4.4.4 Mechanical strength | 25 |
| 1.4.4.5. Strength and Rigidity | 25 |
| 1.4.4.6 Density | 26 |
| 1.4.5 Application of Carbon Nanotubes | 26 |
| 1.4.5.1. Carbon Nanotubes As a Structural Material | 26 |
| 1.4.5.2. Field Effect Transistors | 26 |
| 1.4.5.3. Field Emission Displays | 27 |
| 1.4.5.4. Application in hydrogen storage | 28 |
| 1.4.5.5. In Chemical & biological sensors | 29 |
| 1.4.5.6. In Automotive and aerospace industry | 30 |
| 1.4.5.7 Other Application | 32 |
| 1.5 Carbon Fibers | 32 |
| 1.5.1 Introduction | 33 |
| 1.5.2 History of Carbon Fibers | 34 |
| 1.5.3 Structure and Properties | 35 |
| 1.5.4 Synthesis | 38 |

| | | |
|------------------------------|---|--------------|
| 1.5.5 | Classification of Carbon Fibers | 39 |
| 1.5.6 | Carbon Fiber Reinforced Composites | 41 |
| 1.5.6.1 | Manufacturing Process | 43 |
| 1.5.6.2 | Applications | 45 |
| 1.6 | Epoxy Resin | 45 |
| 1.6.1 | Introduction | 47 |
| 1.6.2 | Applications | 47 |
| 1.6.2.1 | Paints and Coats | 47 |
| 1.6.2.2 | Adhesives | 48 |
| 1.6.2.3 | Industrial Tooling and Composites | 48 |
| 1.6.2.4 | Aerospace Applications | 48 |
| 1.6.2.5 | Electrical and Electronic Systems | 49 |
| 1.6.2.6 | Marine Applications | 49 |
| 1.7 | Composite Materials | 49 |
| | | |
| CHAPTER 2 | | 51-56 |
| LITERATURE REVIEW | | |
| | | |
| CHAPTER 3 | | 57-67 |
| MATERIALS AND METHODS | | |
| | | |
| 3.1. | Materials Used | 57 |
| 3.2. | Chemicals | 57 |
| 3.3. | Method for characterization | 57 |
| 3.3.1. | Scanning Electron Microscope (SEM) | 57 |
| 3.3.2. | Thermal Gravimetric Analysis (TGA) | 58 |
| 3.3.3. | X-Ray Diffraction | 59 |
| 3.3.4. | Resin Casting | 60 |
| 3.4. | Study of properties of MWCNTs-CF epoxy hybrid Composites | 61 |
| 3.4.1 | Mechanical Properties | 61 |
| 3.4.1.1 | Flexural Properties | 62 |
| 3.4.1.2 | Flexural Strength vs. Tensile Strength | 63 |
| 3.4.1.3 | Measuring Flexural Properties | 64 |
| 3.4.1.4 | Hardness | 65 |
| 3.4.2 | Electrical Properties | 66 |
| 3.4.3 | Morphology Study through Electron Scanning Microscope | 67 |

| | |
|--|--------------|
| CHAPTER 4 | 68-70 |
| EXPERIMENTAL | |
| 4.1. Synthesis of MWNTs by CVD method | 68 |
| 4.2 MWCNT-CF-Epoxy Hybrid Composite Fabrication | 70 |
| CHAPTER 5 | 71-83 |
| RESULTS AND DISCUSSION . | |
| 5.1. Characteristic of as grown Carbon Nanotubes | 71 |
| 5.1.1 SEM and TEM | 72 |
| 5.1.2. TGA Analysis | 72 |
| 5.1.3 XRD Analysis | 74 |
| 5.2. Mechanical Properties of Multiwalled Carbon nanotube | 75 |
| Carbon Fiber Epoxy Composites | |
| 5.2.1 Flexural Properties | 75 |
| 5.2.2 Hardness | 76 |
| 5.3 Electrical Properties | 77 |
| 5.3.1 Electrical Conductivity | 78 |
| 5.4 Morphology Study by Scanning Electron Microscope | 79 |
| CHAPTER 6 | 80 |
| CONCLUSIONS | |
| CHAPTER 7 | 81-82 |
| SCOPE FOR FUTURE WORK | |
| REFERENCES | 83-95 |



ABSTRACT

The present investigation was carried out with the objective to synthesize multi-walled carbon nanotubes (MWCNT) by chemical vapor deposition (CVD) technique and to study the use of CNTs and carbon fibers as a reinforcing material to make CNTs/Carbon Fibers reinforced Epoxy hybrid composites for better structural and commercial applications. The objective of the project is to study the effect of both carbon nanotubes and chopped carbon fibers as filler materials on mechanical and electrical properties of the composite material. This included characterization of CNTs and CNT/Carbon Fibers reinforced epoxy composites by techniques such as SEM, TGA and study of characteristic physical properties.

During the course of project MWCNTs were synthesized by CVD process and used as a reinforcing material for the Epoxy. Carbon fiber and MWCNTs were also used as filler in different proportions to bring about the significant improvement in key physical properties. Carbon nanotubes (CNTs) and carbon fibers based epoxy hybrid composites were developed using different percentage of MWCNTs and carbon fibers in epoxy matrix. The hybrid composites of size 70 mm x 12.7mm x 4.5 mm were developed by solvent casting method. Final cured specimens were tested for mechanical and electrical properties. Morphology study was also conducted by Scanning Electron Microscope. Significant improvement in mechanical properties were achieved in 2% MWCNTs and carbon fibers by wt.. Electrical Conductivity also increased considerably compared to neat epoxy. It is observed that effect of carbon nanotubes is more prominent in composite materials.

List of Figures and Tables

Fig.1.1a. Allotropes of Carbon (Carbon family): (a) graphite, (b) diamond, (c) fullerene, C_{60} , (d) single walled carbon nanotube, (e) nanodiamonds

Fig.1.1b Graphite and Diamond

Fig.1.2. A graphene layer folded in to SWNT

Fig.1.3. Multi-walled Nanotube

Fig.1.4. Structure of Single-Walled (SWNT) (a-d) and Multi-Walled (MWNT) carbon NanoTubes (e,f). (a) Shows a schematic of an individual helical SWNT. (b) Shows a cross-sectional view (TEM image) of a bundle of SWNTs [transverse view shown in (d)]. Each nanotube has a diameter of ≈ 1.4 nm and the tube-tube distance in the bundles is 0.315 nm. (c) Shows the high-resolution TEM micrograph of a 1.5 nm diameter SWNT. (e) is the schematic of a MWNT and (f) shows a high resolution TEM image of an individual MWNT. The distance between horizontal fringes (layers of the tube) in (f) is 0.34 nm (close to the interlayer spacing in graphite)

Fig. 1.5. Arc Discharge method

Fig. 1.6. Laser Ablation

Fig.1.7. Schematic diagram of CVD apparatus for vapour phase growth of carbon nanotubes.

Fig.1.8. Chiral Vector configuration in graphene layer

Fig.1.9 A prototype 4.5" field emission display fabricated by Samsung using carbon nanotubes (Image provided by Dr. W. Choi of Samsung Advanced Institute of Technologies)

Fig.1.10 . Temperature-dependent behavior of desorption of hydrogen

Fig.1.11. MWNT array electrode functionalized with DNA/PNA probe as an ultrasensitive sensor.

Fig.1.12 Orientation of fibers in matrix material

Fig.1.13 DGEBA Epoxy resin Molecular structure

Fig.1.14 Triehyltetramine Curing agent Molecular Structure

- Fig.1.15** Ethylene Diphenyl Diamine
- Fig. 3.1.** SEM Instrument used at NPL, New Delhi.
- Fig 3.2** X-Ray Diffractometer
- Fig.3.3.** Instron machine model 4411 at NPL
- Fig.3.4** Beam Under Bending
- Fig.3.5** Shore Schelroscope Hardness Testing Equipment
- Fig.4.1** Schematic diagram of the CVD reactor along with the temperature profile.
- Fig.4.2** Experimental CVD set up at NPL, New Delhi
- Fig. 5.1.** SEM image of as grown MWCNTs synthesized by CVD method
- Fig. 5.2.** TEM image of as grown MWCNTs at lower magnification
- Fig. 5.3** SEM image at lower magnification
- Fig. 5.4** TGA analysis of grown CNTs
- Fig.5.5.** XRD analysis of grown CNTs
- Fig.5.6** Flexural Strength Plot
- Fig.5.7** Flexural Modulus Plot
- Fig.5.8** Shore Schelroscope Hardness Plot
- Fig.5.9** Electrical Conductivity Plot
- Fig.5.10** SEM image of specimen (1% carbon fiber + 1%MWCNT)
- Fig.5.11** SEM image of specimen (1% carbon fiber + 1%MWCNT)
- Fig.5.12** SEM image of specimen at higher magnification (1% carbon fiber + 1%MWCNT)
- Fig.5.13** SEM image of specimen (2% carbon fiber + 2%MWCNT)
- Fig.5.14** SEM image of specimen (2% carbon fiber + 2%MWCNT)
- Fig.5.15** SEM image at of specimen higher magnification (2% carbon fiber + 2%MWCNT)
- Fig.5.16** SEM image of specimen(4% carbon fiber)
- Fig.5.17** SEM image(4 % carbon fiber)
- Fig.5.18** SEM image at lower magnification(4% carbon fiber)

Chapter 1

Introduction of Carbon and its Allotropes

1.1 Carbon

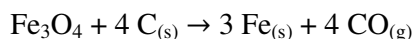
Carbon is the chemical element with symbol **C** and atomic number 6. As a member of group 14 on the periodic table, it is nonmetallic and tetravalent—making four electrons available to form covalent chemical bonds. There are three naturally occurring isotopes, with ^{12}C and ^{13}C being stable, while ^{14}C is radioactive, decaying with a half-life of about 5730 years.^{[1][2][3]}

There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon.^[12] The physical properties of carbon vary widely with the allotropic form. For example, diamond is highly transparent, while graphite is opaque and black. Diamond is among the hardest materials known, while graphite is soft enough to form a streak on paper (hence its name, from the Greek word "to write"). Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions but graphite is the most thermodynamically stable.

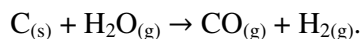
The different forms or *allotropes* of carbon (see below) include the hardest naturally occurring substance, diamond, and also one of the softest known substances, graphite. Moreover, it has an affinity for bonding with other small atoms, including other carbon atoms, and is capable of forming multiple stable covalent bonds with such atoms. As a result, carbon is known to form almost ten million different compounds; the large majority of all chemical compounds.^[4] Carbon also has the highest melting and sublimation point of all elements. At atmospheric pressure it has no melting point as its triple point is at 10.8 ± 0.2 MPa and 4600 ± 300 K,^{[2][3]} so it sublimates at about 3900 K.^{[5][6]}

Carbon sublimates in a carbon arc which has a temperature of about 5800 K. Thus, irrespective of its allotropic form, carbon remains solid at higher temperatures than the highest melting point metals such as tungsten or rhenium. Although thermodynamically prone to oxidation, carbon resists oxidation more effectively than elements such as iron and copper that are weaker reducing agents at room temperature.

Carbon compounds form the basis of all known life on Earth, and the carbon-nitrogen cycle provides some of the energy produced by the Sun and other stars. Although it forms an extraordinary variety of compounds, most forms of carbon are comparatively unreactive under normal conditions. At standard temperature and pressure, it resists all but the strongest oxidizers. It does not react with sulfuric acid, hydrochloric acid, chlorine or any alkalis. At elevated temperatures carbon reacts with oxygen to form carbon oxides, and will reduce such metal oxides as iron oxide to the metal. This exothermic reaction is used in the iron and steel industry to control the carbon content of steel:



with sulfur to form carbon disulfide and with steam in the coal-gas reaction:



Carbon combines with some metals at high temperatures to form metallic carbides, such as the iron carbide cementite in steel, and tungsten carbide, widely used as an abrasive and for making hard tips for cutting tools.

As of 2009, graphene appears to be the strongest material ever tested.^[7] However, the process of separating it from graphite will require some technological development before it is economical enough to be used in industrial processes.^[8]

1.2 Allotropes of Carbon

Atomic carbon is a very short-lived species and, therefore, carbon is stabilized in various multi-atomic structures with different molecular configurations called allotropes. The three relatively well-known allotropes of carbon are amorphous

carbon, graphite, and diamond. Once considered exotic, fullerenes are nowadays commonly synthesized and used in research; they include buckyballs,^{[9][10]} carbon nanotubes,^[11] carbon nanobuds^[12] and nanofibers.^{[13][14]} Several other exotic allotropes have also been discovered, such as lonsdaleite,^[15] glassy carbon,^[16] carbon nanofoam^[17] and linear acetylenic carbon.^[18]

The amorphous form is an assortment of carbon atoms in a non-crystalline, irregular, glassy state, which is essentially graphite but not held in a crystalline macrostructure.

It is present as a powder, and is the main constituent of substances such as charcoal, lampblack (soot) and activated carbon. At normal pressures carbon takes the form of graphite, in which each atom is bonded trigonally to three others in a plane composed of fused hexagonal rings, just like those in aromatic hydrocarbons.^[19] The resulting network is 2-dimensional, and the resulting flat sheets are stacked and loosely bonded through weak van der Waals forces. This gives graphite its softness and its cleaving properties (the sheets slip easily past one another). Because of the delocalization of one of the outer electrons of each atom to form a π -cloud, graphite conducts electricity, but only in the plane of each covalently bonded sheet. This results in a lower bulk electrical conductivity for carbon than for most metals. The delocalization also accounts for the energetic stability of graphite over diamond at room temperature.

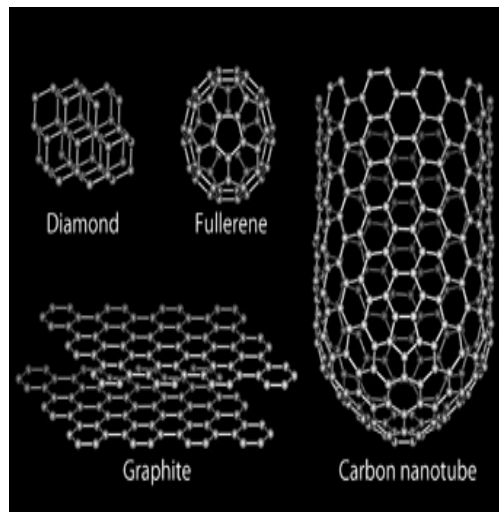


Figure 1.1a Allotropes of carbon



Fig.1.1b Graphite and Diamond

Some allotropes of carbon: a) diamond; b) graphite; c) lonsdaleite; d–f) fullerenes (C_{60} , C_{540} , C_{70}); g) amorphous carbon; h) carbon nanotube.

At very high pressures carbon forms the more compact allotrope diamond, having nearly twice the density of graphite. Here, each atom is bonded tetrahedrally to four others, thus making a 3-dimensional network of puckered six-membered rings of atoms.

Diamond has the same cubic structure as silicon and germanium and because of the strength of the carbon-carbon bonds, it is the hardest naturally occurring substance in terms of resistance to scratching. Contrary to the popular belief that "*diamonds are forever*", they are in fact thermodynamically unstable under normal conditions and transform into graphite.^[20] But due to a high activation energy barrier, the transition into graphite is so extremely slow at room temperature as to be unnoticeable. Under some conditions, carbon crystallizes as lonsdaleite. This form has a hexagonal crystal lattice where all atoms are covalently bonded. Therefore, all properties of lonsdaleite are close to those of diamond.^[15]

Fullerenes have a graphite-like structure, but instead of purely hexagonal packing, they also contain pentagons (or even heptagons) of carbon atoms, which bend the sheet into spheres, ellipses or cylinders. The properties of fullerenes (split into buckyballs, buckytubes and nanobuds) have not yet been fully analyzed and represent an intense area of research in nanomaterials. The names "*fullerene*" and "*buckyball*" are given after Richard Buckminster Fuller, popularizer of geodesic domes, which resemble the structure of fullerenes.

The buckyballs are fairly large molecules formed completely of carbon bonded trigonally, forming spheroids (the best-known and simplest is the soccerball-shaped structure C_{60} buckminsterfullerene).^[9] Carbon nanotubes are structurally similar to buckyballs, except that each atom is bonded trigonally in a curved sheet that forms a hollow cylinder.^{[10][11]} Nanobuds were first published in 2007 and are hybrid bucky

tube/buckyball materials (buckyballs are covalently bonded to the outer wall of a nanotube) that combine the properties of both in a single structure.^[12]

Of the other discovered allotropes, carbon nanofoam is a ferromagnetic allotrope discovered in 1997. It consists of a low-density cluster-assembly of carbon atoms strung together in a loose three-dimensional web, in which the atoms are bonded trigonally in six- and seven-membered rings. It is among the lightest known solids, with a density of about 2 kg/m^3 .^[22] Similarly, glassy carbon contains a high proportion of closed porosity.^[16] But unlike normal graphite, the graphitic layers are not stacked like pages in a book, but have a more random arrangement. Linear acetylenic carbon^[18] has the chemical structure. Carbon in this modification is linear with *sp* orbital hybridization, and is a polymer with alternating single and triple bonds. This type of carbyne is of considerable interest to nanotechnology as its Young's modulus is forty times that of the hardest known material – diamond.^[22]

1.3 Fullerenes

A **fullerene** is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are also called **buckyballs**, Cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.^[23]

The first fullerene to be discovered, and the family's namesake, buckminsterfullerene (C_{60}), was prepared in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University. The name was an homage to Buckminster Fuller, whose geodesic domes it resembles. The structure was also identified some five years earlier by Sumio Iijima, from an electron microscope image, where it formed the core of a "bucky onion."^[24] Fullerenes have since been found to occur in nature.^[25]

The discovery of fullerenes greatly expanded the number of known carbon allotropes, which until recently were limited to graphite, diamond, and amorphous

carbon such as soot and charcoal. Buckyballs and buckytubes have been the subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology.

In mass spectrometry, discrete peaks appeared corresponding to molecules with exact mass of sixty or seventy or more carbon atoms. In 1985, Harold Kroto (then of the University of Sussex), James R. Heath, Sean O'Brien, Robert Curl and Richard Smalley, from Rice University, discovered C_{60} , and shortly thereafter came to discover the fullerenes.^[26] Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry for their roles in the discovery of this class of molecules. C_{60} and other fullerenes were later noticed occurring outside the laboratory (e.g., in normal candle soot). By 1991, it was relatively easy to produce gram-sized samples of fullerene powder using the techniques of Donald Huffman and Wolfgang Krätschmer. Fullerene purification remains a challenge to chemists and to a large extent determines fullerene prices. So-called endohedral fullerenes have ions or small molecules incorporated inside the cage atoms. Fullerene is an unusual reactant in many organic reactions such as the Bingel reaction discovered in 1993. Carbon nanotubes were recognized in 1991.^[27]

1.4 Carbon nanotubes

The discovery of fullerenes [33] provided exciting insights into carbon nanostructures and how architectures built from *sp*² carbon units based on simple geometrical principles can result in new symmetries and structures that have fascinating and useful properties. Carbon nanotubes represent the most striking example. About a decade after their discovery [34], the new knowledge available in this field indicates that nanotubes may be used in a number of practical applications. There have been great improvements in synthesis techniques, which can now produce reasonably pure nanotubes in gram quantities.

Studies of structure–topology–property relations in nanotubes have been strongly supported, and in some cases preceded, by theoretical modeling that has provided insights for experimentalists into new directions and has assisted the rapid expansion of this field [35,36,37,38,39,40]

Quasi-one-dimensional carbon whiskers or nanotubes are perfectly straight tubules with diameters of nanometer size, and properties close to that of an ideal graphite fiber. Carbon nanotubes were discovered accidentally by Sumio *Iijima* in 1991, while studying the surfaces of graphite electrodes used in an electric arc discharge [34].

Carbon nanotubes (CNTs); also known as (bucky tubes) are allotropes of carbon with a cylindrical nanostructure. Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure and they are nanometer in diameter and several millimeters in length. Carbon nanotubes have many structures ,differing in length ,thickness and in the type of helicity and no of layers . Their length -to- diameter ratio is upto 132000000:1.

Carbon nanotubes were discovered accidentally [28] while studying the surfaces of graphite electrodes used in an electric arc discharge [29]. Discovery of carbon nanotubes (CNTs) has the potential of revolutionizing the biomedical research as they can show superior performance because of their impressive structural, mechanical, and electronic properties such as small size and mass, high strength, higher electrical and thermal conductivity, etc. [29,30].

Blood compatibility is an important property for most of the biomedical devices to render their intended functions in vivo. The lack of blood compatibility results in adsorption of plasma proteins, platelet adhesion, and activation, triggering the coagulation and complement cascade and clot formation often leading to device failure [31].It is interesting to note that among the currently available delivery systems, which include liposome's, emulsions, polymers and micro particles, CNTs have recently gained popularity as potential drug carriers, therapeutic agents and for applications in diagnosis [32].

1.4.1 Classification of Carbon Nanotubes

There are two types of Carbon Nanotubes

- **Single Walled Carbon Nanotubes**
- **Multiwalled Carbon Nanotubes**

1.4.1.1. Single Walled Carbon Nanotubes

Among the nanotubes, two varieties, which differ in the arrangement of their grapheme cylinders,. Multi-Walled NanoTubes (MWNT), are collections of several concentric graphene cylinders and are larger structures compared to Single-Walled NanoTubes (SWNTs) which are individual cylinders of 1–2 nm diameter The former can be considered as a mesoscale graphite system, whereas the latter is truly a single large molecule. However, SWNTs also show a strong tendency to bundle up into ropes, consisting of aggregates of several tens of individual tubes organized into a one-dimensional triangular lattice.

Single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many millions of times longer. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n, m) called the chiral vector. SWNTs have only one layer of graphene sheet with diameters of 0.7 to 10 nm (Figure.1.3).

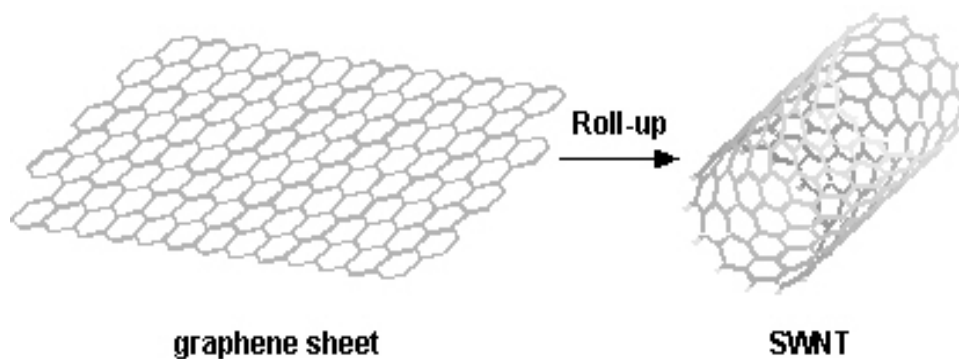


Fig.1.2. A graphene layer folded in to SWNT

Minimum diameter of SWNTs is 0.4 nm and maximum diameter is 2.5 nm and suitable energetic compromise for diameter is 1.2 to 1.4 nm and length up to micrometers or even millimetres. SWNT is the unique example of high aspect ratio.

SWNTs are fundamentally more interesting and unique in electrical, mechanical and optical properties. Single-walled nanotubes are a very important variety of carbon nanotube because they exhibit important electric properties that are not shared by the multi-walled carbon nanotube (MWNT) variants.

In particular, their band gap can vary from zero to about 2eV and their electrical conductivity can show metallic or semiconducting behavior, whereas MWNTs are zero-gap metals. Single-walled nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale currently used in electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors.[41,42]

On the basis of rolling the SWNTs are three types:

There are three different types of SWNTs because the graphite sheet can be rolled in different ways.

- (1) Armchair
- (2) Zigzag
- (3) Chiral

1.4.1.2. Multi-walled carbon nanotubes

Multi-walled nanotubes (MWNT) 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.

In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders, e.g. a (0, 8) single-walled nanotube (SWNT) within a larger (0, 10) single-walled nanotube (SWNT).

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 MWNTs there is no three dimensional ordering between the individual graphite layers, suggesting that the internal layer structure is rotationally disordered.

The aspect ratios of MWNTs are usually smaller than that from SWNTs because diameter is of MWNTs are greater than SWNTs.

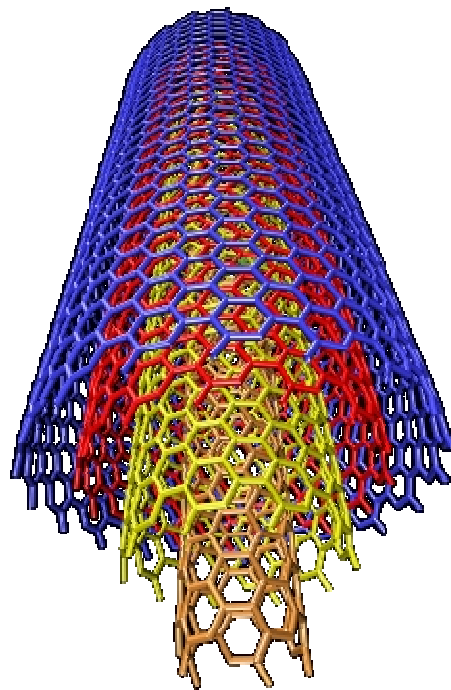


Fig. 1.3. Multiwalled carbon nanotubes

The aspect ratios of nanotubes are varying with diameter but the average length can be several micrometers. Individual SWNTs have uniform diameter, although when they formed they also show a strong tendency to pack together in large bundles [18]. In fact, the packing occurs in a regular triangular lattice structure with an inter-tube spacing in each of the bundles that corresponds to about 0.315 nm and a lattice parameter of 1.7 nm.

The special place of double-walled carbon nanotubes (DWNT) must be emphasized here because they combine very similar morphology and properties as

compared to SWNT, while improving significantly their resistance to chemicals. This is especially important when Functionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, 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 DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 [19] by the catalytic CVD technique, from the selective reduction of oxides solid solutions in methane and hydrogen.

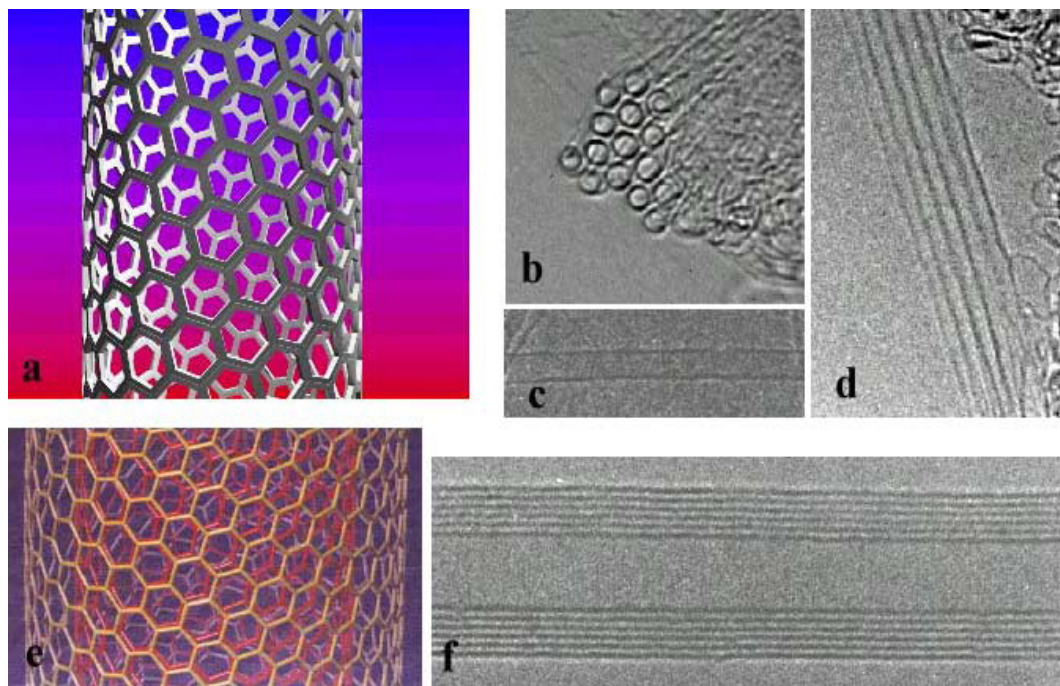


Fig. 1.4. Structure of Single-Walled (SWNT) (a-d) and Multi-Walled (MWNT) carbon NanoTubes (e,f). (a) Shows a schematic of an individual helical SWNT. (b) Shows a cross-sectional view (TEM image) of a bundle of SWNTs [transverse view shown in (d)]. Each nanotube has a diameter of 1.4 nm and the tube-tube distance in the bundles is 0.315 nm. (c) Shows the high-resolution TEM micrograph of a 1.5 nm diameter SWNT. (e) is the schematic of a MWNT and (f) shows a high resolution TEM image of an individual MWNT. The distance between horizontal fringes (layers of the tube) in (f) is 0.34 nm (close to the interlayer spacing in graphite) [43]

1.4.2 Synthesis techniques of Carbon Nanotubes

Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HIPCO), and chemical vapor deposition (CVD). Although carbon nanotube synthesis can occur naturally through flame synthesis most of these processes take place in vacuum or with process gases. CVD growth of CNTs can occur in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

1.4.2.1. Arc discharge

Nanotubes were observed in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps, that was intended to produce fullerenes.[44] However the first macroscopic production of carbon nanotubes was made in 1992 by two researchers at NEC's Fundamental Research Laboratory. [45] The method used was the same as in 1991. During this process, the carbon contained in the negative electrode sublimates because of the high discharge temperatures. Because nanotubes were initially discovered using this technique, it has been the most widely-used method of nanotube synthesis. The yield for this method is up to 30 percent by weight and it produces both single- and multi-walled nanotubes with lengths of up to 50 micrometers with few structural defects. [46].

1.4.2.2 Laser ablation

Laser ablation is the process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates. At high laser flux, the material is typically converted to a plasma. Usually, laser ablation refers to removing material with a pulsed laser, but it is possible to ablate material with a continuous wave laser beam if the laser intensity is high enough.

The depth over which the laser energy is absorbed, and thus the amount of material removed by a single laser pulse, depends on the material's optical properties

and the laser wavelength. Laser pulses can vary over a very wide range of duration (milliseconds to femtoseconds) and fluxes, and can be precisely controlled. This makes laser ablation very valuable for both research and industrial applications.

In the laser ablation process, a pulsed laser vaporizes a graphite target in a high-temperature reactor while an inert gas is bled into the chamber. Nanotubes develop on the cooler surfaces of the reactor as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes. This process was developed by Dr. Richard Smalley and co-workers at Rice University, who at the time of the discovery of carbon nanotubes, were blasting metals with a laser to produce various metal molecules. When they heard of the existence of nanotubes they replaced the metals with graphite to create multi-walled carbon nanotubes.[55] Later that year the team used a composite of graphite and metal catalyst particles (the best yield was from a cobalt and nickel mixture) to synthesize single-walled carbon nanotubes.[56]. The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition.^[46]

Fig. 5 shows the setup of the laser furnace, which consists of a furnace, a quartz tube with a window, a target carbon composite doped with catalytic metals, a water-cooled trap, and flow systems for the buffer gas to maintain constant pressures and flow rates. A laser beam (typically a Argon or CO₂ laser) is introduced through the window and focused onto the target located in the center of the furnace. The target is vaporized in high-temperature Argon buffer gas and forms SWNTs. The Argon flow rate and the pressure are typically 1 cm³•s⁻¹ and 500 torr, respectively. The SWNTs produced are conveyed by the buffer gas to the trap, where they are collected. The vaporization surface is kept as fresh as the possible by changing the focus point or moving the target.

The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the

reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition.

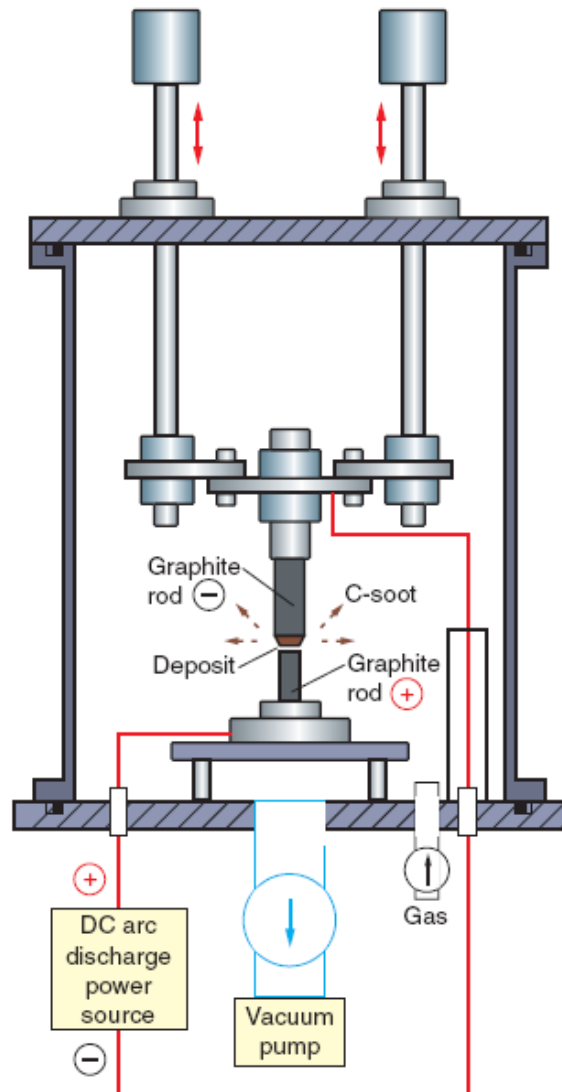


Figure 1.5 Arc discharge Process

- Fullerenes deposited as soot
- SWNT in soot if anode contains metal catalyst (Fe, Co, Ni-Co, etc.)
- MWNT deposited on cathode under hydrogen gas (0.34 nm layer spacing)

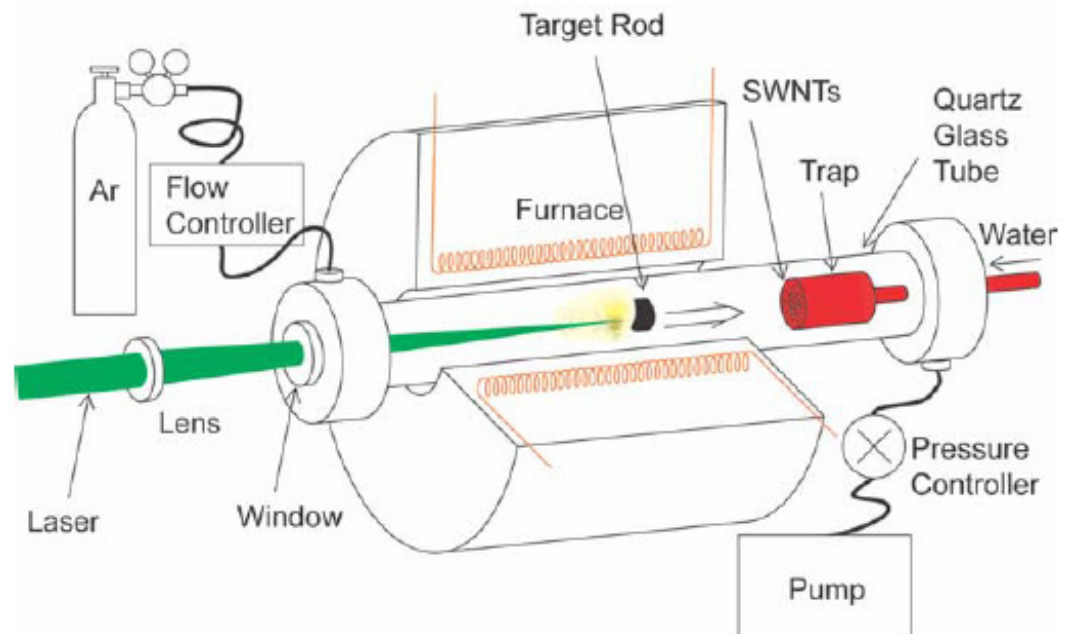


Figure 1.6 Laser Ablation Method

1.4.2.3. Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

The catalytic vapor phase deposition of carbon was first reported in 1959.[26] but it was not until 1993 [47] that carbon nanotubes were formed by this process. In 2007, researchers at the University of Cincinnati (UC) developed a process to grow aligned carbon nanotube arrays of 18 mm length on a First Nano ET3000 carbon nanotube growth system.[48]

During CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt,[49], iron, or a combination[50]. 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 ammonia, nitrogen or hydrogen) and a carbon-containing gas (such as 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 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

.It is a heterogeneous catalysis process. In this method, we can get the high purity carbon nanotubes. It is based on thermal decomposition of hydrocarbons in the presence of catalysts at high temperature of 650-900⁰C in the reactor furnace (Figure.1.6).

Synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The energy source is used to “crack” the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained.

Excellent alignment [51], as well as positional control on nanometre scale [52], can be achieved by using CVD. Compared to arc discharge, 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 appropriate metal catalyst can preferentially grow single rather than multi-walled nanotubes[53].

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. Ammonia may be used as the etchant.[54] Typical yields for CVD are approximately 30%.

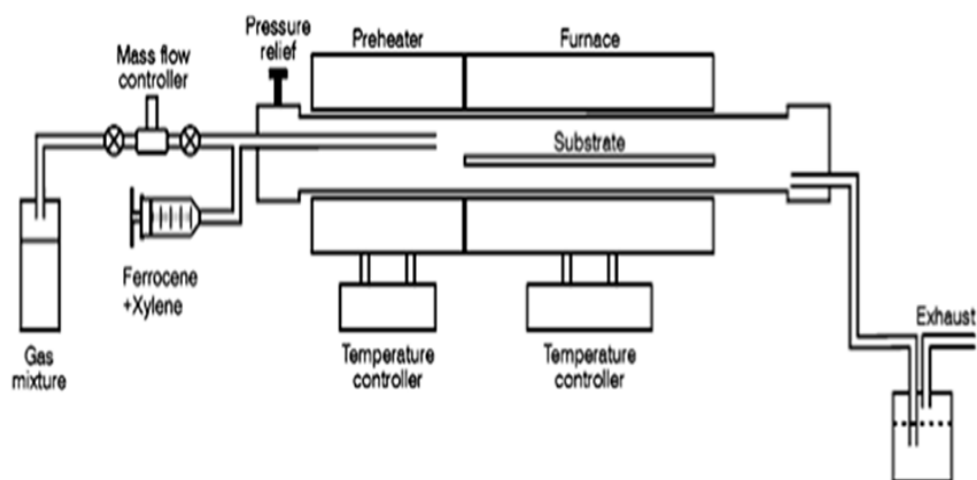


Fig.1.7. Schematic diagram of CVD apparatus for vapour phase growth of carbon nanotubes.

Of the various means for nanotube synthesis, CVD shows the most promise for industrial-scale deposition, because of its price/unit ratio, and because CVD is capable of growing nanotubes directly on a desired substrate, whereas the nanotubes must be collected in the other growth techniques. The growth sites are controllable by careful deposition of the catalyst.

| Methods | Arc discharge Method | CVD Method | Laser ablation Method |
|---------------|---|--|--|
| Who | Ebbesen and Ajayan, NEC, Japan 1992 | Endo, Shinshu University, Nagano, Japan | Smalley, Rice, 1995 |
| How | Connect two graphite rods to a power supply, place them a few mm apart, and throw the switch. At 100 amps, carbon vaporises and forms hot plasma. | Place substrate in oven, heat to 600 ^o C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of CNTs. | Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the CNTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs. |
| Typical yield | | | |
| SWNT | 30 to 90% | 20 to 100 % | Up to 70% |
| MWNT | Short tubes with diameters of 0.6 - 1.4 nm. | Long tubes with diameters ranging from 0.6-4 nm. | Long bundles of tubes (5-20 microns), with individual diameter from 1-2 nm. |
| Properties | Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm. | Long tubes with diameter ranging from 10-240 nm. | Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible. |
| Conclusion | Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible. | Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure. | Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure. |

Table.1.1: A summary of the major production methods and their efficiency

1.4.3 Functionalization and dispersion of carbon nanotubes

CNTs in all their forms are difficult to disperse and dissolve in any organic and aqueous medium. Due to the strong attractive long-ranged van der Waals interaction, nanotubes tend to aggregate and form bundles or ropes, usually with highly entangled network structures. This attraction is fundamental for many body particles and well known for colloids dispersed in polymers. When suspended in a polymer, an attractive force between fillers also arises due to the entropic effects. Polymer chains in the region of the colloidal filler suffer an entropic penalty since roughly half of their configurations are precluded. Therefore, there is a depletion of the polymer in this region, resulting in an osmotic pressure forcing the filler particles to come together. Homogeneous dispersion of CNTs within a supporting medium is crucial for the fabrication of composites with improved properties, well defined and uniform structures. This issue stimulates intensive studies on the exfoliation of carbon nanotubes.

Dispersion broadly falls into two main categories: mechanical/physical and chemical methods. The mechanical techniques involve physically separating the tubes from each other. The chemical methods often use surfactant or chemical treatment of the tube surface. However, certain types of aggressive chemical treatment can lead to the key nanotube properties being compromised. In general, the functionalization of CNTs requires chemical modifications of their surface supported by the mechanical agitation methods such as ultrasonication and shear mixing. Several functionalization strategies have been reported recently. They are mainly based on the covalent (“grafting-to” and “grafting-from”) [and noncovalent (polymer wrapping[57-60], pi-pi stacking interaction adsorption of surfactants coupling of surfactants and functionalities to CNTs.

1.4.4 Special properties of carbon nanotubes

Electronic, molecular and structural properties of carbon nanotubes are determined to a large extent by their nearly one dimensional structure. The most important properties of CNTs and their molecular background are stated below.

1.4.4.1 Chemical reactivity:

The chemical reactivity of a CNT is, compared with a graphene sheet, enhanced as a direct result of the curvature of the CNT surface. 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 behaviour is difficult as the crude nanotube samples are still not pure enough.[61]

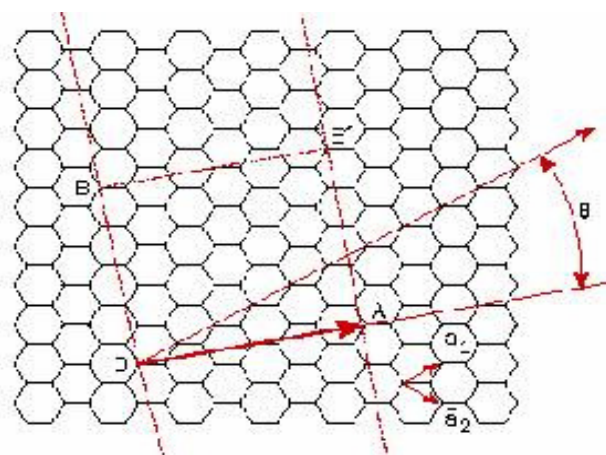


Figure 1.8 : Vector OA is called the chiral vector. It can be defined by the vector $C_h = na_1 + ma_2$ with the zigzag axis. Vectors a_1 and a_2 are the lattice vectors.⁵

1.4.4.2 Electrical conductivity

It is generated when a graphene sheet of a certain size that is wrapped in a certain direction. As the result is cylinder symmetric we can only roll in a discrete set of directions in order to form a closed cylinder. (Figure 1-2). Two atoms in the graphene sheet are chosen, one of which serves the role as origin. The sheet is rolled until the two atoms coincide. The vector pointing from the first atom towards the other is called the chiral vector and its length is equal to the circumference of the

nanotube. The direction of the nanotube axis is perpendicular to the chiral vector. (n,m) are pair of indices.[62]

Depending on their chiral vector, carbon nanotubes with a small diameter are either semi-conducting or metallic. 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 differences in conductivity can easily be derived from the graphene sheet properties. Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n,m) nanotube, if $n = m$, the nanotube is metallic; if $n = 3m$ then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate . Thus all armchair $(n = m)$ nanotubes are metallic, and nanotubes etc. are semiconducting.[63]

However, this rule has exceptions, because curvature effects in small diameter carbon nanotubes can influence strongly electrical properties. Thus, $(5,0)$ SWCNT that should be semiconducting is in fact metallic according to the calculations. And *vice versa*, zigzag and chiral SWCNTs with small diameters that should be metallic have finite gap (armchair nanotubes remain metallic). In theory, metallic nanotubes can carry an electrical current density of 4×10^9 A/cm² which is more than 1,000 times greater than metals such as copper.

Multiwalled carbon nanotubes with interconnected inner shells show superconductivity with a relatively high transition temperature $T_c = 12$ K. In contrast, the T_c value is an order of magnitude lower for ropes of single-walled carbon nanotubes or for MWNTs with usual, non-interconnected shells. The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotube length.[9] For more, general information on electron conductivity is referred to a review by Ajayan and Ebbesen[64]

1.4.4.3 Optical activity:

Theoretical studies have revealed that the optical activity of chiral nanotubes disappears if the nanotubes become larger [11]. Therefore, it is expected that other

physical properties are influenced by these parameters too. Use of the optical activity might result in optical devices in which CNTs play an important role.[65]

1.4.4.4 Mechanical strength:

Carbon nanotubes have a very large Young modulus in their axial direction. The nanotube as a whole is very flexible because of the great length. Therefore, these compounds are potentially suitable for applications in composite materials that need anisotropic properties.

1.4.4.5 Strength and Rigidity:

Strength and rigidity (stiffness) of nanotubes were also seen in the aligning experiment that evolved the cutting of a phenolic and epoxy nanotubes composite. The fact the tube could not break during the cutting and alignment suggests that the strength is much higher than the shear strength of the phenolic and epoxy tube interface. The fracture and deformation modes of nanotubes are intriguing. Fracture can occur in a nanotube via collapse of the hollow, providing extra absorption of energy and increased toughness in a composite. The high value of Young's modulus also suggests that the nanotubes have high bending moment. Deformation experiments, however, suggest that bending in nanotubes depends on various parameters, such as the size of the hollow interior, nanotube wall thickness and tube size. Simulations have suggested the most interesting deformation behaviour in nanotubes (Figure.1.9). Highly deformed nanotubes were seen to reversibly switch into different morphological patterns with abrupt release of energy.

Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa).[66]

Although the strength of individual CNT shells is extremely high, weak shear interactions between adjacent shells and tubes leads to significant reductions in the effective strength of multi-walled carbon nanotubes and carbon nanotube bundles down to only a few GPa's[67]This limitation has been recently addressed by applying high energy electron irradiation which cross links inner shells and tubes and

effectively increases the strength of these materials to ~60 GPa for multi-walled carbon nanotubes^[68] and ~17 GPa for double-walled carbon nanotube bundles^[69].

1.4.4.6 Density:

The hollow structure of nanotubes makes them very light (density varies from ~ 0.8 gcm⁻³ for SWNTs up to 1.8 gcm⁻³ for MWNTs, compared to 2.26 gcm⁻³ for graphite) and this is very useful for a variety of light weight applications from composites to fuel cells. Specific strength (strength/density) is important in the design of structural materials; nanotubes have this value at least 2 orders of magnitudes greater than steel. Traditional carbon fibers have specific strength 40 times that of steel.

1.4.5 Application of Carbon Nanotubes

1.4.5.1 CNT as Structural Material

CNT in concrete increase its tensile strength, and halt crack propagation.^[3] Thin layers of buckypaper can significantly improve fire resistance due to the efficient reflection of heat by the dense, compact layer of CNT or carbon fibers.^[6]

1.4.5.2. Field Effect Transistors

Carbon nanotubes are a new form of carbon with unique electrical and mechanical properties. Varying the diameter of the cylinder can control the band gap of semiconducting nanotubes. The width of the diameter of the nanotube is inversely proportional to the size of the band gap. Semiconducting nanotubes can be used to build molecular field-effect transistors (FETs) while metallic nanotubes can be used to build single-electron transistors. Single wall carbon nanotube transistors are electronic devices based on a single rolled-up sheet of carbon atoms. When the first SWNT transistors were formed, they could not operate at room temperature. However, recent research has developed SWNT transistors that do operate at room temperature. Early nanotube FETs used a non-local back-gate with the nanotube side-bonded to noble metal electrodes. This setup gave large contact resistance and poor characteristics. The recent CNFETs are now built with top-gate geometry and

resemble more conventional silicon CMOS devices. Figure shows the layout of the carbon nanotube transistor along with its I-V characteristics. The SWNT transistors consist of a semiconducting carbon nanotube about 1 nm in diameter bridging two closely separated metal electrodes a top a silicon surface coated with SiO₂. Applying an electric field to the silicon via the gate electrode turns on and off the flow of the current across the nanotube by controlling the movement of charge carriers onto it.

1.4.5.3. Field Emission Displays

The unusual properties of nanotubes make them likely candidates for next-generation display devices. The idea of a Field Emission Device (FED) is to add a high electric field to a wire in order to produce electrons. The efficiency of generating electrons is dependent on the strength of the electric field, and the geometry of the wire. The field amplification increases with a higher electric field and sharper radius. Samsung has been developing a Field-Emission flat display, and has demonstrated a prototype of a 9-inch full color display (576 x 242 pixels) in 1999. The structure of a SWNT based flat panel display is shown in Figure 1.12. Prototype matrix-addressable diode flat panel displays have been fabricated using carbon nanotubes as the electron emission source [96].

One demonstration (demo) structure constructed at North western University consists of nanotube-epoxy stripes on the cathode glass plate and phosphor-coated Indium-Tin-Oxide (ITO) stripes on the anode plate [96]. Each pixel in this device is primarily composed of two glasses: an anode glass, which is coated with a layer of indium-tin-oxide (ITO) phosphor, and a cathode glass that is coated with SWNT. The role of the SWNT in this device is to generate an electron source. Assembling these pixels into a matrix creates the flat panel display. Using the plasma-enhanced or conventional CVD on top of substrates prepatterned with transitional metal catalysts yielded highly aligned arrays of carbon nanotubes growing vertically to the surface of the substrate. This device is only 2.4 mm in depth, has a brightness of 1800 cd/m², and has a low power consumption (3.7 V)

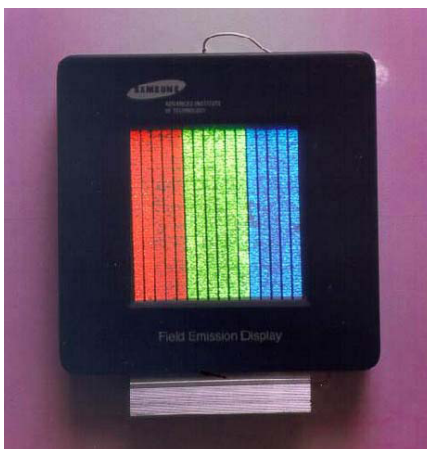


Fig.1.9 A prototype 4.5" field emission display fabricated by Samsung using carbon nanotubes (Image provided by Dr. W. Choi of Samsung Advanced Institute of Technologies)

1.4.5.4. Application in hydrogen storage

Hydrogen storage describes the methods for storing H₂ for subsequent use. The methods span many approaches, including high pressures, cryogenics, and chemical compounds that reversibly release H₂ upon heating. Hydrogen storage is a topical goal in the development of a hydrogen economy. Most research into hydrogen storage is focused on storing hydrogen as a lightweight, compact energy carrier for mobile applications.

CNT have been long heralded as potentially useful for hydrogen storage; for fuel cells that power electric vehicles or laptop computers. Hydrogen is important fuel mainly in three applications: In nickel-hydride battery, in which hydrogen is combined as a metal hydride; in spark ignition engine powered car; and in a fuel cell.

Hydrogen can be converted to electricity with emission of only water with very high efficiency. The most significant news come from the world wide vehicle corporations such as Ford, GM, Toyota, Hondo, etc., that the development of proton exchange membrane fuel cell electric vehicles has made great progress. For conventional porous carbon, the hydrogen uptake is proportional to its surface area and pore volume. However, high hydrogen adsorption capacity can be only obtained at very low temperature. In contrast, in spite of its relatively small surface are and

pore volume, CNT show surprising high hydrogen storage capacity that embarked scientist great interest on this aspect.

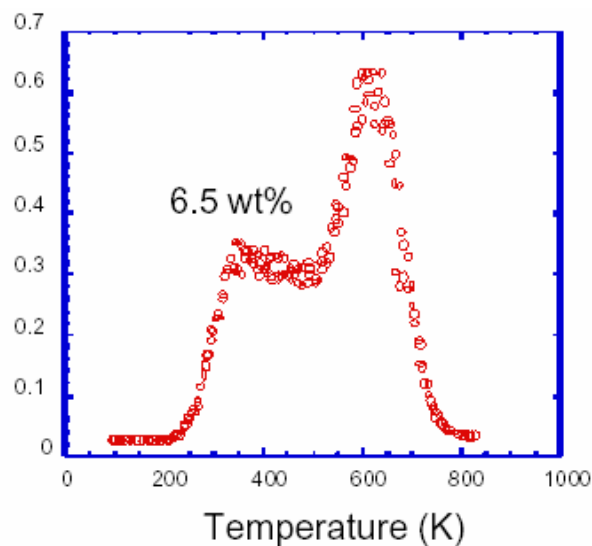


Fig.1.10 Temperature-dependent behaviour of desorption of hydrogen

1.4.5.5. In Chemical & biological sensors

The high surface area, small size, hollow geometry and chemical inertness are the remarkable properties of CNTs that makes them attractive for demanding applications in the field of sensing. Many studies on possible applications of CNTs have been focused either on individual single-walled CNTs as sensitive materials toward O₂, NO₂, and NH₃ or on MWNT mats as NH₃, CO, CO₂ humidity, and O₂ gas sensors.

Nanotube sensors offer significant advantages over conventional metal oxide-based electrical sensor materials in terms of sensitivity and small sizes needed for miniaturization and construction of massive sensor arrays. Nevertheless, it also was found that nanotubes are not sensitive to many types of molecules (i.e. CO, H₂, HCl), indicating an apparent lack of specific interactions between nanotube and these molecules. So, based on the valuable platform of carbon nanotubes, the functionalized CNTs with macromolecules or polymers offer further scope for improving the sensor performance.

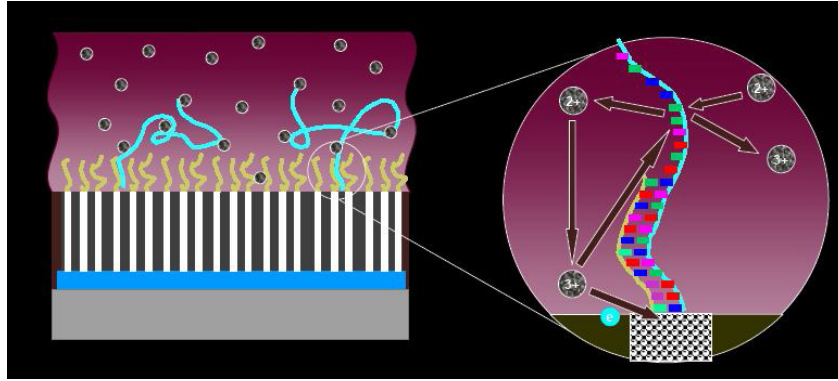


Fig.1.11. MWNT array electrode functionalized with DNA probe as an ultrasensitive sensor. [97]

1.4.5.6. In Automotive and aerospace industry

Carbon fibre is already used to strengthen a wide range of materials, and the special properties of carbon nanotubes mean that they could be the ultimate high strength fibre, which has a tensile strength 20 times, and a strength-to-weight ratio of 100 times that of steel.

Nanotubes have already been used for reinforcement of nano structural composite materials, polymers and concrete. Being stronger than diamond, it is the strongest material known. Because of the low density these materials are very useful for cars, aeroplanes and space vehicles. Whereas a crack in a normal plate will grow because of the concentrated tensions at the tip of the crack, a broken nanotube produces almost no effect on the others. The tiny crack is blocked, and the chain reaction of fracture is terminated. There is good reason to expect a macroscopic 1 in. thick rope, where 10 parallel buckywires are holding together, to be almost as strong as theory predicts, about 40 GPa.

This strength combined with the low density may be crucial for the developing of a space elevator, which uses a rope to reach the stationary orbits of satellites. It can be calculated that the cable made of nanotubes must be as strong as 63 GPa. This is almost achievable whilst no other material known nowadays comes even close to the required strength.

1.4.5.7 Other Applications

- Carbon nanotubes have potential therapeutic applications in the field of drug delivery, diagnostics, and biosensing.
- Bianco and co-workers initially studied the application of CNTs as a template for targeting bioactive peptides to the immune system [70].
- CNTs are currently being considered to be a suitable substrate for the growth of cells for tissue regeneration, as delivery systems for a variety of diagnostic or therapeutic agents or as vectors for gene transfection [71].
- Due to their high tensile strength, carbon nanotubes filled with calcium and arranged/grouped in the structure of bone can act as bone substitute [72].
- Carbon nanotubes and nanohorns are antioxidant in nature. Hence, they are used to preserve drugs formulations prone to oxidation. Their antioxidant property is used in antiaging cosmetics and with zinc oxide as sunscreen dermatological to prevent oxidation of important skin [73].
- Wu et al reported the use of passive cellular uptake to deliver multiwall carbon nanotubes conjugated with amphotericin B (AmB), an antibiotic that is effective in treating fungal infections, but toxic to mammalian cells when it is free in solution [74].
- Dai and co-workers demonstrated SWNTs as nonviral molecular transporters for the delivery of short interfering RNA (siRNA) into human T cells and primary cells [75].
- In genetic engineering, CNTs and CNHs are used to manipulate genes and atoms in the development of bioimaging genomes, proteomics and tissue engineering [76].

- It has been reported that Paclitaxel loaded PEG--CNT's are promising for cancer therapeutics [77].
- Carbon nanotubes could be an important new weapon and act as a boost to fight against cancer after researchers found that they can improve a treatment called adoptive immunotherapy [78].
- They can be used as lubricants or glidants in tablet manufacturing due to nanosize and sliding nature of graphite layers bound with van der waals forces.
- The gelatin CNT mixture (hydro-gel) has been used as potential carrier system for biomedical.
- Antibiotic, Doxorubicin given with nanotubes is reported for enhanced intracellular penetration.
- CNT-based carrier system can offer a successful oral alternative administration of Erythropoietin (EPO), which has not been possible so far because of the denaturation of EPO by the gastric environment conditions and enzymes [79].

1.5 Carbon Fiber

1.5.1 Introduction

Carbon fiber (carbon fibre), alternatively graphite fiber, carbon graphite or CF, is a material consisting of extremely thin fibers about 0.005–0.010 mm in diameter and composed mostly of carbon atoms. The carbon atoms are bonded together in microscopic crystals that are more or less aligned parallel to the long axis of the fiber. The crystal alignment makes the fiber very strong for its size. Several thousand carbon fibers are twisted together to form a yarn, which may be used by itself or

woven into a fabric.

The properties of carbon fibers such as high flexibility, high tensile strength, low weight, high temperature tolerance and low thermal expansion make them very popular in aerospace, civil engineering, military, and motorsports, along with other competition sports. However, they are relatively expensive when compared to similar fibers for example glass fibers or plastic fibers.

Carbon fibers are usually combined with other materials to form a composite. When combined with a plastic resin and wound or molded it forms carbon fiber reinforced plastic (often referred to also as carbon fiber) which is a very high strength-to-weight, extremely rigid, although somewhat brittle material. However, carbon fibers are also composed with other materials, such as with graphite to form carbon-carbon composites, which have a very high heat tolerance.

1.5.2 History of Carbon Fibers

In 1958, Roger Bacon created high-performance carbon fibers at the Union Carbide Parma Technical Center, now GrafTech International Holdings, Inc., located outside of Cleveland, Ohio.^[1] Those fibers were manufactured by heating strands of rayon until they carbonized. This process proved to be inefficient, as the resulting fibers contained only about 20% carbon and had low strength and stiffness properties. In the early 1960s, a process was developed by Dr. Akio Shindo at Agency of Industrial Science and Technology of Japan, using polyacrylonitrile (PAN) as a raw material. This had produced a carbon fiber that contained about 55% carbon.

The high potential strength of carbon fiber was realized in 1963 in a process developed at the Royal Aircraft Establishment at Farnborough, Hampshire. The process was patented by the UK Ministry of Defence then licensed by the National Research Development Corporation (NRDC) to three British companies: Rolls-Royce, already making carbon fiber, Morganite and Courtaulds. They were able to establish industrial carbon fiber production facilities within a few years, and Rolls-Royce took advantage of the new material's properties to break into the American

market with its RB-211 aero-engine.

During the 1970s, experimental work to find alternative raw materials led to the introduction of carbon fibers made from a petroleum pitch derived from oil processing. These fibers contained about 85% carbon and had excellent flexural strength.

1.5.3 Structure and properties

Each carbon filament thread is a bundle of many thousand carbon filaments. A single such filament is a thin tube with a diameter of 5–8 micrometers and consists almost exclusively of carbon. The earliest generation of carbon fibers (i.e., T300, and AS4) had diameters of 7-8 micrometers.[80] Later fibers (i.e., IM6) have diameters that are approximately 5 micrometers.[80]

The atomic structure of carbon fiber is similar to that of graphite, consisting of sheets of carbon atoms (graphene sheets) arranged in a regular hexagonal pattern. The difference lies in the way these sheets interlock. Graphite is a crystalline material in which the sheets are stacked parallel to one another in regular fashion. The intermolecular forces between the sheets are relatively weak Van der Waals forces, giving graphite its soft and brittle characteristics. Depending upon the precursor to make the fiber, carbon fiber may be turbostratic or graphitic, or have a hybrid structure with both graphitic and turbostratic parts present. In turbostratic carbon fiber the sheets of carbon atoms are haphazardly folded, or crumpled, together.

Carbon fibers derived from Polyacrylonitrile (PAN) are turbostratic, whereas carbon fibers derived from mesophase pitch are graphitic after heat treatment at temperatures exceeding 2200 C. Turbostratic carbon fibers tend to have high tensile strength, whereas heat-treated mesophase-pitch-derived carbon fibers have high Young's modulus and high thermal conductivity.

PAN based carbon fibers have following properties[83]**Mechanical Properties**

- High strength and high modulus
- Low density
- Low creep rate
- Good vibration damping

Chemical Properties

- Chemically inert
- Non corrosive
- High resistance to acids and alkalis and organic solvents

Electrical Properties

- High conductivity

Thermal Properties

- Low thermal expansion
- Low thermal conductivity

Electro-Magnetic Properties

- Low X-ray absorption
- Non magnetic

1.5.4 Synthesis of Carbon Fibers

Each carbon filament is produced from a precursor polymer. The precursor polymer is commonly rayon, polyacrylonitrile (PAN) or petroleum pitch.

For synthetic polymers such as rayon or PAN, the precursor is first spun into filaments, using chemical and mechanical processes to initially align the polymer atoms in a way to enhance the final physical properties of the completed carbon fiber. About 90% of fibers are PAN based fibers. Precursor compositions and mechanical processes used during spinning may vary among manufacturers. After drawing or spinning, the polymer fibers are then heated to drive off non-carbon atoms (carbonization), producing the final carbon fiber. The carbon fibers may be further treated to improve handling qualities, then wound on to bobbins. Wound bobbins are then used to supply machines that produce carbon fiber threads or yarn.^[81]

Spinning

- Acrylonitrile plastic powder is mixed with another plastic, like methyl acrylate or methyl methacrylate, and is reacted with a catalyst in a conventional suspension polymerization process to form a polyacrylonitrile plastic.
- The plastic is then spun into fibers using one of several different methods. In some methods, the plastic is mixed with certain chemicals and pumped through tiny jets into a chemical bath or quench chamber where the plastic coagulates and solidifies into fibers. This is similar to the process used to form polyacrylic textile fibers. In other methods, the plastic mixture is heated and pumped through tiny jets into a chamber where the solvents evaporate leaving a solid fiber. The spinning step is important because the internal atomic structure of the fiber is formed during this process. The fibers are then washed and stretched to the desired fiber diameter. The stretching helps align the molecules within the fiber and provide the basis for the formation of the tightly bonded carbon crystals after carbonization.

Stabilizing

- Before the fibers are carbonized, they need to be chemically altered to convert their linear atomic bonding to a more thermally stable ladder bonding. This is accomplished by heating the fibers in air to about 390-590° F for 30-120 minutes. This causes the fibers to pick up oxygen molecules from the air and rearrange their atomic bonding pattern. The stabilizing chemical reactions are complex and involve several steps, some of which occur simultaneously. They also generate their own heat, which must be controlled to avoid overheating the fibers. Commercially, the stabilization process uses a variety of equipment and techniques. In some processes, the fibers are drawn through a series of heated chambers. In others, the fibers pass over hot rollers and through beds of loose materials held in suspension by a flow of hot air. Some processes use heated air mixed with certain gases that chemically accelerate the stabilization.

Carbonizing

- Once the fibers are stabilized, they are heated to a temperature of about 1,830-5,500° F (1,000-3,000° C) for several minutes in a furnace filled with a gas mixture that does not contain oxygen. The lack of oxygen prevents the fibers from burning in the very high temperatures. The gas pressure inside the furnace is kept higher than the outside air pressure and the points where the fibers enter and exit the furnace are sealed to keep oxygen from entering. As the fibers are heated, they begin to lose their non-carbon atoms, plus a few carbon atoms, in the form of various gases including water vapor, ammonia, carbon monoxide, carbon dioxide, hydrogen, nitrogen, and others. As the non-carbon atoms are expelled, the remaining carbon atoms form tightly bonded carbon crystals that are aligned more or less parallel to the long axis of the fiber. In some processes, two furnaces operating at two different temperatures are used to better control the rate of heating during carbonization.

Treating the surface

- After carbonizing, the fibers have a surface that does not bond well with the epoxies and other materials used in composite materials. To give the fibers better bonding properties, their surface is slightly oxidized. The addition of oxygen atoms to the surface provides better chemical bonding properties and also etches and roughens the surface for better mechanical bonding properties. Oxidation can be achieved by immersing the fibers in various gases such as air, carbon dioxide, or ozone; or in various liquids such as sodium hypochlorite or nitric acid. The fibers can also be coated electrolytically by making the fibers the positive terminal in a bath filled with various electrically conductive materials. The surface treatment process must be carefully controlled to avoid forming tiny surface defects, such as pits, which could cause fiber failure.

Sizing

- After the surface treatment, the fibers are coated to protect them from damage during winding or weaving. This process is called sizing. Coating materials are chosen to be compatible with the adhesive used to
- form composite materials. Typical coating materials include epoxy, polyester, nylon, urethane, and others.
- The coated fibers are wound onto cylinders called bobbins. The bobbins are loaded into a spinning machine and the fibers are twisted into yarns of various sizes.[81]

1.5.5 Classification of Carbon Fibers[82]

(i) Based on carbon fiber properties, carbon fibers can be grouped into:

- Ultra-high-modulus, type UHM (modulus $>450\text{Gpa}$)
- High-modulus, type HM (modulus between $350\text{-}450\text{Gpa}$)
- Intermediate-modulus, type IM (modulus between $200\text{-}350\text{Gpa}$)
- Low modulus and high-tensile, type HT (modulus $< 100\text{Gpa}$, tensile strength $> 3.0\text{Gpa}$)
- Super high-tensile, type SHT (tensile strength $> 4.5\text{Gpa}$)

(ii) Based on precursor fiber materials, carbon fibers are classified into;

- PAN-based carbon fibers
- Pitch-based carbon fibers
- Mesophase pitch-based carbon fibers
- Isotropic pitch-based carbon fibers
- Rayon-based carbon fibers
- Gas-phase-grown carbon fibers

(iii) Based on final heat treatment temperature, carbon fibers are classified into:

- Type-I, high-heat-treatment carbon fibers (HTT), where final heat treatment temperature should be above 2000°C and can be associated with high-modulus type fiber.
- Type-II, intermediate-heat-treatment carbon fibers (IHT), where final heat treatment temperature should be around or above 1500°C and can be associated with high-strength type fiber.
- Type-III, low-heat-treatment carbon fibers, where final heat treatment temperatures not greater than 1000°C. These are low modulus and low strength materials.

1.5.6 Carbon Fiber Reinforced Composites.

Carbon-fiber-reinforced polymer or carbon-fiber-reinforced plastic (CFRP or CRP), is a very strong and light fiber-reinforced polymer which contains carbon fibers. The polymer is most often epoxy, but other polymers, such as polyester, vinyl ester or nylon, are sometimes used. The composite may contain other fibers such as Kevlar, aluminium, glass fibers as well as carbon fiber.

The properties of carbon fibre reinforced plastics (CFRP) differ so much from that of their matrix material, that a relationship is barely discernible any more. CFRP materials are distinguished by their extremely high strength and rigidity. Low density, excellent damping properties and a high resistance to impacting combined with exactly modifiable thermal expansion to complement the complex characteristics profile.

Although it can be relatively expensive, it has many applications in aerospace and automotive fields, as well as in sailboats, and notably finds use in modern bicycles and motorcycles, where its high strength-to-weight ratio and good rigidity is of importance.

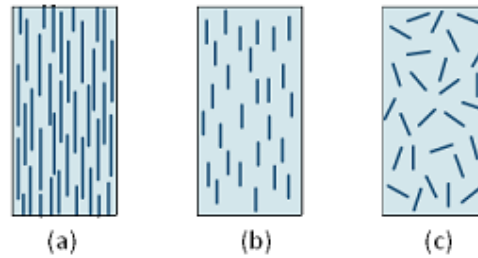
Improved manufacturing techniques are reducing the costs and time to manufacture, making it increasingly common in small consumer goods as well, such as laptops, tripods, fishing rods, paintball equipment, archery equipment, racquet

frames, stringed instrument bodies, classical guitar strings, drum shells, golf clubs, and pool/billiards/snooker cues.

Fiber-reinforced composite materials can be divided into two main categories normally referred to as short fiber-reinforced materials and continuous fiber-reinforced materials. Continuous reinforced materials will often constitute a layered or laminated structure. The woven and continuous fibre styles are typically available in a variety of forms, being pre-impregnated with the given matrix (resin), dry, uni-directional tapes of various widths, plain weave, harness satins, braided, and stitched. The short and long fibers are typically employed in compression moulding and sheet moulding operations. These come in the form of flakes, chips, and random mate (which can also be made from a continuous fibre laid in random fashion until the desired thickness of the ply / laminate is achieved).

Short Fiber Reinforced Blends are partial case of ternary composites, i.e. composites prepared of three ingredients. In particular they can be considered as a combination of an immiscible polymer blend and a short fiber reinforced composite. These blends have the potential to integrate the easy processing solutions available for short fiber reinforced composites with the high mechanical performance of continuous fiber reinforced composites. The performance of these complex, ternary systems is controlled by their morphology.

Depending on the aspect ratio of the filler particles (length/diameter) and their compatibility to the polymeric components one can achieve different morphologies: (i) filler contained within the dispersed phase, (ii) within the matrix phase or (iii) at the interface between the two phases. If the fibers are sufficiently long and are preferentially wetted by the dispersed phase an effectively continuous network consisting of fibers welded together by the dispersed phase can be created. In such manner a pseudo-continuous fibrous reinforcement is spontaneously formed during the processing step and a composite material with better mechanical performance can be obtained.



Typologies of fibre-reinforced composite materials:
 a) continuous fibre-reinforced
 b) discontinuous aligned fibre-reinforced
 c) discontinuous random-oriented fibre-reinforced.

Figure 1.12 Orientation of fibers in a matrix material

1.5.6.1 Manufacturing Processes

- **Molding**

One method of producing graphite-epoxy parts is by layering sheets of carbon fiber cloth into a mold in the shape of the final product. The alignment and weave of the cloth fibers is chosen to optimize the strength and stiffness properties of the resulting material. The mold is then filled with epoxy and is heated or air-cured. The resulting part is very corrosion-resistant, stiff, and strong for its weight. Parts used in less critical areas are manufactured by draping cloth over a mold, with epoxy either pre impregnated into the fibers (also known as *pre-preg*) or "painted" over it. High-performance parts using single molds are often vacuum-bagged and/or autoclave-cured, because even small air bubbles in the material will reduce strength.

- **Vacuum bagging**

For simple pieces of which relatively few copies are needed, (1–2 per day) a vacuum bag can be used. A fiberglass, carbon fiber or aluminum mold is polished and waxed, and has a release agent applied before the fabric and resin are applied, and the vacuum is pulled and set aside to allow the piece to cure (harden). There are two ways to apply the resin to the fabric in a vacuum

mold. One is called a wet layup, where the two-part resin is mixed and applied before being laid in the mold and placed in the bag. The other is a resin induction system, where the dry fabric and mold are placed inside the bag while the vacuum pulls the resin through a small tube into the bag, then through a tube with holes or something similar to evenly spread the resin throughout the fabric. Wire loom works perfectly for a tube that requires holes inside the bag. Both of these methods of applying resin require hand work to spread the resin evenly for a glossy finish with very small pin-holes. A third method of constructing composite materials is known as a dry layup. Here, the carbon fiber material is already impregnated with resin (prepreg) and is applied to the mold in a similar fashion to adhesive film. The assembly is then placed in a vacuum to cure. The dry layup method has the least amount of resin waste and can achieve lighter constructions than wet layup. Also, because larger amounts of resin are more difficult to bleed out with wet layup methods, prepreg parts generally have fewer pinholes. Pinhole elimination with minimal resin amounts generally require the use of autoclave pressures to purge the residual gases out.

- **Compression molding**

A quicker method uses a compression mold. This is a two-piece (male and female) mold usually made out of fiberglass or aluminum that is bolted together with the fabric and resin between the two. The benefit is that, once it is bolted together, it is relatively clean and can be moved around or stored without a vacuum until after curing. However, the molds require a lot of material to hold together through many uses under that pressure.

- **Resin Transfer Molding**

RTM (resin transfer molding) and the VARI (vacuum assisted resin transfer) process. These two processes use so-called preforms (dry fiber structures), into which the resin is injected. This permits the manufacture of component parts with complex contours as well as the use of different types of fiber, such as fabric, multi-axial butts and mesh for a component. This also permits a

reinforced functional integration, through which components can be produced without screwing or welding individual components. Another advantage of the preforms is their improved drapability. In the RTM process, the resin is injected under pressure into a closed mold. In the VARI method, the fibers in the mold are covered with a special distribution medium. The mold is then evacuated, through which the resin is drawn into the mold under atmospheric pressure. On the one hand, the medium permits equal distribution of the resin across the entire surface of the component, and on the other hand it has a distinctly higher permeability than semi-finished fiber products. By applying injection methods, CFRP components can be produced in shorter cycle times. In addition, compared to prepregs, they have a distinctly better surface quality. In order to further reduce process times, a further progressing automation of production as well as a faster and more efficient curing of the plastic resins by microwave radiation, for example, will contribute to the development of innovative manufacturing technologies.

1.5.6.2 Applications

- Carbon fiber is most notably used to reinforce composite materials, particularly the class of materials known as Carbon fiber or graphite reinforced polymers. Non-polymer materials can also be used as the matrix for carbon fibers. Due to the formation of metal carbides and corrosion considerations, carbon has seen limited success in metal matrix composite applications.
- Reinforced carbon-carbon (RCC) consists of carbon fiber-reinforced graphite, and is used structurally in high-temperature applications.
- The fiber also finds use in filtration of high-temperature gases, as an electrode with high surface area and impeccable corrosion resistance, and as an anti-static component.
- Carbon fiber reinforced polymer-[CFRP] has over the past two

decades become an increasingly notable material used in structural engineering applications. Studied in an academic context as to its potential

benefits in construction, it has also proved itself cost-effective in a number of field applications strengthening concrete, masonry, steel, cast iron, and timber structures. Its use in industry can be either for retrofitting to strengthen an existing structure or as an alternative reinforcing (or prestressing material) instead of steel from the outset of a project.

- Retrofitting has become the increasingly dominant use of the material in civil engineering, and applications include increasing the load capacity of old structures (such as bridges) that were designed to tolerate far lower service loads than they are experiencing today, seismic retrofitting, and repair of damaged structures. Retrofitting is popular in many instances as the cost of replacing the deficient structure can greatly exceed its strengthening using CFRP.^[91]
- Specialist ultra-high modulus CFRP (with tensile modulus of 420 GPa or more) is one of the few practical methods of strengthening cast-iron beams. In typical use, it is bonded to the tensile flange of the section, both increasing the stiffness of the section and lowering the neutral axis, thus greatly reducing the maximum tensile stress in the cast iron.
- Fire resistance of polymers or thermoset composites is significantly improved if a thin layer of carbon fibers is molded near the surface—dense, compact layer of carbon fibers efficiently reflects heat.^[92]
- Carbon-fiber-reinforced polymer has found a lot of use in high-end sports equipment
- Each 787 contains approximately 35 short tons of carbon fiber reinforced plastic (CFRP), made with 23 tons of carbon fiber. Carbon fiber composites have a higher strength-to-weight ratio than traditional aircraft materials, and help make the 787 a lighter aircraft. Composites are used on fuselage, wings, tail, doors, and interior.

- Audio equipment, loudspeakers because of good vibration damping, strength, and toughness.
- Automobile hoods, novel tooling, casings and bases for electronic equipments, EMI and RF shielding, brushes.[82]

1.6 Epoxy Resin

1.6.1 Introduction

Epoxy resins are thermosetting polymers that, before curing, have one or more active epoxide or oxirane groups at the end(s) of the molecule and a few repeated units in the middle of the molecule [90]. Chemically, they can be any compounds that have one or more 1,2-epoxy groups and can convert to thermosetting materials. Their molecular weights can vary greatly. They exist either as liquids with lower viscosity or as solids. Through the ring opening reaction, the active epoxide groups in the uncured epoxy can react with many curing agents or hardeners that contain hydroxyl, carboxyl, amine, and amino groups [84,85].

Most common epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A, though the latter may be replaced by similar chemicals.

The hardener consists of polyamine monomers, for example Triethylenetetramine (TETA) and aromatic hardeners like ethylene diphenyl diamine . When these compounds are mixed together, the amine groups react with the epoxide groups to form a covalent bond. Each NH group can react with an epoxide group, so that the resulting polymer is heavily crosslinked, and is thus rigid and strong.^{[1][2]}

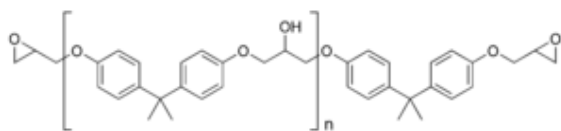


Figure 1.13 Structure of unmodified epoxy prepolymer resin

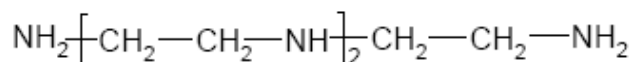


Figure 1.14 Structure of Structure of TETA, a typical hardener. The amine (NH) groups react with the epoxide groups of the resin during polymerization.



Fig 1.15 Structure of Ethylene diphenyl diamine hardener

Compared to other materials, epoxy resins have several unique chemical and physical properties. Epoxy resins can be produced to have excellent chemical resistance, excellent adhesion, good heat and electrical resistance, low shrinkage, and good mechanical properties, such as high strength and toughness. These desirable properties result in epoxy resins having wide markets in industry, packaging, aerospace, construction, etc. They have found remarkable applications as bonding and adhesives, protective coatings, electrical laminates, apparel finishes, fiber-reinforced plastics, flooring and paving, and composite pipes.

Since their first commercial production in 1940s by Devoe-Reynolds Company, the consumption of epoxy resins has grown gradually almost every year [86, 87]. The three main manufacturers of epoxy resins are Shell Chemical Company, Dow Chemical Company and Ciba-Geigy Plastics Corporation. They produce most of the world's epoxy resins. The United States and other industrialized countries such as Japan and those in Western Europe are the main producers and consumers of epoxy resins.

Since the 1930's when the preparation of epoxy resins was patented, many types of new epoxy resins have been developed from epoxides. Most conventional epoxy resins are prepared from bisphenol A and epichlorohydrin. For example, the most

commonly used epoxy resins are produced from diglycidyl ethers of bisphenol A (DGEBA).

Other types of epoxy resins are glycidyl ethers of novolac resins, phenoxy epoxy resins, and (cyclo) aliphatic epoxy resins. Although many accomplishments have been made in the field of epoxy resins, researchers still make efforts to understand better their curing mechanisms, to improve their properties, and to produce new epoxy resins.

1.6.2 Applications of Epoxy Resin

The chemistry of epoxies and the range of commercially available variations allow cure polymers to be produced with a very broad range of properties.

1.6.2.1 Paints and Coats

Polyester epoxies are used as powder coatings for washers, driers and other "white goods". Fusion Bonded Epoxy Powder Coatings (FBE) are extensively used for

corrosion protection of steel pipes and fittings used in the oil and gas industry, potable water transmission pipelines (steel), concrete reinforcing rebar, *et cetera*. Epoxy coatings are also widely used as primers to improve the adhesion of automotive and marine paints especially on metal surfaces where corrosion (rusting) resistance is important. Metal cans and containers are often coated with epoxy to prevent rusting, especially for foods like tomatoes that are acidic. Epoxy resins are also used for high performance and decorative flooring applications especially terrazzo flooring, chip flooring[88] and colored aggregate flooring[89].

1.6.2.2 Adhesives

Epoxy adhesives can be developed to suit almost any application. They can be used as adhesives for wood, metal, glass, stone, and some plastics. They can be made flexible or rigid, transparent or opaque/colored, fast setting or slow setting. Epoxy adhesives are better in heat and chemical resistance than other common adhesives. In general, epoxy adhesives cured with heat will be more heat- and chemical-resistant than those

cured at room temperature. The strength of epoxy adhesives is degraded at temperatures above 350 °F (177 °C)

1.6.2.3 Industrial tooling and composites

Epoxy systems are used in industrial tooling applications to produce molds, master models, laminates, castings, fixtures, and other industrial production aids. This "plastic tooling" replaces metal, wood and other traditional materials, and generally improves the efficiency and either lowers the overall cost or shortens the lead-time for many industrial processes. Epoxies are also used in producing fiber-reinforced or composite parts.

1.6.2.4 Aerospace Applications

In the aerospace industry, epoxy is used as a structural matrix material which is then reinforced by fiber. Typical fiber reinforcements include glass, carbon, Kevlar, and boron. Carbon fiber/epoxy composites find application where high strength to weight ratios are required.

1.6.2.5 Electrical systems and electronics

Epoxy resin formulations are important in the electronics industry, and are employed in motors, generators, transformers, switchgear, bushings, and insulators. Epoxy resins are excellent electrical insulators and protect electrical components from short circuiting, dust and moisture. In the electronics industry epoxy resins are the primary resin used in overmolding integrated circuits, transistors and hybrid circuits, and making printed circuit boards.

Flexible epoxy resins are used for potting transformers and inductors. By using vacuum impregnation on uncured epoxy, winding-to-winding, winding-to-core, and winding-to-insulator air voids are eliminated. The cured epoxy is an electrical insulator and a much better conductor of heat than air. Transformer and inductor hot spots are greatly reduced, giving the component a stable and longer life than unpotted product.

1.6.2.6 Marine Applications

They are also sold in boat shops as repair resins for marine applications. Epoxies typically are not used in the outer layer of a boat because they deteriorate by exposure to UV light. They are often used during boat repair and assembly, and then over-coated with conventional or two-part polyurethane paint or marine-varnishes that provide UV protection.

There are two main areas of marine use.

- Because of the better mechanical properties relative to the more common polyester resins, epoxies are used for commercial manufacture of components where a high strength/weight ratio is required.
- The second area is that their strength, gap filling properties and excellent adhesion to many materials including timber have created a boom in amateur building projects including aircraft and boats.

1.7 Composite Materials

Composite materials, often shortened to composites, are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure.

Composites are made up of individual materials referred to as constituent materials. There are two categories of constituent materials: matrix and reinforcement. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. Wood is a natural composite of Cellulose fibres in a matrix of lignin

Most commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, PEEK, and others.

The reinforcement materials are often fibres but also commonly ground minerals. The various methods described below have been developed to reduce the resin content of the final product, or the fibre content is increased. As a rule of thumb, lay up results in a product containing 60% resin and 40% fibre, whereas vacuum infusion gives a final product with 40% resin and 60% fibre content. The strength of the product is greatly dependent on this ratio.

The greatest advantage of composite materials is strength and stiffness combined with lightness. By choosing an appropriate combination of reinforcement and matrix material, manufacturers can produce properties that exactly fit the requirements for a particular structure for a particular purpose

CHAPTER 2

REVIEW OF LITERATURE

- Carbon filaments prepared by *Hughes and Chambers* in **1889** were probably the **first patent** ever deposited in the field.
- The worldwide enthusiasm came unexpectedly in **1991**, after the catalyst-free formation of nearly perfect concentric multiwall carbon nanotubes (c-MWNTs) was reported as by-products of the formation of fullerenes by the electric-arc technique. In **1991**, Iijima of the NEC Laboratory in Japan reported the first observation of Multi-Walled Carbon Nanotubes.
- In **1992**, a breakthrough in MWCNT growth by arc-discharge was first made by Ebbesen and Ajajyan who achieved growth and purification of high quality MWNTs at the gram level. The synthesized MWNTs have lengths of the order of two microns and diameter in the range 5-30nm.
- In **1992**, Conductivity of carbon nanotubes was measured by J.W. Mintmire, B.I. Dunlap and C.T. White.
- The real breakthrough occurred with the discovery – again unexpected – The first success in producing substantial amounts of SWNTs by arc-discharge was achieved by Bethune and co-workers in **1993**. They used a carbon anode containing a small percentage of Co catalyst in the discharge experiment and found abundant SWNTs generated in the soot material.
- In **1993**, Structural rigidity of carbon nanotubes was seen by G. Overney, W. Zhong, and D. Tománek.
- In **1995**, Nanotubes used as field emitters By A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tománek, P. Nordlander, D.T. Colbert, and R.E. Smalley.

- In **1996**, the growth of high quality SWNTs at the 1-10gm scales was achieved by Richard E Smalley and coworkers using a laser ablation method.
- Dresselhaus et al in **1996** found that good quality yield of nanotubes were obtainable with Fe Co alloy nanoparticles.
- In **1997**, the optimization of SWNT growth by arc-discharge was achieved by Journet and co-workers using a carbon anode containing 1.0 atomic percentage of yttrium and 4.2 atomic % of Ni as catalyst.
- Xie group **1996** and **1998** at the Chinese Academy of Science has grown aligned MWNTs by CVD method. The catalyst used in this case is Fe oxide particles created in the pores of silica; the carbon feedstock is 9% acetylene in Nitrogen at an overall 180 Torr pressure and a growth temperature of 600⁰C.
- In **1998**, Synthesis of nanotube peapods B.W. Smith, M. Monthieux, and D.E. Luzzi.
- Smalley and co-workers in **1998**, who used ethylene as carbon feedstock and growth temperatures around 800⁰C reported another CVD approach to SWNTs.
- Cheng and co-workers in **1998** reported a method that employs benzene as the carbon feedstock, hydrogen as the carrier gas and ferrocene as the catalyst precursor for SWNT growth.
- Ren in **1998** has grown relatively large diameter MWNTs forming oriented 'forests' on glass substrates using a plasma assisted CVD method with Ni as the catalyst and acetylene as the carbon feedstock around 660⁰ C.
- In **1998** and **1999**, high quality SWNTs were grown from Chemical Vapor Deposition process by Dresselhaus et al by using methane as carbon feedstock and reaction temperatures in the range 850-1000⁰C.
- Rao and co-workers in **1999** used a catalyst based on mixed oxide spinels to grow SWNTs.

- Smalley and coworkers **1999** have developed a gas phase catalytic process to grow bulk quantities of SWNTs by taking the carbon feedstock as Co and growth temperature in the range 800-1200⁰C.
- Sandler et al in **1999** reported the dispersion of as produced carbon nanotubes in an epoxy matrix. The use of carbon nanotubes not only reduces the percolation threshold to below 0.04%, but also increases the overall conductivity.
- In **2000**, Thermal conductivity of nanotubes were measured by Savas Berber, Young-Kyun Kwon, and David Tománek.
- Liu made a significant progress and co-workers in **2000**, obtaining a highly active catalyst for methane CVD growth of SWNTs. Liu used sol-gel synthesis and supercritical drying to produce Fe/Mo catalyst supported on alumina sol-gel. Using the aerogel catalyst, Liu and co-workers were able to obtain nearly 200% yield of high quality CNTs.
- Colomer and coworkers in **2000** recently reported the growth of bulk quantities of SWNTs by CVD of methane using a cobalt catalyst supported on MgO. On the acidic treatment of the material produced 70-80% of the SWNTs were obtained.
- In **2001**, Integration of carbon nanotubes for logic circuits. by C. Collins, M.S. Arnold, and P. Avouris.
- In **2001**, Intrinsic superconductivity of carbon nanotubes was discovered by M. Kociak, A. Yu. Kasumov, S. Guéron, B. Reulet, I. I. Khodos, Yu. B. Gorbatov, V. T. Volkov, L. Vaccarini, and H. Bouchiat.
- Carbon nanotubes–Polymer composites were initially reported by Ajayan et al in **1994**. They just mechanically mixed the purified MWNTs with epoxy resin. Since then, attention has been paid to composite materials with uniform and high nanotube loading.

- Ago et al in **1998** obtained uniform film of MWNTs and poly (p-phenylene vinylene) (PPV) widely studied was prepared by spin-coating highly concentrated MWNT dispersion.
- Gong et al in **2000** reported that using surfactants as wetting agents might improve dispersion and thermo chemical properties of carbon nanotubes/polymer composites, but even with the addition of surfactants, complete homogeneous dispersion of nanotubes was not obtained.
- Allaoui et al in **2002** found two to three times improvement in Young's modulus and yield strength respectively when 1 wt% MWNTs were added to the epoxy matrix.
- Tai et al in **2003 & 2004** showed a 100% improvement in tensile strength of the MWNTs / phenolic resin composites when 3 wt% CNTs network was introduced into the phenolic matrix.
- Zeng et al in **2004** reported a 50% increase on Young's Modulus in CNT/PMMA composites when 5 wt % carbon nanofibres were introduced into the composites.
- Zhi Wang et al in **2004** have prepared Bucky paper/ epoxy resin, dissolved in acetone, composites. A hot press molding process was used for curing to produce the final nano composites of multiple layer bucky papers with high SWNTs loading (up to 39 wt %). Dynamic mechanical analysis results show that the storage moduli of the resulting nano composites were as high as 15 GPa.
- Iijima S (1991) Nature 354-56 provided a major breakthrough to make CNTs by CVD process specifically optimized for pitch composite fabrication.
- Tilimans H. , Pietzka G., Pauls H., Influence of the quinoline Insoluble Matter in the Pitch on Carbonization Behaviour and Structure of Pitch Coke Fuel 1978:57;171-7
- Feng *et.al.* (**2003**) have prepared MWCNTs well-aligned polyaniline (PANI)/MWCNT composite films were prepared by in situ polymerization of aniline [52].

- Zengin et al., (2002), mixed multiwalled carbon nanotubes (MWCNTs) with aniline via stirring followed by in situ polymerization. They reported that the MWCNT / PANI composites exhibit drastic increase in electrical conductivity.
- Deng et al., (2002) used a similar method to prepare CNT / PANI hybrid materials, and studied the conductivity in these composites. They proposed that even 0.2% of CNTs can improve the conductivity of the CNT / PANI composite more than three times than that of PANI [53].
- A new approach for the synthesis of size-controllable polyaniline/carbon nanotube (CNT) nanocables by in situ chemical oxidative polymerization directed by the cationic surfactant cetyltrimethyl ammonium bromide (CTAB) have been described by Zhang et.al., (2004) [55].
- Galvanostatic electro polymerization of aniline on multi-walled carbon nanotubes (MWCNTs)-modified gold electrode was used for fabricate a polyaniline (PANI)/carbon nanotubes (CNTs) composite modified electrode by Manli et. al., (2005). The prepared electrode thus exhibits enhanced electro catalytic behavior to the reduction of nitrite and facilitates the detection of nitrite at an applied potential of 0.0 V. Although the amperometric responses toward nitrite at MWCNTs/gold and PANI/gold electrodes have also been observed and the effects of electropolymerization time, MWCNTs concentration and pH value of the detection solution on the current response of the composite modified electrode toward sodium nitrite, were also
- Yijun et al., (2005), have been prepared multi-walled carbon nanotubes/polyaniline composites (MWCNTs/PANI) by the in situ inverse micro emulsion, Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) showed that the nanotubes were coated with a PANI layer. Fourier transform infrared (FT-IR) spectra suggested that the -bonded surface of the carbon nanotubes (CNTs) interact strongly with the conjugated structure of the PANI shell layer. The thermal stability and electrical conductivity of the MWCNTs/PANI composites were examined by Thermogravimetric analysis (TGA) and conventional four-probe method.
- Xiao et al., (2005) has been observed that the Polymer/carbon nanotube (CNT)

composites are expected to have good processability characteristics of the polymer and excellent functional properties of the CNTs. They have also studied the critical challenge, how to enhance dispersion and alignment of CNTs in the matrix and on mechanical, thermal, electrical, electrochemical,

- optical and super-hydrophobic properties; and applications of polymer/CNT composites.
- Nanocomposites of polyaniline (PANI) and single-wall carbon nanotubes (SWCNTs) were prepared and characterized via resonance Raman and electronic absorption spectroscopy (ultraviolet–visible/near-infrared). The chemical synthesis of PANI was performed in the presence of SWCNTs in concentrations ranging from 10 to 50-wt % (SWCNT/PANI) by GUSTAVO M et.al **2005**. The chemical interaction between PANI and metallic and semi conducting nanotubes was investigated. The emeraldine salt form of the polymer was significantly stabilized in the composite in comparison with plain PANI.
- Layered composites of polyaniline (PAn), single-walled carbon nanotubes (CNTs) and polypyrrole (PPy) were produced by coating PAn or PAn/CNT on a PPy hollow fibre containing a platinum (Pt) helix (Spinks et. al. **2005**). The actuation behaviour of PAn/PPy and PAn/CNT/PPy composites was compared with that of neat PPy. The Pt helix reduces the IR drop along the fibre, thus enhancing the actuation strain. A minimal quantity of CNT (1.3 wt.%) in the composite leads to a discernible decrease in actuation strain but also increases the Young's modulus and tensile strength of the composite [56].
- The synthesis of doped polyaniline in its emeraldine salt form (PANI-ES) with carboxylic acid and acylchloride groups contained multi-walled carbon nanotubes (designated as c-MWCNTs and a-MWCNTs) by in situ polymerization was reported by Tzong-Ming et.al **2006**. They have analysed both Raman spectra and HRTEM images indicate that carboxylic acid and acylchloride groups formed at both ends and on the sidewalls of the MWCNTs.

CHAPTER 3

MATERIALS AND METHODS

3.1 Material Used

- Multiwalled carbon nanotubes used in the study are synthesized by CVD method at carbon technology unit, NPL New Delhi in the laboratory and Carbon Fibers used as a filler material in the composites
- Uni-directional carbon fibers

3.2. Chemicals

Different Chemicals used in this study were

- Acetone
- Ferrocene
- Toulene
- Epoxy Resin
- Diphenyl Diamine Ethylene

3.3 Characterization of Multi-Walled Carbon Nanotubes

- Scanning Electron Microscope(SEM)
- Thermogravemetric Analysis(TGA)
- X-Ray Diffraction (XRD)

3.3.1 Scanning Electron Microscope

SEM is an important tool to characterize surface morphology and growth structure of the material. SEM micrograph of the MWCNTs as produced in the form of carbon soot, after purification and MWCNT/CF/Epoxy composites have been taken by LEO S-440 PC Based Digital SEM having 3.5 nm SEI Mode, 5.5 nm BEI Mode and accelerating voltage is available 300-40kV in steps of 10 volts at NPL, New Delhi (fig.3.1). The tungsten filament or lanthanum hex boride LaB₆ is used as the source of electrons. Direct surface morphology and surface structure has been examined for

conducting sample however, the specimen was coated with a very thin layer (10 nm) of conducting material.



Figure 3.1. SEM Instrument used at NPL, New Delhi

3.3.2. Thermo Gravimetric Analysis (TGA)

Thermo gravimetric Analysis (TGA) is a thermal analysis technique used to measure changes in the weight of a sample as a function of temperature. TGA is one of the important tool to determine the thermal stability, absorbed moisture content and different impurities present along with the CNTs, polymer and polymer composite.

Thermo gravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results

may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials,

A constant supply of dry air @ 10ml/min was maintained at the heating rate of 10⁰C/min with Mettler Toledo, TGA/SDTA 851^o Thermal Analysis System from room temperature to a maximum temperature of 850⁰C. A sample is placed into a TGA sample pan, which is attached to a sensitive microbalance assembly. The balance assembly measures the initial sample weight at room temperature and then continuously monitors changes in sample weight with increase in temperature. The weight loss curves are analyzed for the amount or percent of weight loss at any given temperature and the temperatures of various sample degradation processes, was recorded by the software provided with the instrument.

3.3.3. X-Ray Diffraction

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

A Bruker made D-8 ADVANCE Powder X-ray diffractometer at NPL, New Delhi (Figure.27) was used to characterize the MWCNTs composite.

The heart of D-8 ADVANCE is the high precision, two-circle goniometer with independent stepper motors and optical encoders for the 8 and 28 circles. The central

opening in the Theta ring provides the maximum possible flexibility for different samples and sample stages.

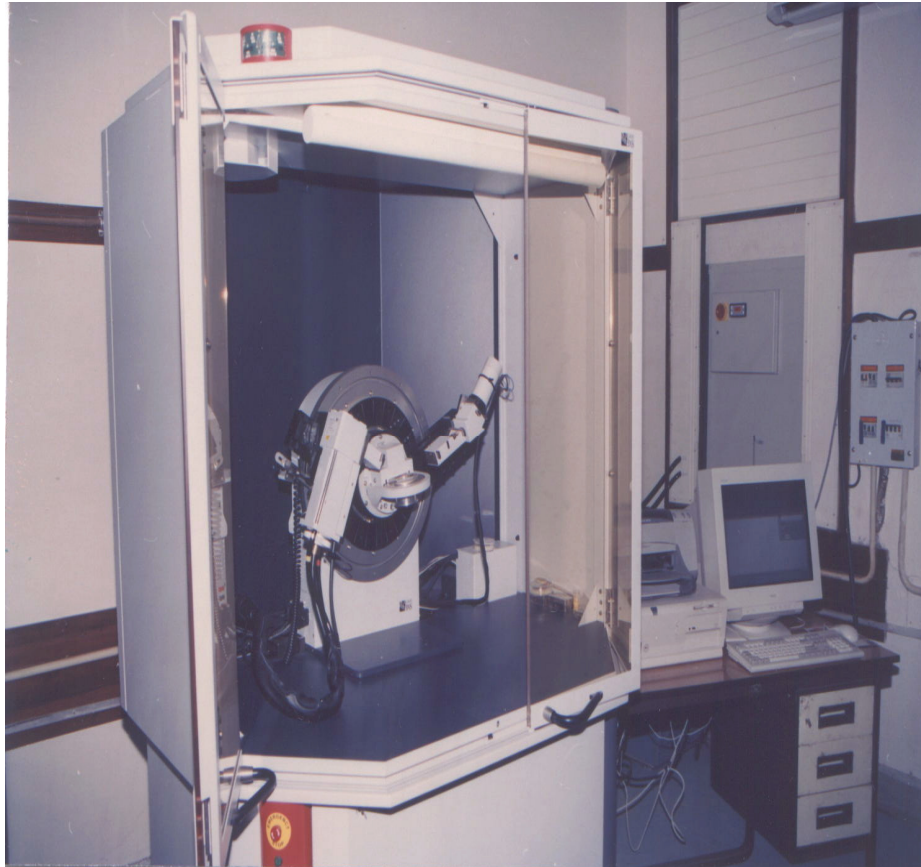


Fig 3.2 Photograph of Brukers D8 ADVANCE X-ray diffractometer used for the characterization of composites in X-ray section at NPL, New Delhi.

3.3.4 Resin Casting

Resin casting is a method of plastic casting where a mold is filled with a liquid synthetic resin, which then hardens. The synthetic resin for such processes is a monomer for making a plastic thermosetting polymer. During the setting process, the liquid monomer polymerizes into the polymer, thereby hardening into a solid.

Most commonly a thermosetting resin is used that polymerizes by mixing with a curing agent (polymerization catalyst) at room temperature and normal pressure. The synthetic resins used include epoxy resin polystyrene resin, polyurethane resin, , unsaturated polyester resin, acrylic resin and silicone resin.

There are two categories of resin casting. One is single-part molding and other is two-part molding. In single-part molding or open casting sing part mold is used. The top surface of the castings will be unfinished, which requires sanding. In two part molding resin is subjected to contact pressing. Molds consists of two halves between which resin is cured. In two-part cured resin have better finish.

For the preparation of composite material, fillers or reinforcements are added to the uncured thermoset resin. However it is required to heat the resin a little to reduced its viscosity so that fillers can be added. After adding reinforcements curing agent or hardener is added to the mix. Before casting molds are applied with wax polish to prevent the cured specimen from sticking on to the mold Thereafter resin is immediately poured into the mold. Depending upon the curing agent, resin is allowed to set either at room temperature or is heated at high temperatures for curing of mix. Cured specimens are then cooled gradually. Final cooled cured specimen are ejected out of mold cavity. Curing can be as quickly as in overnight for room temperature curing. In case of high temperature curing, process however takes considerable less time.

Finally the cured specimens are grinded or sanded with emery paper

3.4. Study of properties of MWCNTs-CF reinforced epoxy hybrid composites:

3.4.1. Mechanical Properties of the Polymer Composites:

The samples were tested on an Instron machine model 4411 to determine their flexural properties and on Shore Schleroscope Hardness Testing Equipment to determine Hardness.

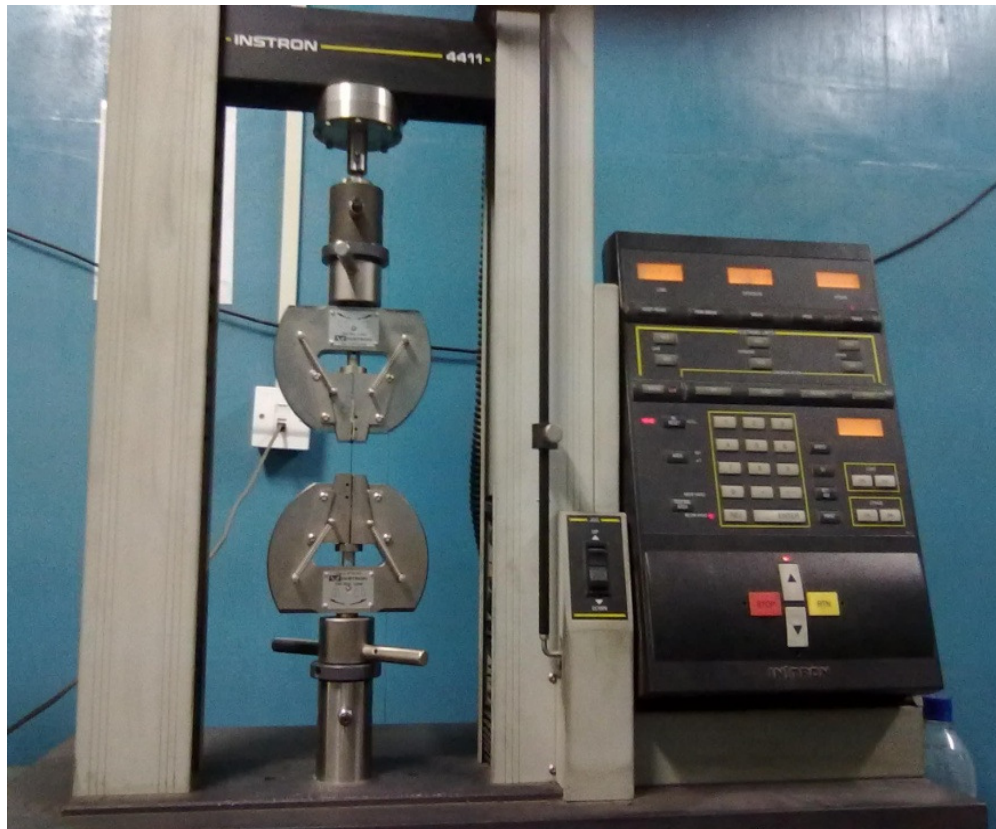


Fig.3.3. Instron machine model 4411 at NPL

3.4.1.1 Flexural Properties

Flexural strength, also known as modulus of rupture, bend strength, or fracture strength a mechanical parameter for brittle material, is defined as a material's ability to resist deformation under load. The transverse bending test is most frequently employed, in which a rod specimen having either a circular or rectangular cross-section is bent until fracture using a three point flexural test technique. The flexural strength represents the highest stress experienced within the material at its moment of rupture. It is measured in terms of stress, here given the symbol σ_f .

In mechanics, the flexural modulus is the ratio of stress to strain in flexural deformation, or the tendency for a material to bend. It is determined from the slope of

a stress-strain curve produced by a flexural test (such as the ASTM D 790), and uses units of force per area. It is an intensive property. It is given symbol E_f .

3.4.2.2 Flexural Strength vs. Tensile strength

The flexural strength would be the same as the tensile strength if the material was homogeneous. In fact, most materials have small or large defects in them which act to concentrate the stresses locally, effectively causing a localized weakness. When a material is bent only the extreme fibers are at the largest stress so, if those fibers are free from defects, the flexural strength will be controlled by the strength of those intact 'fibers'. However, if the same material was subjected to only tensile forces then all the fibers in the material are at the same stress and failure will initiate when the weakest fiber reaches its limiting tensile stress.

Therefore it is common for flexural strengths to be higher than tensile strengths for the same material. Conversely, a homogeneous material with defects only on its surfaces (e.g. due to scratches) might have a higher tensile strength than flexural strength.

If we don't take into account defects of any kind, it is clear that the material will fail under a bending force which is smaller than the corresponding tensile force. Both of these forces will induce the same failure stress, whose value depends on the strength of the material.

For a rectangular sample, the resulting stress under an axial force is given by the following formula :

$$\sigma_f = F/(b \times d)$$

This stress is not the true stress, since the cross section of the sample is considered to be invariable (engineering stress).

- F is the axial load (force) at the fracture point

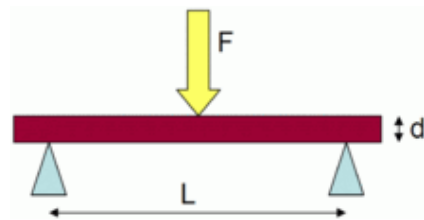
- b is width
- d is thickness


The resulting stress for a rectangular sample under a load in a three-point bending setup (Fig. 3) is given by the formula below (see "Measuring flexural strength").

Usually, L (length of the support span) is much bigger than d , so the fraction is $3L/2d$ bigger than

3.4.2.3 Measuring flexural Properties

(i) Flexural Strength



 Fig. 3.4 - Beam under 3 point bending

For a rectangular sample under a load in a three-point bending setup (Fig. 3):

$$\sigma_f = 3FL/2bd^2$$

- F is the load (force) at the fracture point
- L is the length of the support span
- b is width
- d is thickness

(ii) Flexural Modulus

Flexural modulus:

$$E(\text{bend}) = \frac{L^3 F}{4wh^3 d}$$

For a 3-point deflection test of a beam, where: w and h are the width and height of the beam, L is the distance between the two outer supports and d is the deflection due to load F applied at the middle of the beam.

3.4.2.4 Hardness

Hardness is a property of penetration strength, deformation strength, etc, but in most, hardness test depends on the penetration strength of the material surface. [48]The Shore Scleroscope Equipment used to carry out hardness test determines hardness in relation elastic behavior of the material.

Shore Scleroscope Hardness Test

- The Shore Scleroscope hardness is associated with the elasticity of the material. The appliance consists of a diamond-tipped hammer, falling in a graduated glass tube from a definite height. The tube is divided into 140 equal parts.
- The height of the first rebound is the hardness index of the material. The harder the material, the higher the rebound.
- The Shore method is widely used for measuring hardness of large machine components like rolls, gears, dies, etc.
- The Shore scleroscope is not only small and mobile, it also leaves no impressions on the tested surface.



Fig 3.5 Shore Scleroscope at NPL

3.4.2 Electrical Properties Of Hybrid Composites

Electrical conductivity or **specific conductance** is the reciprocal quantity, and measures a material's ability to conduct an electric current. It is commonly represented by the Greek letter σ (sigma), Its SI unit is siemens per metre ($S \cdot m^{-1}$) and electrostatic unit is reciprocal second (s^{-1}):. ρ is the electrical resistivity.

$$\sigma = \frac{1}{\rho}$$

The electrical conductivity of the composite specimens was measured by 4-point contact method. Kiethley 224 programmable current source was used for providing current. The voltage drop was measured by Keithley 197 A auto ranging micro volt DMM.

The polymer composite sample was cut into rectangular strips of size 60mm in length and 20 mm in width. Current was passed along the length of the strip and the voltage drop was measured across different points separated by unit length. Each sample reading was averaged over 10 to 15 readings. The room temperature current–voltage (I – V) characteristics were measured and resistance values were obtained from the slope of these plots.

The electrical conductivities of the pellets can be calculated by considering the sample dimensions as:

$$\sigma = \frac{L}{RA}$$

where “ L ” is the length of the composites “ R ” is resistance and “ A ” is cross-sectional area of the composite normal to direction of current flow. Conductivity is measured in seimens/cm/(S/cm).

3.4.3 Morphology Studies through Scanning Electron Microscope and Transmission Electron Microscope

Hybrid composite samples were cut into small strips having one surface as the fractured surface. Specimens' fractured surface was scanned by Scanning electron microscope for microstructure and morphology studies.

CHAPTER 4

EXPERIMENTAL

4.1. Synthesis of MWNTs by CVD

It is heterogeneous catalysis process. In this method, we can get the high purity carbon nanotubes. It is based on thermal decomposition of hydrocarbons in the presence of catalysts at high temperature of 650-900⁰C in the reactor furnace (Figure.1.8). Synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The energy source is used to “crack” the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained. Excellent alignment [31], as well as positional control on nanometre scale [32], can be achieved by using CVD. Compared to arc discharge, 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 appropriate metal catalyst can preferentially grow single rather than multi-walled nanotubes.

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. Ammonia may be used as the etchant. Typical yields for CVD are approximately 30%.

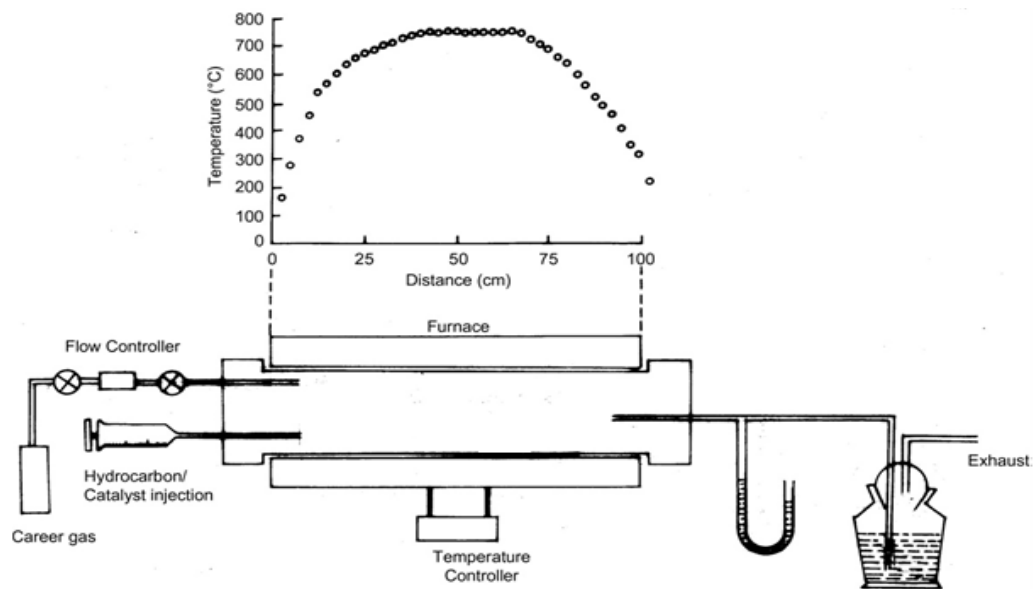


Fig. 4.1. Schematic diagram of the CVD reactor along with the temperature profile.



Fig. 4.2. CVD Experimental setup at NPL, New Delhi.

4.2 MWCNT-CF-Epoxy Hybrid Composite Fabrication by resin Casting

Uni-directional Carbon fibers were chopped manually. Chopped fibers were then dispersed in epoxy resin using magnetic stirrer at temperature of 50°C for four hrs. Carbon Fiber content in epoxy was varied as 1%,2% and 4% by weight.

MWCNT dispersed in acetone and sonicated for 2hr. and then added in the same epoxy resin with dispersed carbon fiber as explained in the fig.MWCNT content was also varied as 1%, 2% and 4% by weight. The mix however became too viscous for dispersion when both carbon fiber and MWCNT were mixed in epoxy resin at 4% concentration. The mixture was therefore subjected to magnetic stirring at 60 °C for 24 h. Once the uniform dispersion of MWCNT-CF(Carbon fiber) was achieved the curing agent (hardener) was added into the mix at a stoichiometric weight ratio to epoxy, 32/100 and stirred for 1 h before cast into mould having dimensions 70 × 12.7 mm² and thickness 2.5 mm. Mix was first heated to 140°C for 1 hr and then at 200°C for two hrs. Specimen with 4% carbon fiber wt. were cast into mould of dimension 60 x 19.8mm² and thickness 3.5mm. Five samples were prepared of each type of specimen and there average values were reported.

Final cured specimen was ejected out of the mould.

Specimens with varying amount of carbon fiber and carbon nanotube were prepared .

- 0.5% carbon fiber
- 0.5% carbon fiber + 0.5% carbon nanotube
- 1% carbon fiber
- 1% carbon fiber + 1% carbon nanotube
- 2% carbon fiber
- 2% carbon fiber + 2% carbon nanotube
- 4 % carbon fiber

All the specimens prepared by resin casting were tested determining flexural properties, hardness, compressive strength, electrical conductivity

Prepared Specimens morphology were studied through SEM micrographs.

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Characteristic of as grown MWCNT synthesized by CVD technique:

MWCNTs were synthesized using toluene as a carbon source and ferrocene as catalyst precursor by CVD method. These as synthesized MWCNTs were characterized by several techniques such as SEM, TEM, TGA, and XRD as given below:

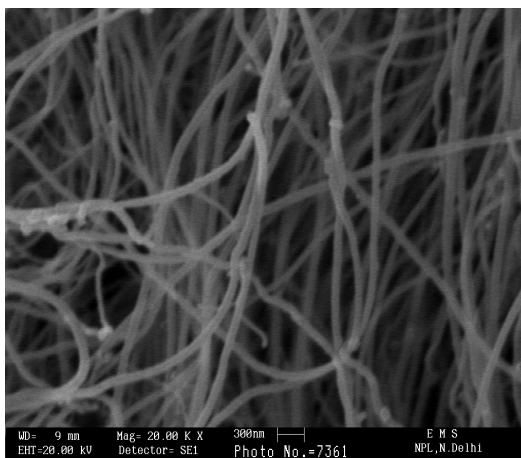


Fig.5.1. SEM image of as grown MWCNTs synthesized by CVD method

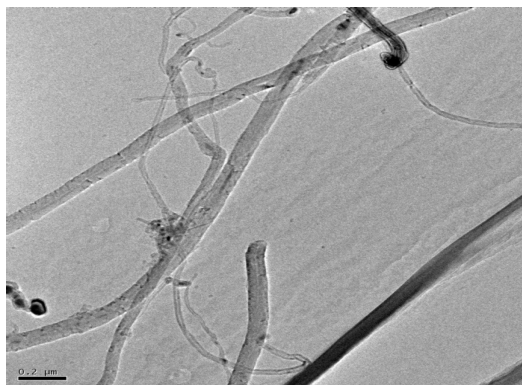


Fig.5.2. TEM image of As grown CNTs synthesized by CVD Technique

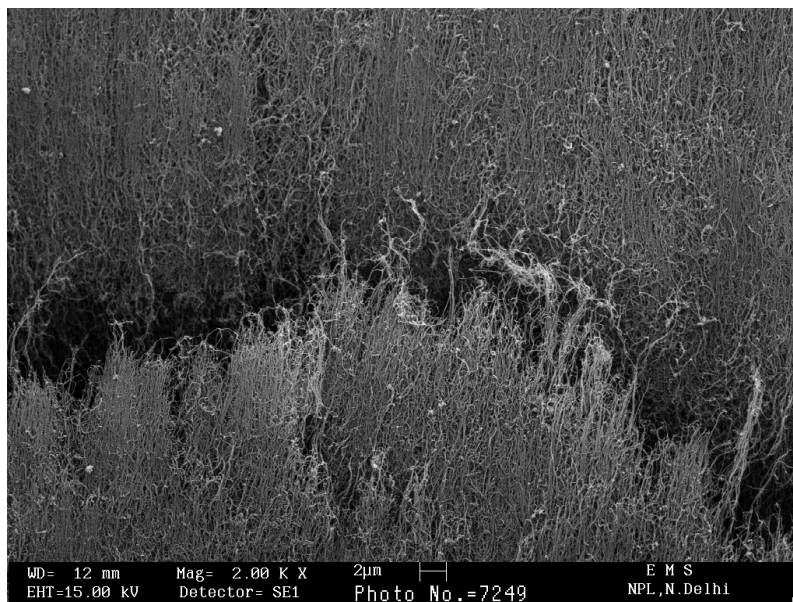


Fig. 5.3. SEM image of as grown MWCNTs at lower magnification

5.1.1. SEM:

Fig.5.1 and Fig 5.2 show the SEM images of the carbon nanotubes produced inside the reactor chamber at higher and lower magnification respectively. The carbon nanotubes are having almost similar character i.e. straight and uniformity in diameter of 10-60 nm and lengths in several μm . These SEM images clearly revealing the presence of high quality CNTs

5.1.2. TGA

TGA is one of the techniques used for ascertaining the catalyst contents as well as the other carbon impurities present in the as produced soot. TGA run of the as produced CNTs was carried out on Mettler Toledo, TGA/SDTA 851e thermal analysis system in flowing dry air at a heating rate of $10^{\circ}\text{C}/\text{min}$ up to a maximum temperature of 1000°C .

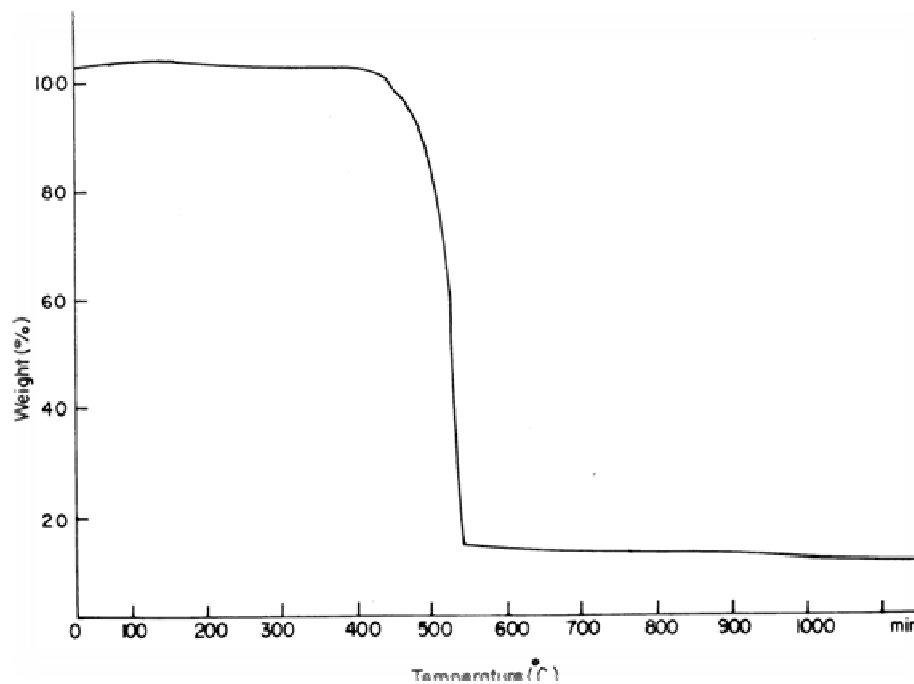


Fig.5.4. TGA analysis of the as produced CNTs inside the reactor

The TGA studies also gave an indication whether other forms of carbon were present in the deposits or not.

Fig.5.5. shows the TGA graph where we can see that there is no weight loss up to 450°C, after which a sharp weight loss is observed. The weight loss in this region is due to the oxidation of MWNTs present in the sample. Absence of any weight loss in the low temperature region, i.e. between 200 and 400°C suggests the absence of amorphous carbon in the sample. However, we do not observe any weight gain in the temperature range <200°C, which generally results from the oxidation of the catalyst present in the sample, suggesting the absence of bare catalyst particles, i.e. Fe in the deposits. No weight loss is observed beyond 600°C. The total weight loss up to 1000°C was calculated to be around 88% due to oxidation or burn out of carbon nanotubes. The remaining 12% weight could, therefore, be due to either iron catalyst or its oxide present in the sample as impurity.

5.1.3. XRD

Fig.5.5. shows the XRD patterns of pure MWCNT. The pure MWCNT shows a sharp peak centered on 2θ value of 26 which corresponds to the (0 0 2) planes of MWCNT. The peaks around 43° are due to the (1 1 0) and (1 0 0) graphitic planes plus small amount of catalyst particle encapsulated inside the walls of the MWCNTs.

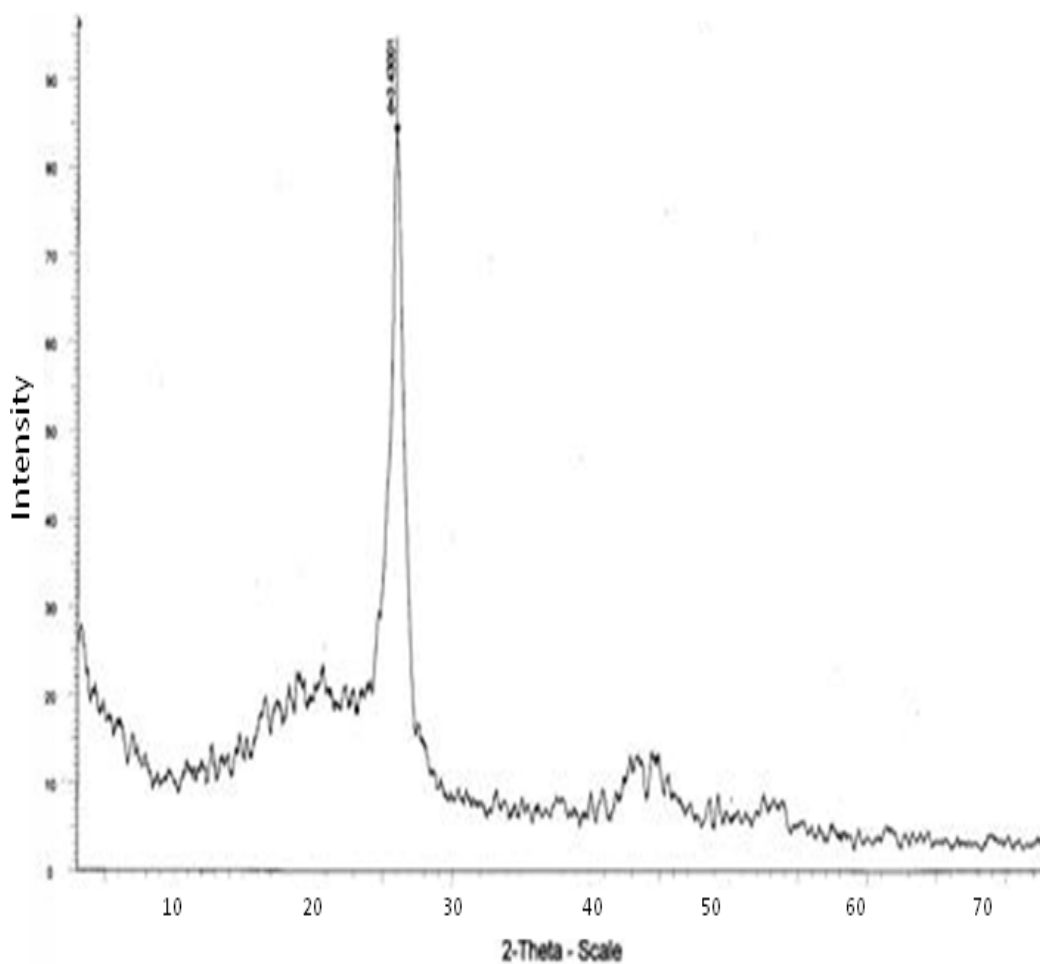


Figure 5.5 XRD pattern of Multi-walled carbon nanotubes

5.2 Mechanical Properties of Multiwalled Carbon Nanotubes Carbon Fiber Epoxy Composites

5.2.1 Flexural Properties

Figure 5.6 and 5.7 show variation in flexural strength and flexural modulus of different samples prepared by solvent casting method with varying amount of carbon fibers and carbon nanotubes.

Strength of neat Epoxy Resin = 70 MPa

Flexural Modulus of Neat Epoxy = 1.8 GPa

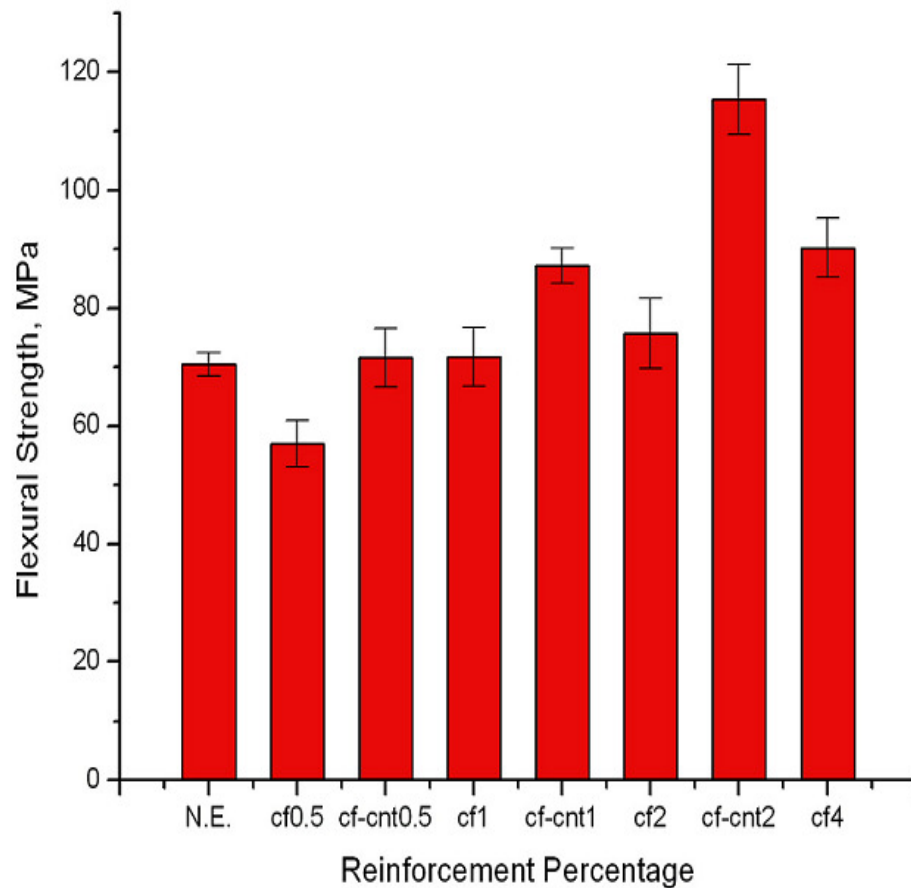


Figure 5.6 Flexural Strength

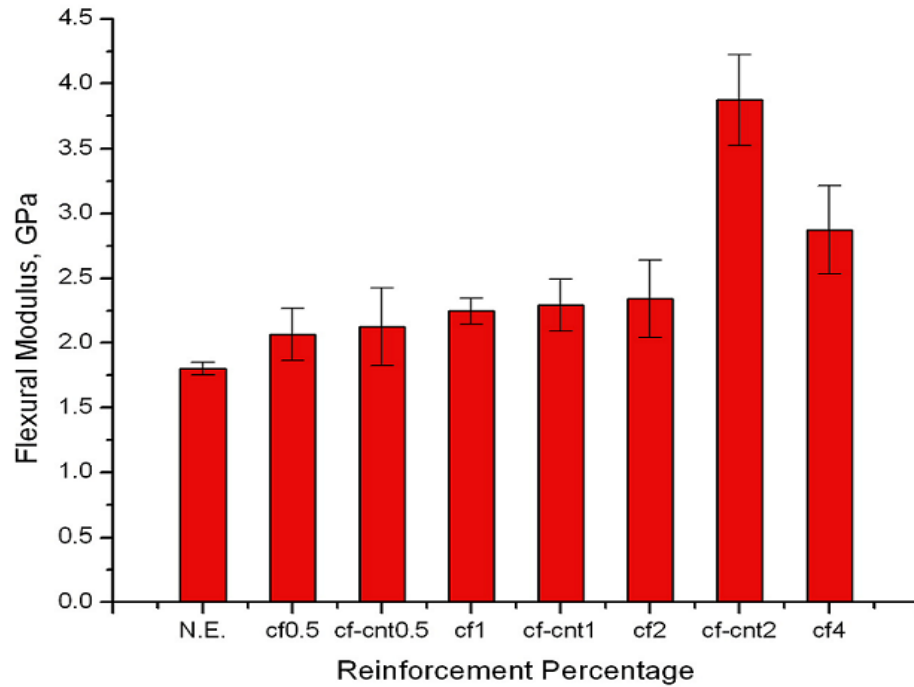


Figure 5.7 Flexural Modulus

5.2.2 Hardness

Fig 5.8 Shows the variation in Shore schleroscope hardness for various specimens

Shore Schelroscope Hardness of Neat Epoxy = 80

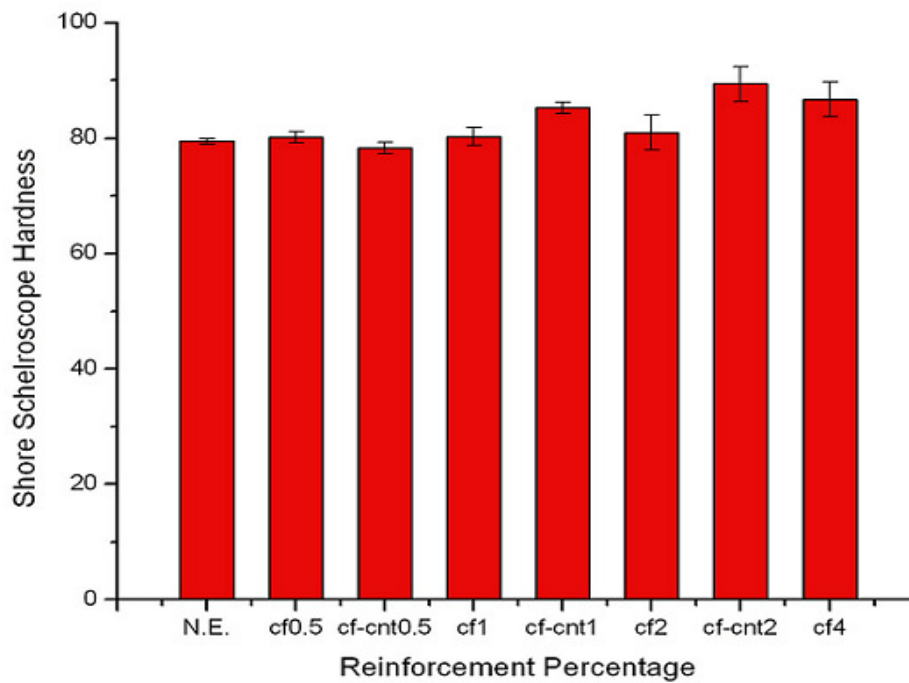


Figure 5.8 Shore Schleroscope Hardness

For specimens with 0.5% carbon fiber and carbon nanotube and 1% carbon fiber by wt. in polymer matrix the strength is same as that of neat epoxy. No significant effect was observed. However we observe that highest strength is achieved at specimen with 2% carbon fiber and multiwalled carbon nanotube by wt. each showing improvement of 64% compared to neat epoxy. This can be attributed to proper dispersion of carbon nanotubes and carbon fiber in polymer matrix. In case if 1% carbon fiber and carbon nanotubes by wt. there is improvement of 24% compared to neat epoxy. For 4% carbon fiber by wt. there is improvement of 28%. The decrease compared to 2% carbon fiber and carbon nanotube by wt. is due to relatively poor wetting of carbon fiber. There is gradual increase in flexural modulus from neat epoxy to 2% carbon fiber by wt. in epoxy matrix until there is steep increase for 2% carbon fiber and carbon nanotubes. This is due to proper wetting and rigidity provided by carbon nanotubes. Effect of carbon nanotube is more prominent due to its high abstract ratio. All the samples with different filler content showed density 1.15-1.2g/cc.

There is no significant improvement in hardness compared to neat epoxy for 0.5%, carbon fibers and carbon nanotubes by weight. However for 2% carbon fiber and carbon nanotubes by wt. there is relatively better improvement of 12.5% over the neat epoxy. This is due to rigidity provided by well dispersed carbon fibers and carbon nanotubes.

5.3 Electrical Properties

5.3.1 Electrical Conductivity

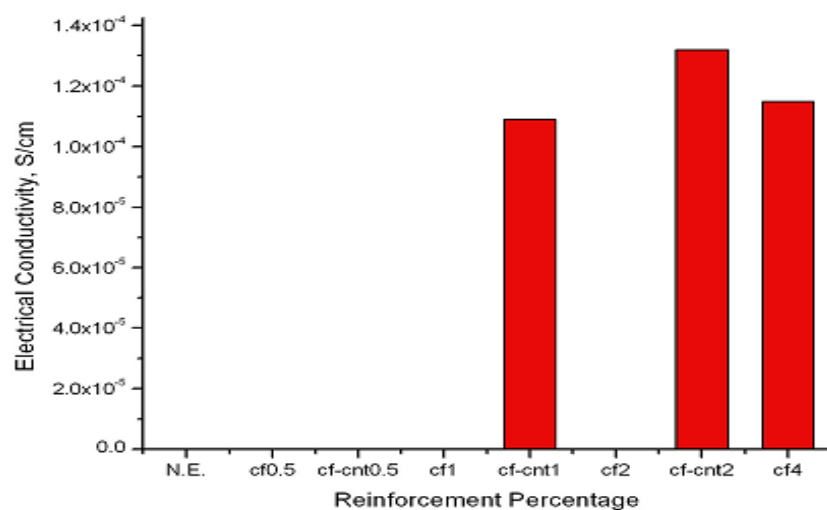


Figure 5.9 Variation in electrical conductivity in different specimens

The electrical conductivity of the composite specimens was measured by 4-point contact method. Kiethley 224 programmable current source was used for providing current. The voltage drop was measured by Keithley 197 A auto ranging micro volt DMM. The electrical conductivities of the pellets can be calculated by considering the sample dimensions as:

$$\sigma = \frac{L}{RA}$$

Electrical Conductivity measured in Seimens/cm is observed highest for 2% carbon fiber and carbon nanotube by wt. at 1.2×10^{-4} . For 4% carbon fiber specimen and 1% carbon fiber and carbon nanotube by wt. electrical conductivity is less. For other specimens on conductivity is observed due to the lower limit of 10^{-5} S/cm of the instrument.

5.4 Morphology study by Scanning Electron Microscope

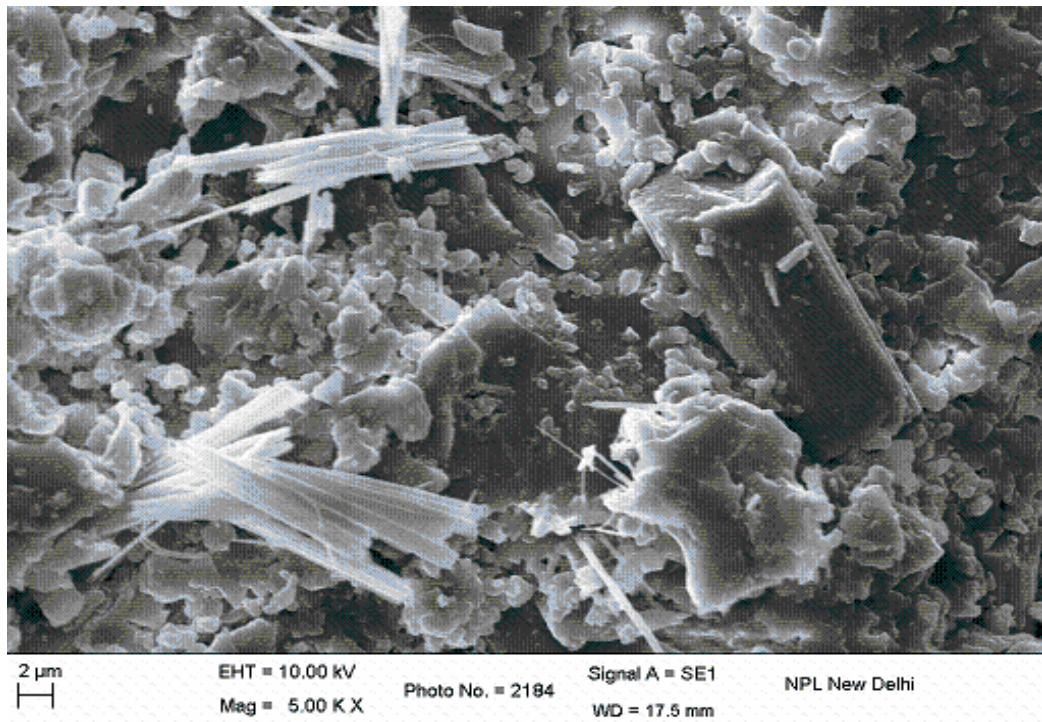


Figure 5.10

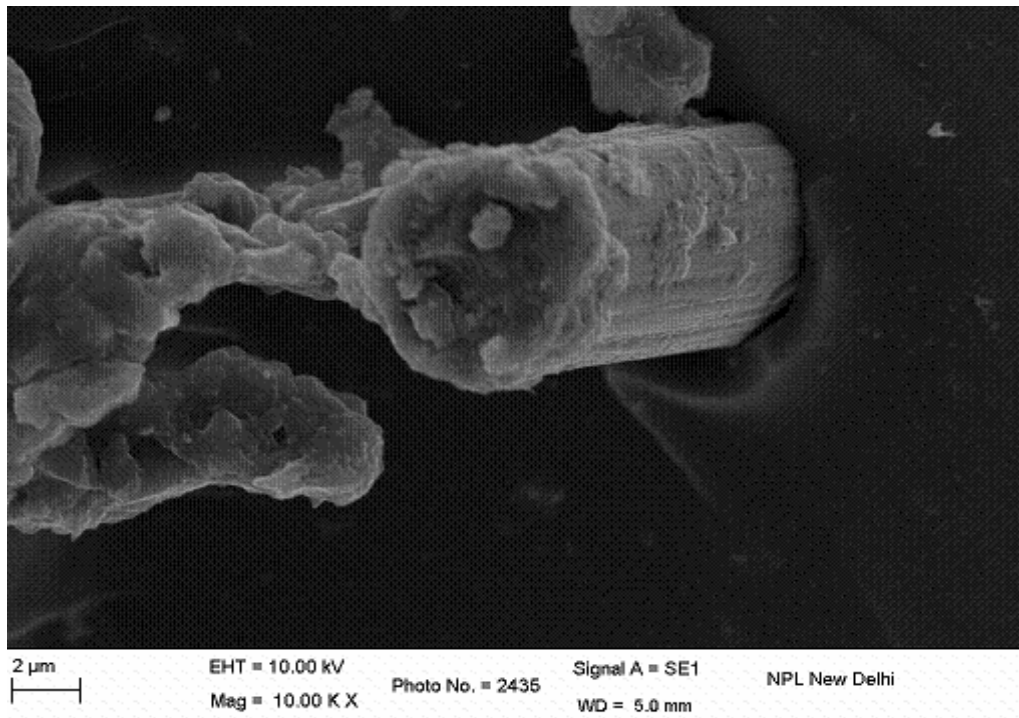


Figure 5.11

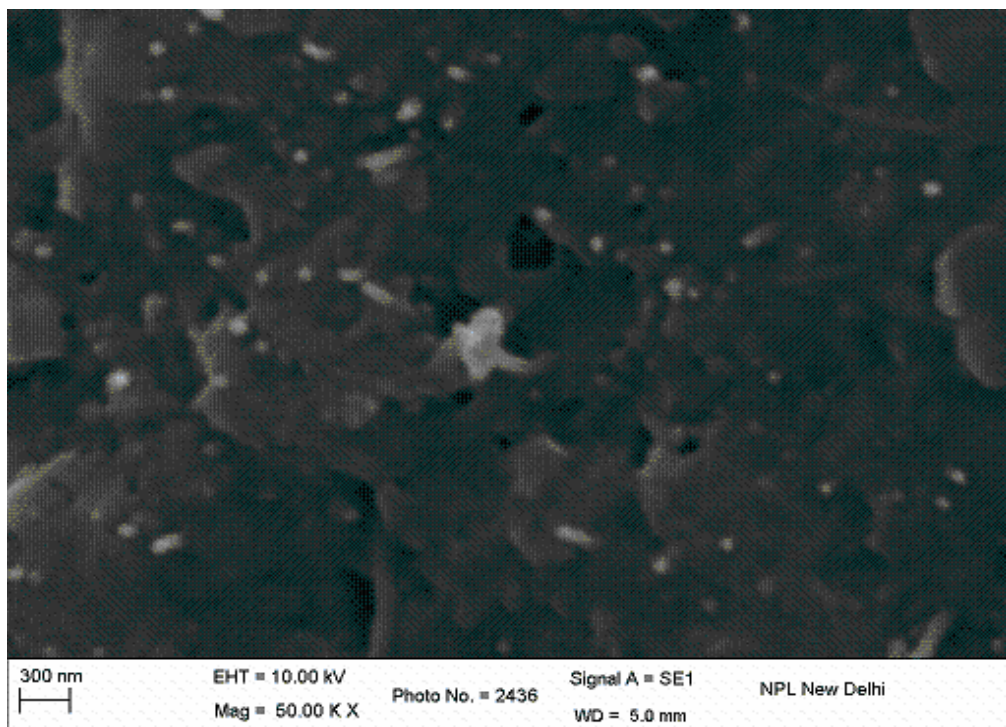


Figure 5.12

Fig 5.10, 5.11 and 5.12 show the SEM micrograph of 1%carbon fiber + 1% MWCNT epoxy composite specimen

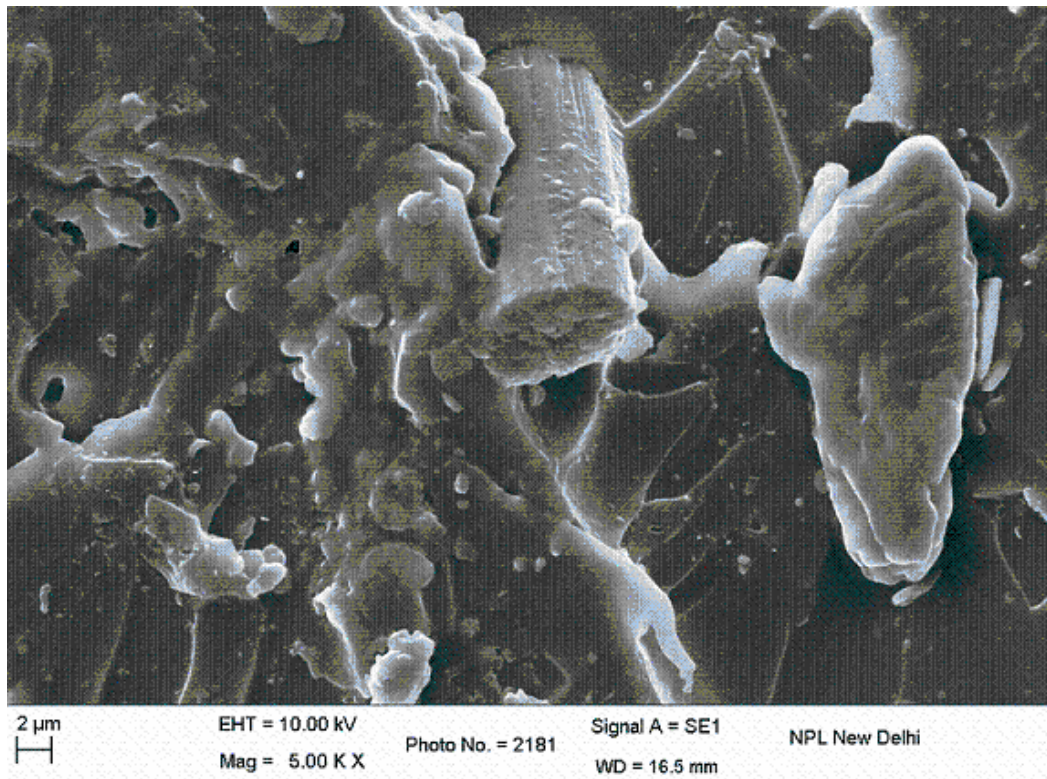


Figure 5.13

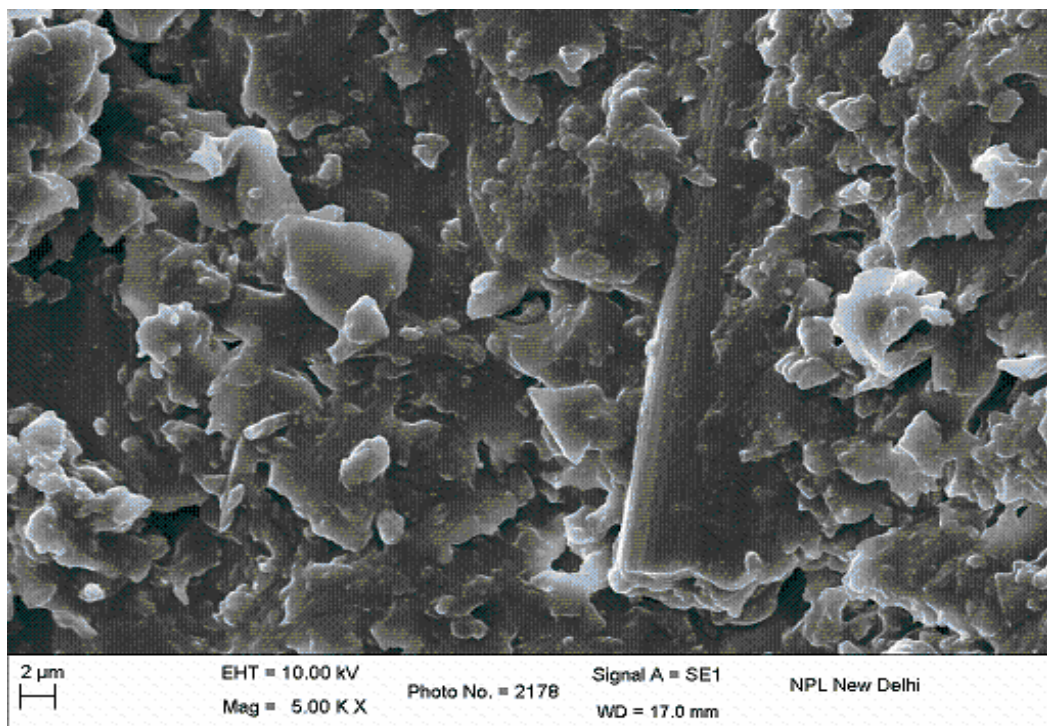


Figure 5.14

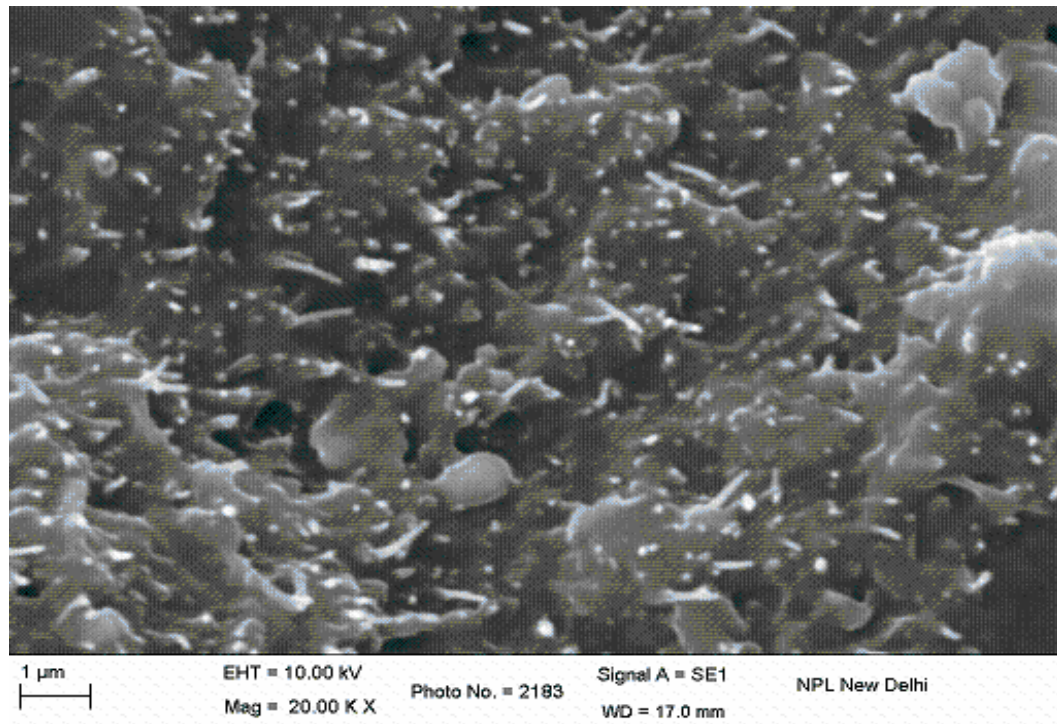


Figure 5.15

Fig 5.13, 5.14 and 5.15 shows SEM micrographs of 2% carbon fiber + 2% MWCNT epoxy composite specimen

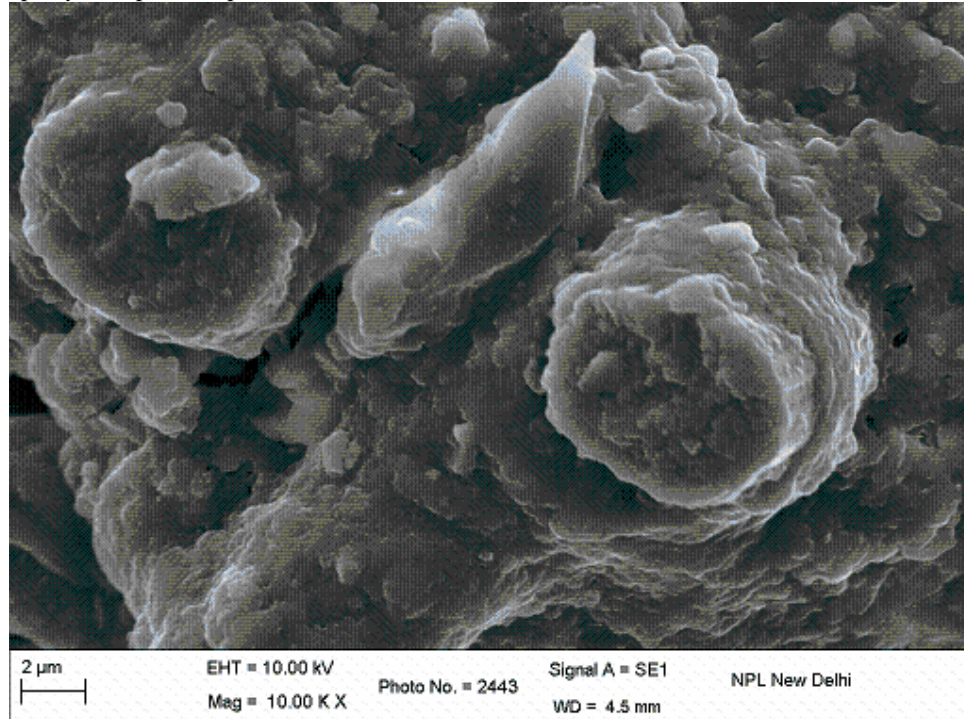


Figure 5.16

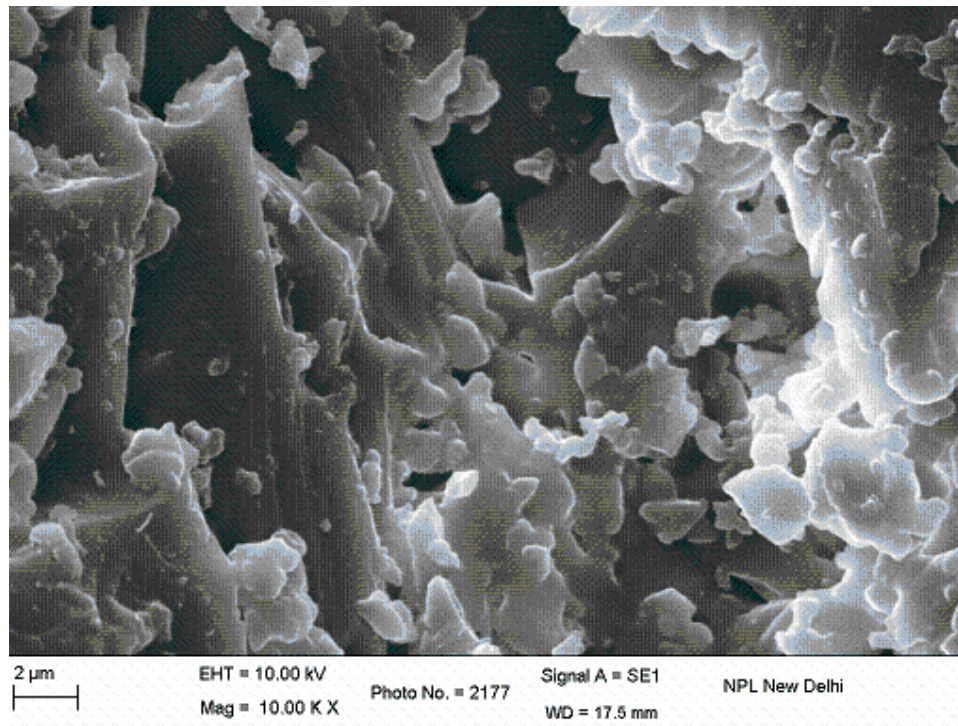


Figure 5.17

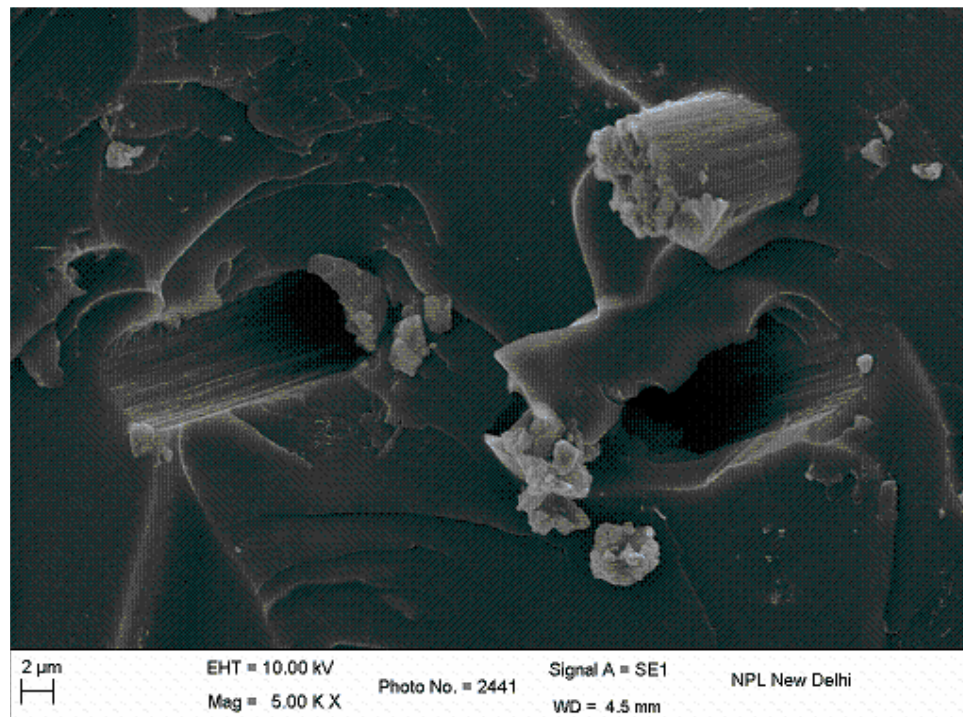


Figure 5.18

Fig 5.16, 5.17 and 5.18 show the SEM micrographs of 4% carbon fiber epoxy composite specimen

In figs. 5.10, 5.11 and 5.12 we can observe carbon fibers and carbon nanotubes dispersed in epoxy matrix in 1% carbon fiber and carbon nanotube by wt. .

In figs. 5.13, 5.14 and 5.15 concentration of carbon fibers and carbon nanotubes have increased.

In figs 5.16, 5.17 and 5.18 higher concentration of carbon fibers are observed. However in fig. 5.18 we can see some fibers are ejected off. This is the reason for decrease in mechanical properties of 4% carbon fibers by wt. in epoxy matrix. Epoxy resin does not completely wet with the fibers.

CHAPTER 6 CONCLUSIONS

MWCNTs have been synthesized by Chemical Vapour Deposition Method using toluene as precursor and ferrocene as catalyst in inert atmosphere. The yield of MWCNTs obtained is approximately 25%. The successful fabrications of MWCNT-carbon fiber-epoxy hybrid composites with varying the fraction of as produced MWCNTs and carbon fiber were carried out by resin casting .

The SEM, TEM, XRD, and TGA study confirmed the better quality of as produced MWCNTs. The Mechanical and electrical properties of carbon fibers and MWCNTs and carbon fibers reinforced epoxy composites were studied.

From our study we conclude that flexural strength improved by 64% in 2% carbon fiber-MWCNTS reinforced epoxy composites compared to neat epoxy. With density of 1.16g/cc specific strength of 103.5 kN·m/kg, slightly higher than steel. The Flexural Modulus increased by 200% in 2% carbon fiber-MWCNTS reinforced epoxy composites compared to neat epoxy. Hardness also improved by nearly 12%. The maximum electrical conductivity is observed for 2 wt% MWCNT/carbon fiber/epoxy hybrid composites composite is 1.2×10^{-4} S/cm. The morphology and degree of dispersion of MWCNT and carbon fibers in the epoxy matrix at different magnification was investigated using scanning electron microscope (SEM). The hybrid composites be used in automobile components. They can be used as anti static agent, in electrostatic discharge applications and in electronic casings

CHAPTER 7

SCOPE FOR FUTURE WORK

Polymers and polymer matrix composite materials are being utilized in an increasing number of industrial applications including transportation, automotive, aerospace, defence, sporting goods, energy and infrastructure sectors. This is due to their high durability, high strength, light weight, design and process flexibility, etc. Polymers such as epoxy (Ruiz et al 1998), thermoplastics (Fiege et al 1999), gels (Gomes et al 1999), as well as poly (methyl methacrylate) (PMMA) (Laurie et al 1998) have been used as the matrix.

The conductivity, strength, elasticity, toughness, and durability of formed composites may all be substantially improved by the addition of nanotubes. The very high aspect ratio of some carbon nanotubes may also enable them to be aligned with one axis of the composite. This high axial electrical conductivity offers the potential for fabricating conducting polymers. Carbon nanotubes could replace conventional conductive fillers for a range of applications like electrostatic discharge (ESD) and electromagnetic interference (EMI) shielding, and a much lower loading of carbon nanotubes can be used to achieve desired conductivity levels

For nearly a decade of research, many studies have been conducted and it has been expected that CNTs could play a role as an excellent reinforcement in the polymer composite that has not yet been fully realized (Schadler et al 1998; Allaoui et al 2002; Wong et al 2003). Such studies were of value in understanding the reasons for composite failure and in identifying the critical issues, which need to be addressed.

The factors like intratube load transfer in MWNTs and shearing in SWNT bundles are the central issues for the production of composites with exceptional mechanical properties. In spite of the obstacles in the development of nanotube-based composites, the good load transfer measured between a matrix and CNTs is very encouraging for the future. Now that these problems have been identified, we believe that solutions will be found for making CNT polymer composites in which the exceptional Young's modulus and theoretical strength of CNTs is achieved.

Since filler content could not be increased further beyond 4% due to increased high viscosity of the filled matrix. Chopped fiber and carbon nanotubes content could be increased by other methods or techniques like compression molding or vacuum assisted resin transfer molding.

Other fibers like glass and aramid fibers could also be filled along with carbon nanotubes. Aramid fiber may provide high impact strength. Such Composites could be used as armor shield in military applications

References

- 1 "Carbon – Naturally occurring isotopes". WebElements Periodic Table. Retrieved 2008-10-09.
- 2 "Periodic Table: Date of Discovery". Chemical Elements.com. Retrieved 2007-03-13.
- 3 "Timeline of Element Discovery". Retrieved 2007-03-13.
- 4 Chemistry Operations (December 15, 2003). "Carbon". Los Alamos National Laboratory. Retrieved 2008-10-09.
- 5 Greenville Whittaker, A. (1978). "The controversial carbon solid–liquid–vapour triple point". *Nature* 276 (5689): 695–696. doi:10.1038/276695a0.
- 6 Zazula, J. M. (1997). "On Graphite Transformations at High Temperature and Pressure Induced by Absorption of the LHC Beam". CERN. Retrieved 2009-06-06..
- 7 Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. (2008). "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene". *Science* 321 (5887): 385. Bibcode 2008Sci...321..385L. doi:10.1126/science.1157996. PMID 18635798. Lay summary.
- 8 Sanderson, Bill (2008-08-25). "Toughest Stuff Known to Man : Discovery Opens Door to Space Elevator". nypost.com. Retrieved 2008-10-09.
- 9 Peter Unwin. "Fullerenes(An Overview)". Retrieved 2007-12-08.
- 10 Ebbesen, T. W., ed (1997). *Carbon nanotubes—preparation and properties*. Boca Raton, Florida: CRC Press. ISBN 0849396026.
- 11 Dresselhaus, M. S.; Dresselhaus, G.; Avouris, Ph., ed (2001). "Carbon nanotubes: synthesis, structures, properties and applications". *Topics in Applied Physics* (Berlin: Springer) 80. ISBN 3540410864.

12 Nasibulin, Albert G.; Pikhitsa, P. V.; Jiang, H.; Brown, D. P.; Krasheninnikov, A. V.; Anisimov, A. S.; Queipo, P.; Moisala, A. et al. (2007). "A novel hybrid carbon material". *Nature Nanotechnology* 2 (3): 156–161. doi:10.1038/nnano.2007.37. PMID 18654245.

13 Nasibulin, A; Anisimov, Anton S.; Pikhitsa, Peter V.; Jiang, Hua; Brown, David P.; Choi, Mansoo; Kauppinen, Esko I. (2007). "Investigations of NanoBud formation". *Chemical Physics Letters* 446: 109–114. doi:10.1016/j.cplett.2007.08.050.

14 Vieira, R (2004). "Synthesis and characterisation of carbon nanofibers with macroscopic shaping formed by catalytic decomposition of C₂H₆/H₂ over nickel catalyst". *Applied Catalysis A* 274: 1–8. doi:10.1016/j.apcata.2004.04.008.

15 Clifford, Frondel; Marvin, Ursula B. (1967). "Lonsdaleite, a new hexagonal polymorph of diamond". *Nature* 214 (5088): 587–589. doi:10.1038/214587a0.

16 Harris, PJF; Gallagher, J. G.; Hargreaves, J. S. J.; Harris, P. J. F. (2004). "Fullerene-related structure of commercial glassy carbons". *Philosophical Magazine*, 84, 3159–3167 116 (3–4): 122. doi:10.1007/s10562-007-9125-6.

17 Rode, A. V.; Hyde, S. T.; Gamaly, E. G.; Elliman, R. G.; McKenzie, D. R.; Bulcock, S. (1999). "Structural analysis of a carbon foam formed by high pulse-rate laser ablation". *Applied Physics A-Materials Science & Processing* 69 (7): S755–S758. doi:10.1007/s003390051522.

18 Carbyne and Carbynoid Structures Series: Physics and Chemistry of Materials with Low-Dimensional Structures, Vol. 21 Heimann, R.B.; Evsyukov, S.E.; Kavan, L. (Eds.) 1999, 452 p., ISBN 0-7923-5323-4

19 Jenkins, Edgar (1973). *The polymorphism of elements and compounds*. ISBN 9780423875003. Retrieved 2011-05-01.

- 20 "World of Carbon – Interactive Nano-visualisation in Science &Engineering Edukation (IN-VSEE)". Retrieved 2008-10-09.
- 21 Carbon Nanofoam is the World's First Pure Carbon Magnet". Retrieved 2007-12-2
- 22 Lior Itzhaki; Altus, Eli; Basch, Harold; Hoz, Shmaryahu (2005). "Harder than Diamond: Determining the Cross-Sectional Area and Young's Modulus of Molecular Rods". *Angew. Chem. Int. Ed.* 44 (45): 7432.
- 23 Fullerene, Encyclopedia Britannica on-line
- 24 Iijima, S (1980). "Direct observation of the tetrahedral bonding in graphitized carbon black by high resolution electron microscopy". *Journal of Crystal Growth* 50: 675. doi:10.1016/0022-0248(80)90013-5.
- 25 ^{a b} Buseck, P.R.; Tsipursky, S.J.; Hettich, R. (1992). "Fullerenes from the Geological Environment". *Science* 257 (5067): 215–7. doi:10.1126/science.257.5067.215. PMID 17794751.
- 26 Kroto, H.W.; *et al.* (1985). "C₆₀: Buckminsterfullerene". *Nature* 318 (6042): 162–163. Bibcode 1985Natur.318..162K. doi:10.1038/318162a0.
- 27 Mraz, S.J. (14 April 2005). "A new buckyball bounces into town". *Machine Design*. 27 Pushparaj, V.L.; *et al.* (2007). "Flexible energy storage devices based on nanocomposite paper". *Proceedings of the National Academy of Sciences* 104 (34): 13574–7.
- 28 S Iijima. *Nature* 1991; 354: 56.
- 29 S Iijima. Helical microtubules of graphitic carbon. *Nature* 1991;354: 56–58.
- 30 M S Dresselhaus. Fullerenes: Down the straight and narrow. *Nature* 1992;358: 195–196.

- 31 Saravanababu Murugesan, Tae-Joon Park, Hoichang Yang, Shaker Mousa and Robert J. Linhardt, Blood Compatible Carbon Nanotubes - Nano-based Neoproteoglycans, *Langmuir* 2006; 22: 3461-3463.
- 32 Bianco A. et al. In *Nanotechnologies for the Life Sciences*. 2007 ; 10: 85–142
- 33 . H. W. Kroto, J. R. Heath, S. C. O'Brien, S. C. Curl, R. E. Smalley, *Nature* 318, 162 (1985) 391
34. S. Iijima, *Nature* 354, 56 (1991) 391
35. M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York 1996) 391
36. T. W. Ebbesen, *Carbon Nanotubes: Preparation and Properties* (CRC, Boca Raton 1997) 391
37. R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London 1998) 391
38. B. I. Yakobson, R. E. Smalley, *American Scientist* 85, 324 (1997) 391
39. P. M. Ajayan, *Chem. Rev.* 99, 1787 (1999) 391, 407
- 40 .C. Dekker, *Phys. Today*, 22 (May 1999) 391, 392
- 41 Mintmire, J.W.; Dunlap, BI; White, CT (3 February 1992). "Are Fullerene Tubules Metallic?". *Physical Review Letters* 68 (5): 631–634. Bibcode 1992PhRvL..68..631M. doi:10.1103/PhysRevLett.68.631. PMID 10045950.
- 42 Dekker, Cees (1999). "Carbon nanotubes as molecular quantum wires" (PDF). *Physics Today* 52 (5): 22–28. Bibcode 1999PhT....52e..22D. doi:10.1063/1.882658.
- 43 Applications of Carbon Nanotubes Pulickel M. Ajayan¹ and Otto Z. Zhou²
- 44 Iijima, Sumio (1991). "Helical microtubules of graphitic carbon". *Nature* 354 (6348): 56–58. Bibcode 1991Natur.354...56I. doi:10.1038/354056a0.

45 Ebbesen, T. W.; Ajayan, P. M. (1992). "Large-scale synthesis of carbon nanotubes". *Nature* 358 (6383): 220–222. Bibcode 1992Natur.358..220E. doi:10.1038/358220a0.

46 Lam CW, James JT, McCluskey R, Arepalli S, Hunter RL (2006). "A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risks". *Crit Rev Toxicol.* 36 (3): 189–217. doi:10.1080/10408440600570233.

47 Walker Jr., P. L.; Rakszawski, J. F.; Imperial, G. R. (1959). "Carbon Formation from Carbon Monoxide-Hydrogen Mixtures over Iron Catalysts. I. Properties of Carbon Formed". *J. Phys. Chem.* 63 (2): 133. doi:10.1021/j150572a002.

48 José-Yacamán, M.; Miki-Yoshida, M.; Rendón, L.; Santiesteban, J. G. (1993). "Catalytic growth of carbon microtubules with fullerene structure". *Appl. Phys. Lett.* 62 (6): 657. Bibcode 1993ApPhL..62..657J. doi:10.1063/1.108857.

49 Beckman, Wendy (2007-04-27). "UC Researchers Shatter World Records with Length of Carbon Nanotube Arrays". University of Cincinnati

. 50 N. Inami et al. "Synthesis-condition dependence of carbon nanotube growth by alcohol catalytic chemical vapor deposition method" *Sci. Technol. Adv. Mater.* 8 (2007) 292 free download

51 N. Ishigami; Ago, H; Imamoto, K; Tsuji, M; Iakoubovskii, K; Minami, N (2008). "Crystal Plane Dependent Growth of Aligned Single-Walled Carbon Nanotubes on Sapphire". *J. Am. Chem. Soc.* 130 (30): 9918–9924. doi:10.1021/ja8024752. PMID 18597459.

52 Pinilla JL, Moliner R, Suelves I, Lazaro M, Echegoyen Y, Palacios J (2007). "Production of hydrogen and carbon nanofibers by thermal decomposition of methane using metal catalysts in a fluidized bed reactor". *International Journal of Hydrogen*

53 Muradov N (2001). "Hydrogen via methane decomposition: an application for decarbonization of fossil fuels". *International Journal of Hydrogen Energy* 26 (11): 1165–1175. doi:10.1016/S0360-3199(01)00073-8.

54 Eftekhari, A.; Jafarkhani, P; Moztarzadeh, F (2006). "High-yield synthesis of carbon nanotubes using a water-soluble catalyst support in catalytic chemical vapor deposition". *Carbon* 44 (7): 1343. doi:10.1016/j.carbon.2005.12.006.

55 Guo, Ting; Nikolaev, Pavel; Rinzler, Andrew G.; Tomanek, David; Colbert, Daniel T.; Smalley, Richard E. (1995). "Self-Assembly of Tubular Fullerenes". *J. Phys. Chem.* 99 (27): 10694–10697. doi:10.1021/j100027a002.

56 Guo, Ting; Nikolaev, P; Thess, A; Colbert, D; Smalley, R (1995). "Catalytic growth of single-walled nanotubes by laser vaporization" (PDF). *Chem. Phys. Lett.* 243: 49–54. Bibcode 1995CPL...243...49B. doi:10.1016/0009-2614(95)00825-O.

56 Jordan, J.; Jacob, K. I.; Tannenbaum, R.; Sharaf, M. A.; Jasiuk, I.; "Experimental trends in polymer nanocomposites - a review", *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing* 393 (1-2), 1-11, (2005).

57 J.U. Park, S. Cho, K.S. Cho, K.H. Ahn, S. J. Lee, and S.J. Lee, *Korea-Australia Rheology Journal*, 17, 41 (2005). [71] J.N. Coleman, U. Khan, W.J. Blau, and Y.K. Gun'ko, *Carbon*, 44, 1624 (2006).

58 Kim, J. A.; Seong, D. G.; Kang, T. J.; Youn, J. R.; "Effects of surface modification on rheological and mechanical properties of CNT/epoxy composites", *Carbon* 44 (10), 1898-1905, (2006).

59 K.W. Putz, C.A. Mitchell, R. Krishnamoorti, and P.F. Green, *J. Polym. Sci. Part B: Polym Phys.*, 42, 2286 (2004).

60 Jung, S. H., Kim, M. R., Jeong, S. H., Kim, S. U., Lee, O. J., Lee, K. H., Suh, J. H., and Park, C. K., *Applied Physics A-Materials Science & Processing*, 76, (2), 285-286,(2003).

61. Niyogi, S., Hamon, M. A., Hu, H., Zhao, B., Bhowmik, P., Sen, R., Itkis, M. E., and Haddon, R. C. Chemistry of Single-Walled Carbon Nanotubes. *Accounts of Chemical Research* 35(12), 1105-1113. 2002.
62. P. Avouris, *Chemical Physics* 281, 429-445 (2002).
63. Tans, Sander J., Devoret, Michel H., Dal, Hongjie, Thess, Andreas, Smalley, Richard E., Geerligs, L. J., and Dekker, Cees. Individual single-wall carbon nanotubes as quantum wires. *Nature (London)* 386(6624), 474-477. 1997.
64. P. M. Ajayan and O. Z. Zhou, *Carbon Nanotubes* 80, 391-425 (2001).
65. M. Damnjanovic, I. Milosevic, T. Vukovic, R. Sredanovic, *Physical Review B*.
- 66 Yu, Min-Feng; Lourie, Oleg; Dyer, Mark J.; Moloni, Katerina; Kelly, Thomas F.; Ruoff, Rodney S. (28 January 2000). "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load". *Science* 287 (5453): 637–640. Bibcode 2000Sci...287..637Y. doi:10.1126/science.287.5453.637. PMID 10649994.
- 67 T. Filleter, R. A. Bernal, S. Li, and H. D. Espinosa, "Ultra-high Strength and Stiffness in Cross-Linked Hierarchical Carbon Nanotube Bundles," *Adv. Mater.*, (in press), 2011.
- 68 B. Peng, M. Locascio, P. Zapol, S. Li, S. L. Mielke, G. C. Schatz, and H. D. Espinosa, "Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements," *Nature Nanotechnology*, vol. 3, pp. 626 - 631, 2008.
- 69 T. Filleter, R. A. Bernal, S. Li, and H. D. Espinosa, "Ultra-high Strength and Stiffness in Cross-Linked Hierarchical Carbon Nanotube Bundles," *Adv. Mater.*, (in press), 2011.
- 70 Guiseppi-Elie A, Lei C H and Baughman R H. Direct electron transfer of glucose oxidase on carbon nanotubes. *Nanotechnology* 2002; 3: 559–64.

71 Chen X, Tam U C, Czapinski J L, Lee G S, Rabuka D, Zettl A and Bertozzi C R J Am Chem Soc 2006; 128: 6292–3.

72 Ding R, Lu G, Yan Z, Wilson M. J Nanosci & Nanotech 2001: 17-29.

73 Rajashree Hirlekar, Manohar Yamagar, Harshal Garse, Mohit Vilasrao Kadam. Asian J Pharm & Cli Res 2009;2(4).

74 Morinobu Endo, Michael S Strano & Pulickel M Ajayan. Appl Physics 2008;111:13–62.

75 Wenrong Yang, Pall Thordarson, J Justin Gooding, Simon P Ringer and Filip Braet. Nanotechnology 2007;18: 412001.

76 Pai P, Nair K, Jamade S, Shah R, Ekshinge V, Jadhav N. Cur Pharma Res J 2006;1:11-15.

77 Galanzha El et al. Nat Nanotech 2009;12: 855-860.

78 Sarojini S, Rajasekar S and Koumaravelou K. Int J Pharm & Bio Sci 2010;1(4).

79 Pai P, Nair K, Jamade S, Shah R, Ekshinge V, Jadhav N. Curr Pharma Res J 2006;1:11-

80 W.J. Cantwell, J Morton (1991). "The impact resistance of composite materials - a review". *Composites* 22 (5): 347–62. doi:10.1016/0010-4361(91)90549-V

81 "How It Is Made". Retrieved 2010-04-04., <http://www.zoltek.com/carbonfiber/made.php>

82 CARBON FIBERS Updated: April, 2004 - Raghavendra R. Hegde, Atul Dahiya, M. G. Kamath (Monika Kannadaguli & Haoming Rong)
<http://www.engr.utk.edu/mse/Textiles/CARBON%20FIBERS.htm>

83 <http://www.tohotenax-eu.com/en/products/whats-carbon-fiber.html>

84. Lee, H., and Neville, K., "*Handbook of Epoxy Resins*", McGraw-Hill, Inc., New York, 1975.

85. Saunders, K. J., "*Organic Polymer Chemistry*", Chapman & Hall, New York, p. 412-435, 2 nd ed., 1988.

86. Pham, H. A. Q., Maurice and Marks, J., "*Encyclopedia of Polymer Science and Technology*", John Wiley and sons, New York, v. 9, p. 678-795, 1986.

87. May, C. A., "*Introduction to Epoxy Resins*", in *Epoxy Resins Chemistry and Technology*, May, C. A., 2 nd ed., Marcel Dekker, Inc., New York, p. 1-12, 1988.

88 .Norm Lambert. "Chips Flooring". Epoxy.com. Retrieved 2010-07-24.

89 .Norman L. Lambert. "Quartz Flooring". Epoxy.com. Retrieved 2010-07-24.

90. Barton, J. M., Hamerton, I., Howlin, B. J., Jones, J. R., and Liu, S., "*Studies of Cure Schedule and Final Property Relationships of a Commercial Epoxy Resin Using Modified Imidazole Curing Agents*", *Polymer*, v. 39, p. 1929-1936, 1998

91 Ismail, N. "Strengthening of bridges using CFRP composites." Beijing, 217-224.

92. Z. Zhao and J. Gou "Improved fire retardancy of thermoset composites modified with carbon nanofibers" *Sci. Technol. Adv. Mater.* 10 (2009) 015005