SYNTHESIS OF CARBON NANOTUBES AND THEIR USE IN PHENOLIC COMPOSITES

A major project submitted in the partial fulfillment of the requirement for
the award of the degree of

MASTER OF ENGINEERING
IN
POLYMER TECHNOLOGY

<u>SUBMITTED BY</u>

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CERTIFICATE

This is to certify that Mr. Kunwar Devendra Swaroop has satisfactorily completed the project work entitled **“synthesis of carbon nanotubes and their use in phenolic composites”** in partial fulfillment of the award of the degree of Master of Technology in Polymer Technology of Delhi College of Engineering, University of Delhi, Delhi, during the session of 2006-2007. This work has not been submitted in part or full in any other university or institution for the award of any degree or diploma.

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ACKNOWLEDGEMENT

I would like to thank *Dr. R. B. Mathur, Scientist 'F'* of the *Carbon Technology Unit*, National Physical Laboratory, New Delhi for giving me the opportunity to work and complete my entire project under his valuable guidance.

I am heartily thankful to my head of department Dr. G. L. Verma for his valuable support in recommending me in such a reputed organization and unconditional support throughout the project work.

I am greatly indebted to my internal supervisor *Dr. D. Kumar, Department of Applied Chemistry & Polymer Technology,* Delhi University, for guiding me and helping me in all the related problems before and during the project period from such a long apart.

I am thankful to *Mr. B.P. Singh, Scientist 'B'* of the same unit for his valuable and continuous guidance during the course of the entire project.

I am highly indebted to *Dr. T. L. Dhami* for all their guidance. They gave significant inputs in terms of methodological guidance as the work progressed. It was almost impossible to come up with this kind of work without the valuable insights provided by them during discussions.

I would like to thank *Dr. C. Lal and Dr. S. R. Dhakate* for their moral support and valuable suggestions. They were the back bone of my inspiration during the entire work.

I would not like to miss the opportunity of giving my heartiest gratitude to *Dr. Vikram Kumar, Director,* National Physical Laboratory, a Govt. of India Organization and *Dr. A. K. Agarwal,* head *Human Resource and Management Group,* for giving me the opportunity to complete my M. E. Project and placing me to the right department of such a prominent and leading laboratory of the nation. I convey my sincere thanks to Dr. A. K. Gupta, Head Engineering Material Division of N.P.L.

I would like to convey special thanks to D. D. Saklani, J.C.Ghawana, V.K.Chaddah, N.K. Sharma, B.D. Chauhan, Ms. Shaveta Sharma and Mrs. Shailja Pandey for helping me in related works. They improved the quality of the work with their best experience in practical work.

Last but not the least I would like to convey my heartiest and warmth gratitude to all the scientists and supporting staff of Carbon Technology Unit, National Physical Laboratory through out the entire Project and giving me valuable suggestion, support and inspiration during the project sharing their valuable time.

Lastly, I would like to thank the people that made my stay here in N.P.L. an exciting and memorable experience forwarding helping hands in all the concerned matter. I convey my special thanks to our teachers and our H.O.D.

Finally, to my father, my beloved brothers, go my eternal gratitude for their constant love and support.

Kunwar Devendra Swaroop

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ABSTRACT

Carbon nanotube is a fascinating material having outstanding properties have inspired the researchers to adopt their properties for application point of view. In this study firstly carbon nanotubes have been synthesized by dc arc discharge technique. The parameters such as pressure inside the chamber, amount of the catalysts and the amount of the catalyst Fe were tried to optimize to get higher yield. Carbon nanotubes were obtained by the same technique on chamber deposits.

Carbon nanotubes synthesized by above technique have been characterized by scanning electron microscopy, X-ray diffraction, and TGA.

The outstanding mechanical properties of carbon nanotubes have also attracted researcher to adopt CNTs as reinforcement for composites. In this study carbon nanotubes were reinforced with phenolic resin in 0 and 2% volume fraction. The Composite samples prepared in this study were of dog bone shape with volume of 1 cc^3 approximate. The mechanical properties, tensile strength and tensile modulus of these samples were obtained by universal testing machine (INSTRON).

Chapter 1: Objective of the project

1. The synthesis of carbon nanotubes from electric arc discharge method by using different catalyst proportions.

2. The characterization of produced carbon nanotubes by scanning electron microscopy, Thermo gravimetric analysis & X-ray diffraction techniques.

3. To prepare reinforced Carbon nanotubes composite and to investigate its mechanical properties

Chapter 2: Introduction

2. Introduction

2.1 General

Carbon is a remarkable element, which possesses the exceptional ability of stable clusters in the vapor phase. Yet until recently we knew for certain of just two types of all carbon crystalline structure, the naturally occurring allotropes diamond and graphite. In August 1985, Kroto discovered the Fullerene, which was called third allotrope of carbon.

2.2 Discovery of fullerenes and Carbon Nanotubes

Fullerenes are large, closed-cage, carbon clusters and have several special properties that were not found in any other compound before. Therefore, fullerenes in general form an interesting class of compounds that surely will be used in future technologies and applications. Before the first synthesis and detection of the smaller fullerenes C_{60} and C_{70}, it was generally accepted that these large spherical molecules were unstable. However, some Russian scientists already had calculated that C_{60} in the gas phase was stable and had a relatively large band gap.

As is the case with numerous, important scientific discoveries, fullerenes were accidentally discovered. In 1985, Kroto and Smalley found strange results in mass spectra of evaporated carbon samples. Herewith, fullerenes were discovered and their stability in the gas phase was proven. The search for other fullerenes had started.

Carbon Nanotubes were discovered by Iijima and Coworkers in 1991, while examining fullerenes and containing carbon soot. Carbon Nanotubes have been investigated by many researchers all over the world. Their large length (up to several microns) and small diameter (A few nanometers) result in a large aspect ratio. They can be seen as the nearly one-dimensional form of fullerenes. Therefore, these materials are expected to possess additional interesting electronic, mechanical and molecular properties. Especially in the beginning, all theoretical studies on carbon nanotubes focused on the influence of the nearly one-dimensional structure on molecular and electronic properties.

The all four allotropes of carbon are shown in the figure 2.1.

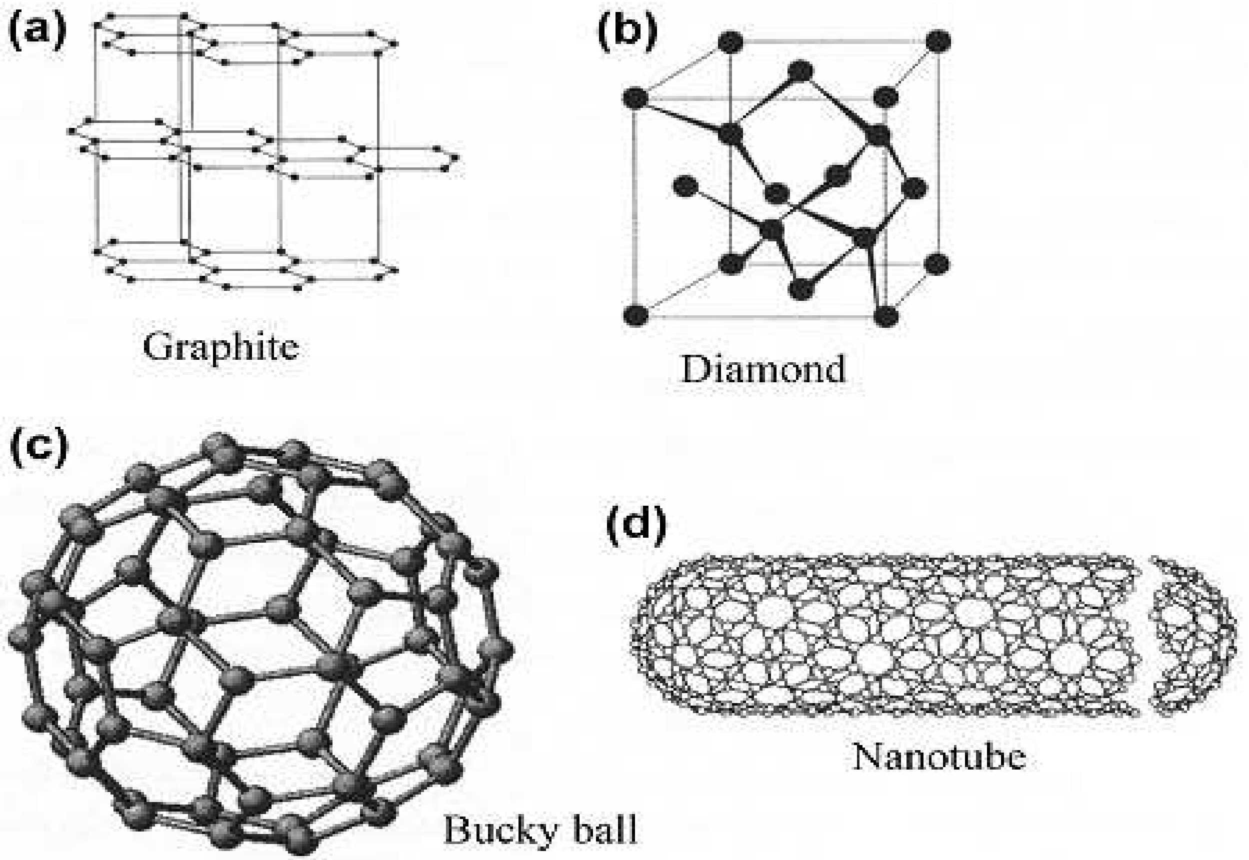


Figure 2.1- Allotropes of carbon

2.3 Classification of Carbon Nanotubes

Two variations of carbon nanotubes exist that contrast in general appearance, structure and graphitization.

1) Multi-walled nanotubes (MWNTs)
2) Single-walled nanotubes (SWNTs)

A graphitic multi-walled carbon nanotubes, which are the first type were found in 1991, and single-walled carbon nanotubes were found in 1993. The former may be considered to be single-crystal nanosized ideal graphite fibers the later are true elongated Fullerene tubes.

SWNTs consist of singular graphene cylindrical walls with diameter ranging between 1and 2 nm as shown in figure 2.2 (a). MWNTs have thicker walls, consisting of several coaxial grapheme cylinders separated by a spacing of about D 0.34nm (about 3-5% larger than single crystal graphite spacing) as shown in figure 2.2 (b). The outer diameter of MWNTs range between 2 - 25nm and the inner hollows range from 1 to 8 nm.
The aspect ratio of nanotubes varies with diameter, but the average length can be several micrometers. Individual SWNTs have uniform diameter, although when formed they also show a strong tendency to pack together in large bundles.

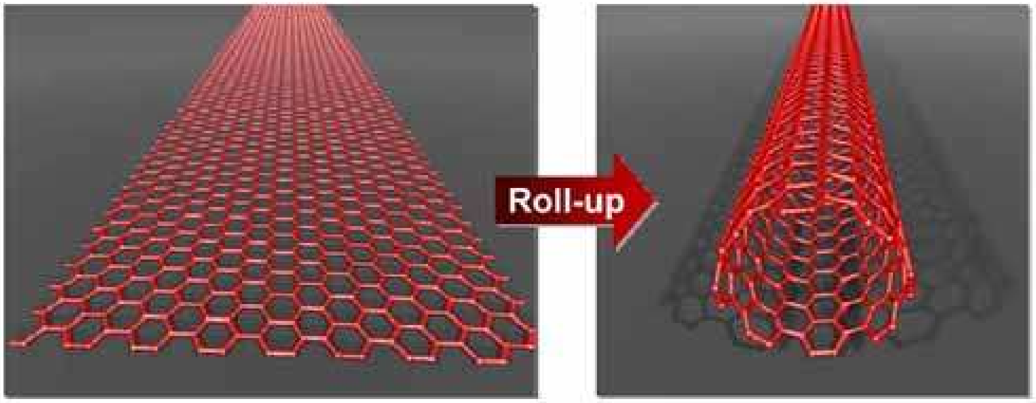


Figure 2.2 (a): A graphene layer folded into the single walled carbon nanotube

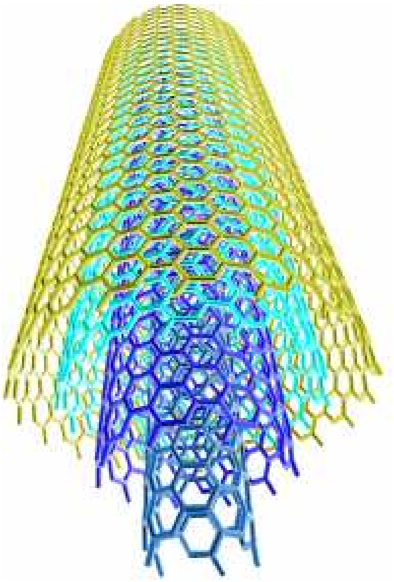


Figure 2.2 (b): Multi-walled nanotube

A multi-wall carbon nanotube (MWCNT) can similarly be considered to be a coaxial assembly of cylinders of SWCNTs, one within another; the separation between tubes is about equal to that between the layers in natural graphite.

2.4 Carbon Nanotubes structure and defects

Many exotic structures of fullerenes exist: regular spheres, cones, tubes and also more complicated and strange shapes. Here we will describe some of the most important and best-known structures.

Single Walled Nanotubes (SWNT) can be considered as long wrapped graphene sheets. As stated before, nanotubes generally have a length to diameter ratio of about 1000 so they can be considered as nearly one-dimensional structures.

A SWNT consists of two separate regions with different physical and chemical properties. The first is the sidewall of the tube and the second is the end cap of the tube. The end cap structure is similar to or derived from a smaller fullerene, such as C_{60}.

C-atoms placed in hexagons and pentagons form the end cap structures. It can be easily derived from Euler's theorem that twelve pentagons are needed in order to obtain a closed cage structure which consists of only pentagons and hexagons. The combination of a pentagon and five surrounding hexagons results in the desired curvature of the surface to enclose a volume. A second rule is the isolated pentagon rule that states that the distance between pentagons on the fullerene shell is maximized in order to obtain a minimal local curvature and surface stress, resulting in a more stable structure. The smallest stable structure that can be made this way is C_{60} the one just larger is C_{70} and so on. Another property is that all fullerenes are composed of an even number of C-atoms because adding one hexagon to an existing structure means adding two C-atoms.

The other structure of which a SWNT is composed is a cylinder. 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 discreet set of directions in order to form a closed cylinder. Two atoms in the graphene sheet are chosen, one of which servers 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.

SWNTs with different chiral vectors have dissimilar properties such as optical activity, mechanical strength and electrical conductivity

After ideal structures without flaws, we discuss the possible desirable or undesirable defects. Deformations, such as bends and nanotube junctions, are introduced by replacing a hexagon with a heptagon or pentagon. Deformations can be inward or outward and, among others, electrical properties are seriously changed by these deformations. Another class of defects is caused by impurities that are built in during or after the nanotube growth process; Compounds that can be incorporated into the structure are for example catalyst particles.

A graphene sheet can be rolled more than one way, producing different types of carbon nanotubes. The three main types are armchair, zigzags, and chiral.

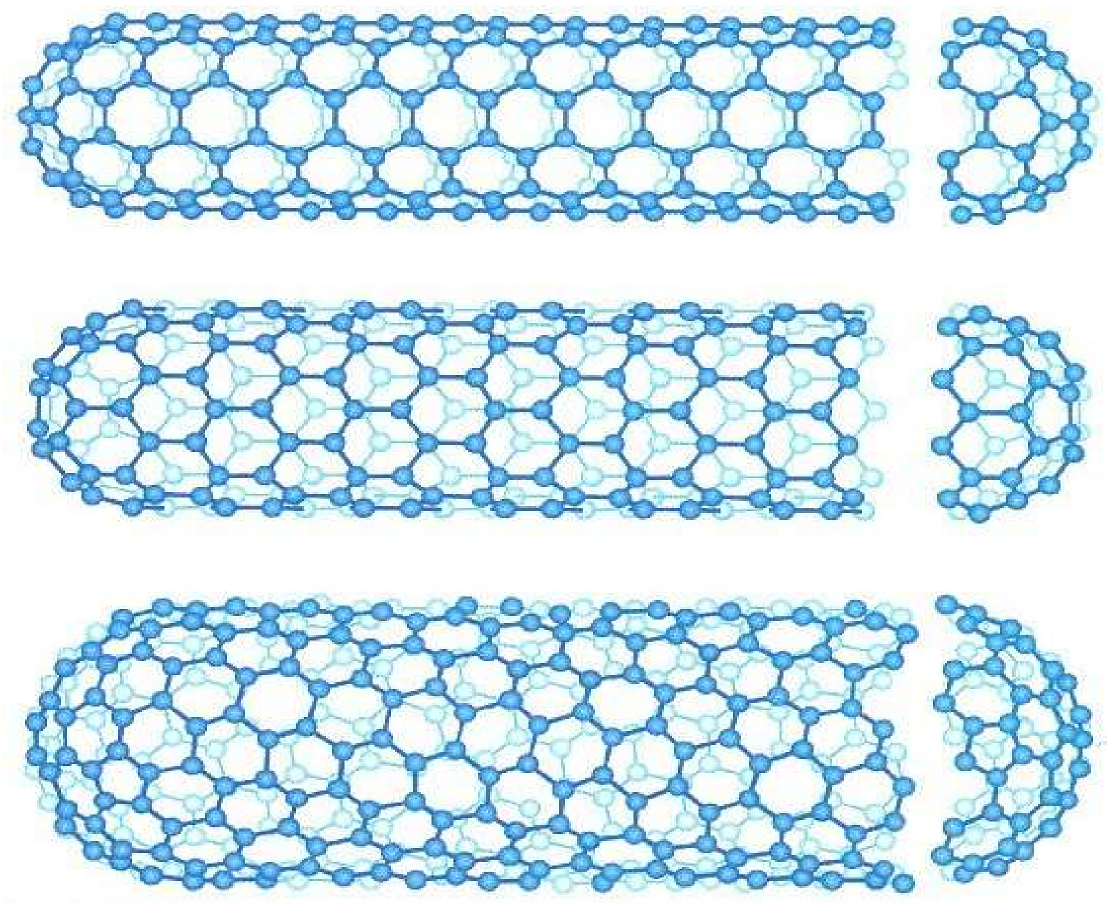


Figure 2.4: Structure of Single Walled Carbon Nanotube

Multi Walled Nanotubes (MWNT) can be considered as a collection of concentric SWNTs with different diameters. The length and diameter of these structures differ a lot from those of SWNTs and, of course, their properties are also very different.

Carbon cones are also shown. It can be considered as a gradual transition from a large diameter to a smaller one without defects in the wall of the cone but with fewer pentagons in the end cap.

Introduction of defects can also result in various new structures such as Y -branches T -branches or SWNT junctions. Under certain circumstances, these defects can be introduced in a 'controlled' way.

These defects result in special structures that will have other, but even more interesting, properties than their original forms. Defects are also being studied with great effort, but they will not be treated in this report.

A final type of interesting structures is the so-called peapods, carbon nanotubes with C_{60} molecules enclosed in the nanotube.

The derived carbon products (carbon nanotubes) are normally characterized by following techniques.

1-Scanning electron microscope (SEM)
2-Transmission electron microscope (TEM)
3-Raman spectrum
4- Thermo gravimetric and energy dispersive X-ray analysis
5-XRD

2.5 Properties of Carbon Nanotubes

2.5.1 Mechanical Properties

The mechanical properties of carbon nanotubes (strength stiffness) should approach that of an ideal carbon fiber, which has perfect orientation for graphene layers in the axial direction (single crystal) and a negligible number of structural defects. Since the in plane C-C covalent bond in graphite is one of the strongest bond in nature, the axial strength of the nanotubes would surpass that of most known materials some theoretical studies have suggested that the smallest single shell nanotubes might have young modulus as high as 5 TPa, while other have predicted a softening with decreasing tube radius. The reference point is of course the values of graphite for which the best estimate of the in-plane elastic modulus 1.06 TPa and that of the tensile stiffness 0.8TPa .For multi-wall nanotubes, the actual strength in particular situation would be further affected by propensity for individual graphene cylinders to slide with respect to each other.

There are no direct tensile tests available that could be performed on nanoscopic specimens to determine directly their axial strength. Hence the measurement of elastic modulus of individual carbon nanotubes and had to await the thought of a novel method to measure the intrinsic thermal vibration of nanotubes during imaging inside a TEM. The Nanotubes projecting out onto holes in a TEM specimen grid were assumed to be equivalent to clamped homogeneous cantilevers and the horizontal vibration amplitude at the tube end was measured and related to the young modulus and the vbrational energy. The analysis performed on several nanotubes give the average value for young’s modulus as 1.8 TPa, which is higher than the in-plane modulus for single crystal graphite. This value is higher than the expected considering that the diameter of the multi wall nanotubes studied and the reference value of graphite. At the same time it should be remembered that the accepted young’s modulus of graphite is a best estimated. The high stiffness and strength combined with low density implies that nanotubes could serve as ideal reinforcement in composite materials.

2.5.2 Strength and rigidity

Strength and rigidity (stiffness) of nanotubes were also seen in the aligning experiment that envolved the cutting of a phenolic and epoxy Nanotubes composite. The fact that the tube could not break during the cutting and alignment suggests that its strength is much higher that the shear strength of the phenolic and epoxy tube interface. The fracture mode of structure like Nanotubes is also intriguing, e.g. it could happen via the collapse of the inside providing absorption of energy and increased toughness. Their high young's modulus also suggests that the nanotubes have high bending moment. This is seen from images of nanotubes that appear also straight. Deformation experiments, however, suggest that the bending in nanotubes depend on various parameters such as the size of the inside hallows number of the layer on the nanotube wall and nanotubes size. It is generally seen that the single wall nana tubes are, more flexible and less prone to buckling compared with their multi-wall nanaotubes counterparts. Simulation has also suggested interesting deformation, behavior for nanotubes. Highly deformed nanotubes were seen reversibly switch into different morphological patterns with an abrupt release of energy. Nanotubes could sustain extreme strain of 40% without showing signs of brittleness, plastic deformation or atomic rearrangements and bond rupture. The reversibility of deformations such as buckling has been recorded under TEM and supports the notion that the tubes can recover from sever structural distortions. This flexibility is related to the ability of the carbon atoms to the rehybridize, the degree of sp2 –sp3 rehybirdization depends on the strain.

All these results show that nanotubes do indeed have exceptional mechanical properties both strength and elasticity, which combined with their low density, should make them ideal for reinforcement applications.

2.5.3 Density

The hollow structure of carbon nanotubes makes them very light (density varies from 0.8g/cm3 for SWNTs up to 1.8g/cm3 for MWNTs, compared to 2.26g/cm3 for graphite) and this is very useful for a variety of lightweight applications from composites to fuel cells. Specific strength (strength/density) is important in the design of structural materials nanotubes have this value at least two orders of magnitude greater than steel. Traditional carbon fibers have specific strength 40 times that of steel.

2.5.4 Chemical attack and thermal stability

As carbon nanotubes are made of graphitic carbon, they have good resistance to chemical attack and have high thermal stability. Oxidation studies have shown that the onset of oxidation shifts by a 100^0C to higher temperature in nanotubes compared to high modulus graphite fibers. The oxidation in nanotubes begins at the tubes tips and this leads to the possibility of opening nanotubes by oxidation. In vacuum or reducing atmosphere, nanotubes structures will be stable to any practical services temperatures.

2.5.5 Thermal Conductivity

Electron transport in carbon nanotubes is unique and the nanotubes are highly conducting in the axial direction. Similarly, the thermal conductivity of carbon nanotubes also should be high in the axial direction and should close to the in-plane value of graphite (one of the highest among materials). No experiment to date has tested the thermal conductivity of carbon nanotubes material or carbon nanotube composite. In the case of composites, although the high aspect ratio of carbon nanotubes will aid in improving conductivity, the interface between the carbon nanotubes and the matrix could have a deleterious effect.

2.5.6 Catalytic Nature of Carbon Nanotubes

The catalytic nature of carbon nanotubes surfaces has been studied and the indications are that nanotubes are catalytically active. It has been demonstrated that MWNTs decorated with metals can show selectivity in heterogeneous catalysis (that is heterogeneous reaction of cinnamaldehyde in liquid phase using Ru nanotubes) compared to the same attached on other carbon substrates. Microelectrodes made from carbon nanotubes have been used to carry out bioelectrochemical reactions. Electrode made from carbon nanotubes show superior properties (reversibility and efficient electron transfer) during in vitro oxidation studies of biomolecules (dopamine) compared to electrodes made from graphite paste. MWNTs microelectrodes were used to study the oxygen reduction reaction in aqueous acid and natural media. It was observed that electron transfer occurred at a much faster rate (determined from the exchange current density measured at the electrodes) on carbon nanotubes compared to graphite.

Ab intio calculations on the electron transfer rates of nanotubes indicate that curvature do not enhance the rates significantly, although the presence of topological defects on the surface can cause a significant improvement in the electron transfer rates, especially at the pentagon sites, which are electrophonic in nature compared to the hexagonal rings. The electrodic efficiency can be increased by electrode activation (treatment of nanotubes in concentrated HNO3 for a short period) and through the deposition of small amounts of metal catalysts (Pt. Pd. Ag)

2.6 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.

2.6.1 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 behavior is difficult as the crude nanotube samples are still not pure enough.

2.6.2 Electrical conductivity

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. It was shown that a *(n, m)* nanotube is metallic as accounts that: n = m or $(n-m) = 3i$, where I is an integer and n and m are defining the nanotube. The resistance to conduction is determined by quantum mechanical aspects and was proved to be independent of the nanotube length. For more, general information on electron conductivity reader is referred to a review by Ajayan and Ebbesen.

2.6.3 Optical activity

Theoretical studies have revealed that the optical activity of chiral nanotubes disappears if the nanotubes become larger. Therefore, it is expected that other physical properties be influenced by these parameters too. Use of the optical activity might result in optical devices in which CNTs play an important role.

2.6.4 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 isotropic properties.

Chapter 3: Application 0f carbon Nanotubes

Bucky tubes have extraordinary electrical conductivity, heat conductivity and mechanical properties. They are probably the best electron field-emitter possible. They are polymers of pure carbon and can be reacted and manipulated using the tremendously rich chemistry of carbon. This provides opportunity to modify the structure and to optimise solubility and dispersion.

Very significantly, Bucky tubes are molecularly perfect, which means that they are free of property- degrading flaws in the nanotubes structure. Their material properties can therefore approach closely the very high levels intrinsic to them.

These extraordinary characteristics give Bucky tubes potential in numerous applications.

1→Nanotubes can be opened and filled with materials such as biological molecules, raising the possibility of applications in biotechnology.

2→They can be used to dissipate heat from tiny computer chips.

3→The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering. The highest tensile strength individual SWNTs has been tested to be 63 GPa.

4→In earth's upper atmosphere, atomic oxygen erodes the carbon nanotubes, but other applications of carbon nanotubes rarely need the surface to be protected. Though it is debatable if nanotube materials can ever be made with a tensile strength approaching that of individual

Tubes, composites may still yield incredible strength potentially sufficient to allow the building of such things as space is working on combat jackets utilizing carbon nanotubes for ultra strong fibers and for monitoring its whereas condition.

5→Carbon nanotubes additionally can also be used to produce nanowires of other materials, such as gold or zinc oxide. These nanowires in turn can be used to cast nanotubes of other materials, such as gallium nitride. These can have very different properties from CNTs –for example, gallium nitride nanotubes are hydrophilic, while CNTs are hydrophobic, giving them possible uses in organic chemistry that CNTs could not be used for.

6→One use for nanotubes that has already been developed is as extremely fine electron guns, which could be used as miniature cathode ray tubes in thin high-brightness low-energy low-weight display. This type of display would consist of a group of many tiny CRTs, each providing the electrons to hit the phosphor of one pixel, instead of having one giant CRT whose electrons are aimed using electric and magnetic fields. These displays are known as filed emission display (FEDs). A nanotube formed by joining nanotubes of two different diameters end to end act as diode, suggesting the possibility of constructing electronic computer circuits entirely out of nanotubes. Nanotubes have been shown to be super conducting at low temperatures.

3.1 Current Progress

One application for nanotubes that is currently being researched is high tensile strength fibers. Two methods are currently being tested for the manufacture of such fibers. A French team has developed a liquid spun system that involves pulling a fiber of nanotubes from a bath that yield a product that is approximately 60% nanotubes. The other method, which is simpler but produces weaker fibers, uses traditional melt-drawn polymer. After drawing, the fibers can have the polymer burned out of them to make purely nanotube fiber or they can be left as they are.

Ray Baughman’s group from the NanoTech Institute at University of Texas at Dallas produced the current toughest material known in mid-2003 by spinning fibers of single wall carbon nanotubes with poly vinyl alcohol. Beating the previous contender, spider silk, by a factor of four, the fibers require 600j/g to break. In comparison, the bullet-resistant fiber Kevlar is 27-33j/g.

In 2004 Alan Windle's group of scientist at the Cambridge-MIT Institute developed a way to make carbon nanotube fiber continuously at the speed of several centimeters per second just as nanotubes are produced. One thread of carbon nanotubes was more than 100 meters long.

In June 2004 scientists from China's Tsinghua University and Louisiana State University demonstrated the use of nanotubes in incandescent lamps, replacing a tungsten filament in a light bulb with a carbon nanotube one.

Nanomechanical computer storage devices using nanotubes are currently at the prototype stages. Both high speed non-volatile memories which can be used to replace nearly all solid state memory in computers today, and high density storage that may replace hard drives, are being developed. Major limiting factors in the development of nanotubes include their cost and difficulties in orienting the nanotubes, which tend to tangle because of their length.

As of 2003, nanotubes cost upwards from 20 euro per gram to 1000 euro per gram, depending on purity, composition (single-wall, double-wall and multi-wall carbon nanotubes) and other characteristics.

Japanese manufacturer Mitsui & Company has announced plans to build the world's first mass production facility for Carbon Nanotubes. Using technology developed at their research facility, they expect to reduce the selling price of Nanotubes to less than 100 Yen per gram.

3.2 Carbon Nanotubes in Electrical Circuits

Carbon nanotubes have many properties-from their unique dimensions to an unusual current conduction mechanism-that make them ideal components of electrical circuits, and it is exciting to envision, or even to implement, novel transistor, MEMS devices, interconnects, and other circuit elements.

The major hurdles that must be jumped for carbon nanotubes to find prominent places in circuits related to fabrication difficulties. The carbon nanotubes production processes are very different from the traditional IC fabrication process. The IC fabrication process is somewhat like sculpture-films are deposited on to wafer and pattern-etched away. Carbon nanotubes are fundamentally from films; they are like atomic level spaghetti (and every bit as sticky).

Today, there is a no reliable way to arrange carbon nanotubes in a circuit. Researchers sometimes resort to manipulating nanotubes one-by-one with the tip of an atomic force microscope in a painstaking, time-consuming process. Perhaps the best hope is that carbon nanotubes can be grown through a chemical vapor deposition process from patterned catalyst materials on a wafer. Though such a CVD process has been shown to allow a circuit designer to locate one end of a nanotube, there is no obvious way to control where the other end goes as the nanotubes grows out of the catalyst. Another way for the self-assembly of the carbon nanotube transistors consist in using chemical or biological technique to place the nanotubes from the solution to determinate place on the substrate.

Even if nanotubes could be precisely positioned, there remains the problem that, to this date, engineers have been unable to control the type of nanotubes- metallic, semi-conducting, single walled, multi-walled, produced. This is a problem that chemical engineers must solve if nanotubes are to find a place in commercial circuits.

The special nature of carbon combines with the molecular perfection of Bucky tubes (single-wall carbon nanotubes) to endow them with exceptionally high material properties such as electrical and thermal conductivity, strength, stiffness, and toughness. No other element in the periodic table bonds to itself in an extended network with the strength of the carbon-carbon bond. The delocalised pi-electron donated by each atom is free to move about the entire structure, rather than stay home with its donor atom, giving rise to the first molecule with metallic-type electrical conductivity. The high-frequency carbon-carbon bond vibrations provide an intrinsic thermal conductivity higher than even diamond.

In most materials, however, the actual observed material properties - strength, electrical conductivity, etc. - are degraded very substantially by the occurrence of defects in their structure. For example, high strength steel typically fails at about 1% of its theoretical breaking strength. Bucky tubes, however, achieve values very close to their theoretical limits.

Because of their perfection of structure - their molecular perfection. This aspect is part of the unique story of Bucky tubes. Bucky tubes are an example of true nanotechnology only a nanometre in diameter, but molecules that can be manipulated chemically and physically. They open incredible applications in materials, electronics, chemical processing and energy management.

3.3 Field Emission

Bucky tubes are the best-known field emitters of any material. This is understandable, given their high electrical conductivity, and the unbeatable sharpness of their tip (the sharper the tip, the more concentrated will be an electric field, leading to field emission; this is the same reason lightening rods are sharp). The sharpness of the tip also means that they emit at especially low voltage, an important fact for building electrical devices that utilize this feature. Bucky tubes can carry an astonishingly high current density, possibly as high as 1013 A/cm^2. Furthermore, the current is extremely stable [B.Q. Wei, et al. Appl. Phys. Lett. 79 1172 (2001)].

An immediate application of this behaviour receiving considerable interest is in field emission flat-panel displays. Instead of a single electron gun, as in a traditional cathode ray tube display, here there is a separate electron gun (or many) for each pixel in the display. The high current density, low turn-on and operating voltage, and steady, long-lived behaviour make Bucky tubes attract field emitters to enable this application.

Other applications utilising the field-emission characteristics of Bucky tubes include: general cold-cathode lighting sources, lightning arrestors, and electron microscope sources.

3.4 Conductive Plastics

Much of the history of plastics over the last half-century has been as a replacement for metal. For structural applications, plastics have made tremendous headway, but not where electrical conductivity is required, plastics being famously good electrical insulators.

This deficiency is overcome by loading plastics up with conductive fillers, such as carbon black and graphite fibres (the later one used to make golf clubs and tennis racquets). The loading required to provide the necessary conductivity is typically high, however, resulting in heavy parts, and more importantly, plastic parts whose structural properties are highly degraded.

It is well established that the higher aspect ratio of filler, the lower loading required achieving a given level of conductivity. Bucky tubes are ideal in this sense, since they have the highest aspect ratio of any carbon fibre. In addition, their natural tendency to form ropes provides inherently very long conductive pathways even at ultra-low loadings.

Applications that exploit this behaviour of Bucky tubes include EMI/RFI shielding composites and coatings for enclosures, gaskets, and other uses; electrostatic dissipation (ESD), and antistatic materials and (even transparent!) coatings; and radar-absorbing materials.

3.5 Energy Storage

Bucky tubes have the intrinsic characteristics desired in material used as electrodes in batteries and capacitors, two technologies of rapidly increasing importance. Bucky tubes have a tremendously high surface area (~1000 m^2/g), good electrical conductivity, and very importantly, their linear geometry makes their surface highly accessible to the electrolyte.

Research has shown that Bucky tubes have the highest reversible capacity of any carbon material for use in lithium-ion batteries [B. Gao, Chem. Phys. Lett. 327, 69 (2000)]. In addition, Bucky tubes are outstanding materials for super capacitor electrodes [R.Z. Ma, et al., Science in China Series E-Technological Sciences 43 178 (2000)] and are now being marketed.

Bucky tubes also have applications in a variety of fuel cell components. They have a number of properties including high surface area and thermal conductivity that make them useful as electrode catalyst supports in PEM fuel cells. They may also be used in gas diffusion layers as well as current collectors because of their high electrical conductivity. Bucky tubes' high strength and toughness to weight characteristics may also prove valuable as part of composite components in fuel cells that are deployed in transport applications where durability is extremely important

3.6 Conductive Adhesives and Connectors

The same issues that make Bucky tubes attractive as conductive fillers for use in shielding, ESD materials, etc., make them attractive for electronics materials, such as adhesives and other connectors (e.g., solders).

3.7 Molecular Electronics

The idea of building electronic circuits out of the essential building blocks of materials - molecules - has seen a revival for the past five years, and is a key component of nanotechnology. In any electronic circuit, but particularly as dimensions shrink to the nano scale, the interconnections between switches and other active devices become increasingly important.

Their geometry, electrical conductivity, and ability to be precisely derived, make Bucky tubes the ideal candidates for the connections in molecular electronics. In addition, they have been demonstrated as switches themselves.

3.8 Thermal Materials

The record-setting anisotropic thermal conductivity of Bucky tubes is enabling applications where heat needs to move from one place to another. Such an application is electronics, particularly advanced computing, where uncooled chips now routinely reach over 100^{o}C.

CNT's technology for creating aligned structures and ribbons of Bucky tubes [D.Walters, et al., Chem. Phys. Lett. 338, 14 (2001)] is a step toward realising incredibly efficient heat conduits. In addition, composites with Bucky tubes have been shown to dramatically increase the bulk thermal conductivity at small loadings.

3.9 Structural Composites

The world-record properties of Bucky tubes are not limited to electrical and thermal conductivities, but also include mechanical properties, such as stiffness, toughness, and strength. These properties lead to a wealth of applications exploiting them, including advanced composites requiring high values in one or more of these properties.

3.10 Fibres and Fabrics

Fibres spun of pure Bucky tubes have recently been demonstrated [R.H. Baughman, Science 290, 1310 (2000)] and are undergoing rapid development, along with Bucky tube composite fibres. Such super strong fibres will have applications including body and vehicle armour, transmission line cables, woven fabrics and textiles.

3.11 Catalyst Supports:

Bucky tubes have an intrinsically high surface area; in fact, every atom is not just on a surface - each atom is on two surfaces, the inside and outside! Combined with the ability to attach essentially any chemical species to their sidewalls provides an opportunity for unique catalyst supports. Their electrical conductivity may also be exploited in the search for new catalysts and catalytic behaviour.

3.12 Biomedical Applications

The exploration of Bucky tubes in biomedical applications is just underway, but has significant potential. Cells have been shown to grow on Bucky tubes, so they appear to have no toxic effect. The cells also do not adhere to the Bucky tubes, potentially giving rise to applications such as coatings for prosthetics and anti-fouling coatings for ships.

The ability to chemically modify the sidewalls of Bucky tubes also leads to biomedical applications such as vascular stents, and neuron growth and regeneration.

3.13 Quantum Wires and Tiny Electronic Devices

The application of nanotubes as quantum wires and tiny electronic devices has received the most coveted attention. The Delft group, which pioneered the measurements of electron transport in individual SWNTs [IS], has built the first single molecule field effect transistor based on a semi conducting SWNT, the device, which operates at room temperature, comprises a nanotube bridging two metal electrodes. The band structure suggested for this device is similar to traditional semiconductor devices (two Scotty-type diodes connected back to back), and the performance of this device is comparable to existing devices in terms of switching speeds. Although the demonstration of such a device is exciting, the next stage of integrating devices into circuits will be crucial. None of the procedures developed so far for nanotube fabrication enables the construction of complex architectures that the semi-conductor industry needs today. New ideas based on the self-assembly of carbon structures into integrated nanotube assemblies have to be realized before nanotube electronics become practical reality.

3.14 Fabrication of Heterojunction Devices

The possibility of connecting nanotubes of different helicity (and hence different electronic character) through the incorporation of 5-7 defect pairs could lead to the fabrication of heterojunction devices. Although this concept has never been shown experimentally on an individual nanotube structure, STS studies of nanotube rope and MWNTs have indicated spatially varying changes in electronic properties along the length of the rope similar junction devices can be designed from two nanotube segments, one of which is semi conducting and the other made metallic by doping with impurity elements such as boron.

3.15 Electron Emitters

Another application that has caught the attention of the scientific and engineering communities is the use of nanotubes as electron emitters Field emission has been observed from arrays of partially aligned MWNTs that have been aligned by pulling slurry of nanotube dispersion through a ceramic filter The film of aligned tubes is then transferred onto a substrate and a voltage is applied across the suppor1ing film and a collector. Such nanotube films act like field emission sources with turn-on voltages of a few tens of volts and electron emission at current densities of a few hundred mill amperes per centimeter squared The nanotube electron source remains stable over several hours of field emission and is air stable One of the practical issues that still needs to be resolved is obtaining uniformly aligned tubes, which would guarantee uniform emission.

3.16 Nanoprobes

Due to high aspect ratio, mechanical strength, and elasticity, nanotubes could be used as Nan probes for example, as tips of scanning probe microscopes This idea has been demonstrated successfully and a nanotube tip on an atomic force microscope was used to image the topography of TIN coated aluminum film A bundle of MWNTs is first attached to a Si cantilever through adhesive bonding and then the bundle is sheared to expose one tube at the end of the bundle that performs as the tip. Due to the flexibility of nanotubes. The nanotube tips do not suffer the common problem of tip crashes also, such a slender structure as the nanotube is ideally suited to image deep features like surface cracks Due to the conducting nature of the tubes. They also can be used as STM tips, Images of charge density waves on TaS2 have been obtained at high-resolution using nanotube tips. Nanotube tips also have been used to image biological systems [68]. The proposal to use nanotube tips is enticing, but the vibration of individual freestanding tips can spoil some resolution imaging.

3.17 Filler-Based Applications of Nanotubes

(Filler-based applications of nanotubes for polymer composites are another area being hotly researched One of the biggest applications of traditional carbon fibers is in reinforcing polymers in high strength, high toughness lightweight structural composites. Epoxy based MWNT composites have been made and tested, but the results are not very conclusive. Substantial increase in modulus has been reported together with high strain to failure, but the strength of the composite is less than expected. The success of nanotube-reinforced composites depends on how strong the interface (between tubes and the matrix) can be made The atomically smooth surfaces of nanotubes do not guarantee a strong interface Molecular interlocking of the nanotubes by incorporation of 5-7 defect pairs could lead to the fabrication of heterojunction devices [4]. Although this concept has never been shown experimentally on an individual nanotube structure, STS studies of nanotube rope and MWNTs have indicated spatially varying changes in electronic properties along the length of the rope Similar junction devices can be designed from two nanotube segments, one of which is semi conducting and the other made metallic by doping with impurity elements such as boron.

Lity of hydrogen storage inside the well-defined SWNT pores and temperature-programmed desorption spectroscopy in traditional porous carbon material. The hydrogen uptake is already in use is high and can be compared to the best presently available material (metal hydrides) for hydrogen storage If an optimum nanotube diameter can be selected.

3.18 High conductivity composites

High conductivity composites (electrical and thermal) using nanotube-filled polymers could be useful, but the problems is getting well distributed nanotubes in matrix; heavy settling of nanotubes is seen when larger nanotubes epoxy composites are made [120], probably due to the lack of interaction with the tubes and the matrix. One advantage, however, is the negligible breakdown of nanotubes during processing of the composites. This is a big problem in carbon fiber composites because the fibers are extremely brittle

3.19 Electrode Applications

The potential of nanotubes Torr electrode applications is being explored especially because carbon-based electrodes have been used for decades in important electrode applications such as fuel cell and batteries. The unique surface constitution of nanotubes permits high selectivity for reactions more recent studies indicate that nanotubes much higher compared to on other carbon electrodes the catalytic activity (graphite and glassy carbon) supports. Oxygen reduction is an important fuel cell reaction, and the experiments show the potential of nanotube catalysts in energy production and storage

3.20 Hydrogen Storage

Finally, another interesting and exciting area of application has been demonstrated in SWNTs, the possibility of hydrogen storage inside the well defined SWNT pores Temperature-programmed desorption spectroscopy in traditional porous carbon material. The hydrogen uptake is high and can be compared to the best presently available material (metal hydrides) for hydrogen storage If an optimum nanotube diameter can be established for the best intake and release of hydrogen, high-energy storage efficiency can be obtained and the process could operate at ambient temperature. Advance in controlling the nanotube size during production can have an impact in this field whereas fuel cells are increasingly becoming part of future technology, the role of nanotubes as energy storage material is significant.

3.21 Some Unique Applications

Other than structural composites, some unique properties are being pursued by physical doping (filling) polymers with nanotubes. Such a scheme was demonstrated in a conjugated luminescent polymer, poly (m-phenylenevinglene-co 2, 5 dioctoxy-p-phenylenevinglene) (PYC) filled with MWNTs and SWNTs Compared *to* the pristine polymer. Nanotube/PPY composites have shown a large increase in electrical conductivity of nearly 8 orders of magnitude, with little increase in photoluminescence/ electroluminescence yield

3.22 Other Applications

There is a wealth of other potential applications for Bucky tubes, such as solar collection; nonporous filters; catalyst supports; and coatings of all sorts. There are almost certainly many unanticipated applications for this remarkable material that will come to light in the years ahead and which may prove to be the most important and valuable of all.

Most applications are based on the unique electronic structure, mechanical strength, flexibility, and dimensions of nanotubes whereas the electronic applications are based on SWNTs; no distinction has been made between SWNTs and MWNTs in other fields of applications.

Chapter 4: Literature Survey

Literature survey

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.

The first success in producing substantial amounts of SWNTs by arc-discharge was achieved was achieved by Bethune and coworkers 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.

The growth of high quality SWNTs at the 1-10gm scales was achieved by Richard E Smalley and coworkers using a laser ablation method.

The optimization of SWNT growth by arc-discharge was achieved by Journet and coworkers using a carbon anode containing 1.0 atomic percentage of yttrium and 4.2 atomic % of Ni as catalyst.

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 850-1000^{0}C.

Smalley and coworkers who used ethylene as carbon feedstock and growth temperatures around 800^{0}C reported another CVD approach to SWNTs.

Liu made a significant progress and coworkers in 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 coworkers were able to obtain nearly 200% yield of high quality CNTs.

Roar and coworkers used a catalyst based on mixed oxide spinels to grow SWNTs.

Dresselhaus et al found that good quality yield of nanotubes were obtainable with Fe Co alloy nanoparticles.

Colomer and coworkers 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.

Cheng and coworkers reported a method that employs benzene as the carbon feedstock, hydrogen as the carrier gas and ferrocene as the catalyst precursor for SWNT growth.

Smalley and coworkers 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 800-1200^{0}C.

Xie group 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 600^{0}C.

Ren 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 660^0 C.

The Carbon nanotubes –Polymer composites were initially reported by Ajayan et al. 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.

Sandler et al. reported that untreated carbon nanotubes were dispersed 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.

Gong et al. reported that using surfactants as wetting agents might improve dispersion and thermo chemical properties of carbon nanotubes /polymer (epoxy) composites, but even with the addition of surfactants, complete homogeneous dispersion of nanotubes was not obtained

Ago et al. reported that a uniform film of MWNTs and poly (p- phenylene vinylene)(PPV) widely studied was prepared by spin –coating highly concentrated MWNT dispersion.

Zeng et al. reported a 50% increase on Young's Modulus in CNT/PMMA composites when 5 wt % carbon nanofibres were introduced into the composites.

Allaoui et al.found twice and triple improvement in Young's modulus and yield strength resp. when 1 wt% MWNTs were added to the epoxy matrix.

Tai et al. showed a 100% improvement in tensile strength of the MWNTs / phenolic resin composites when 3 wt% CNTs network was introduced into the phenolic matrix.

Zhi Wang et al. have prepared Bucky paper/ epoxy resin, dissolved in acetone, composites. A hot press molding process was used for curing to produce the final nanocomposites 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 nanocomposites were as high as 15 Gpa.

Chapter 5: Experimental

5.1 Synthesis of Carbon nanotubes

5.1.1 Arc Discharge method

The samples were prepared using standard arc chamber with a pair of electrodes as shown in Fig. 4.1.1 The cathode is a graphite carbon rod 10 mm diameter and Anode as 8 mm diameter rod. The center hole in anode is 3 mm diameter and 60 mm in depth and was filled with Fe element in 1, 2, 3, 4 atomic wt percent of the carbon electrode. The arc was generated by a dc current of 100A at 22V between the electrodes. The reaction chamber was filled with He gas and the pressure inside the chamber was maintained 0.5 bar. The sample was received in the form of collarate deposited on the cathode rod and in the form of soot from the walls of the reaction chamber. The physical nature of the soot varied from fine fluffy powder to rolled-up mat depending on the experimental conditions. The samples were observed under Jeol scanning electron microscope model ISM 35 CF

Figure 5.1.1: Set-up for producing carbon nanotubes by dc electric arc discharge

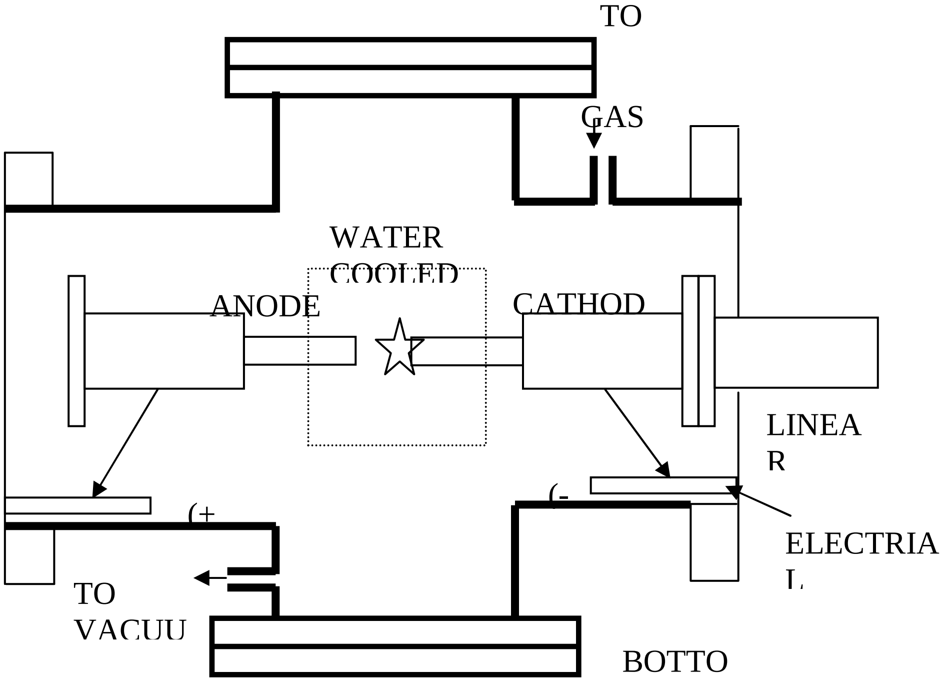


Figure 5.1.2: Block Diagram of Arc Discharge Method

Experiment-1

3mm diameter hole was drilled up to depth of 60mm in one of the graphite electrodes of diameter 8mm and length 90mm. The hole was filled with 1at% Fe powder, purity 99.9%. This electrode was arced against a cathode of diameter 10mm. Current of 100A and 20 volts was maintained during arcing. Helium pressure was maintained at 500 Torr. The electrode was moved to and fro by stepping up motor to maintain 1mm separation between the electrodes to achieve suitable arcing condition during the arcing process. The soot, which was collected from the chamber, contains carbon Nanotubes as characterized by SEM and XRD.

Experiment-2

3mm diameter hole was drilled up to depth of 60mm in one of the graphite electrodes of diameter 8mm and length 90mm. The hole was filled with 2at% Fe powder, purity 99.9%. This electrode was arced against a cathode of diameter 10mm. A current of 100A and 20 volts was maintained during arcing. Helium pressure was maintained at 500 Torr. The electrode was moved to and fro by stepping up motor to maintain 1mm separation between the electrodes to achieve suitable arcing condition during the arcing process. The soot, which was collected from the chamber, contained more of nanotubes compared to previous experiment.

Experiment-3

3mm diameter hole was drilled up to depth of 60mm in one of the graphite electrodes of diameter 8mm and length 90mm. The hole was filled with 3at% Fe powder, purity 99.9%. This electrode was arced against a cathode of diameter 10mm. A current of 100A and 20 volts was maintained during arcing. Helium pressure was maintained at 500 Torr. The electrode was moved to and fro by stepping up motor to maintain 1mm separation between the electrodes to achieve suitable arcing condition during the arcing process. The carbon soot, which was collected from the chamber, was found to be increased as compared to the soot in experiment no. 1 and 2. The amount of the catalyst in the soot was measured by TGA was also found increased with respect to previous experiments.
Additionally the soot was also found to contain amorphous carbon and confirmed by Thermal Gravimetric Analysis and X-ray difractrometry.

Experiment-4

3mm diameter hole was drilled up to depth of 60mm in one of the graphite electrodes of diameter 8mm and length 90mm. The hole was filled with the catalyst comprising of 4% Fe powder, purity 99.9%. This electrode was arced against a cathode of diameter 10mm. A current of 100A and 20 volts was maintained during arcing. Helium pressure was maintained at 500 Torr. The electrode was moved to and fro by stepping up motor to maintain 1mm separation between the electrodes to achieve suitable arcing condition during the arcing process. The carbon soot, which was collected from the chamber, was found to contain sea urchin like deposits when viewed under the SEM. The tubes were of much shorter length as compared to one produced in experiment 1-3. The amount of catalyst in the soot was measured by TGA was also found to be greatest of the other experimental runs though the amount of the nanotubes produced was greatest of all other deposits. Additionally the soot was also found to contain amorphous carbon and confirmed by Thermal Gravimetric analysis and X-ray defracrometry. The cathode deposit weighs about 70% of the total carbon evaporated during the arching.

Table below gives the different carbon products in nanotubes produced.

Nanotubes produced

	Coil deposit(gm)	Wall deposit(gm)	Total amount of CNT’s(gm)
Exp.1	1.95	1.85	3.60
Exp.2	2.85	2.70	5.55
Exp.3	2.45	2.35	4.80
Exp.4	2.24	2.06	4.30

Table 5.1 Comparative amounts of CNT’s produced in each experiment

5.2 Fabrication of Samples

From virtually the moment nanotubes were discovered it was expected that they would display superlative mechanical properties by analogy with graphite. It had long been known that graphite had an in-plane modulus of 1.06 TPa and nanotubes were expected to display similar stiffness.

In this study as such carbon nanotubes were reinforced in phenolic resin for composite preparation of the 1.5mm thickness.

Typical dog bone shape sample is shown in figure.

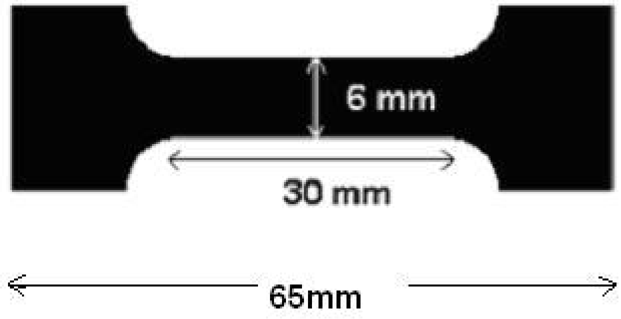


Fig. 5.2.1: Dimensional view of dog bone shape sample

5.2.1 Procedure

CNTs reinforced and phenolic resin (phenol formaldehyde) composites have been prepared with 2 volume% of CNTs. The preparation of this polymer nanocomposite involves the following steps: -

1. Dispersion of CNTs in the polymer matrix.
2. Casting of sample material in a mould of appropriate dimensions
3. Curing (polymerization) of the material at the specific pressure and temperature required for effective polymerization

In order to achieve maximum interaction between CNTs and polymer molecules it is necessary to separate the agglomerated bundles of CNTs. This is done through proper dispersion of the CNTs in polymer matrix. There are two methods generally employed i.e. dry mixing and wet mixing.

Dry mixing comprises of mixing dry phenolic resin and carbon nanotubes with the help of mortar and pestle or with by Ball mill, while wet mixing involves the sonication of CNTs and resin separately in a solvent and then sonication of their mixture in a sonicator. Later by the evaporation of the solvent wet mixture or semisolid contents obtained were used in the die.

A unique process comprising of the both processes was employed. Contents were sonicated separately in the same solvent and then the mixture was sonicated. This insures the liquid phase dispersion of nanotubes. Later this mixture was evaporated until the solid phenol with nanotubes dispersed in it was not obtained. This solid layer was scratched and dry mixed with the help of mortar. This mixture was continuously screened with the help of 300 mesh screen and the oversize was grinded until all the mixture was in the form of homogenized powder.

The same powder were placed in the die mould of the required size and kept under the press. Firstly temperature of the press was fixed at 90^0C and when the temp reaches near to 90^0Cthe sample material was pressed very slowly. After pressing these samples were cured at 180^0C for two hr. For comparisons composites with neat resin (0% CNTs) were also prepared with similar dimension. The samples were prepared with different volume fraction of carbon nanotubes as 0, 1 and 2% with same resin.

5.3 Mechanical properties (Tensile) of the Polymer Composite

The composite samples were characterized for their mechanical properties (tensile strength and tensile modulus) on Instron Universal Testing machine as per the American Society for Testing of Materials (ASTM) standard (ASTM D-638).

Tensile Analysis

Tensile testing determines the Young's modulus of elasticity which is used to figure out the load carrying ability and the amount of deformation of a sample before fracture.

Under light stress, a material will go temporary deformation, which is an elastic displacement of the atoms in the space lattice. If the stress is removed, the material will return to its original shape and dimensions. Thus, in the elastic range of a material, the strain is proportional to the stress. Hook's experimental law gives the relationship between the load and the extension: $\delta = \frac{pl}{AE}$

p: load producing extension of the sample (N).

l: original length of the sample (m).

A: cross sectional area of the sample (m^2)

E: the modulus of elasticity or Young's modulus (N/m^2).

From the above formula we can see that the extension of the sample is directly proportional to the load and the length of the sample, and is inversely proportional to the cross sectional area of the sample and the modulus of elasticity.

The tensile stress was defined as the load applied per cross sectional area perpendicular to the load: $\sigma = \frac{p}{A}$ where σ is stress (N/m^2 or Pa). The tensile strain, or the extension of a bar per unit length, is determined by $\varepsilon = \frac{\delta}{l}$ where ε is strain (m/m). Thus, $E = \frac{\sigma}{\varepsilon}$. In other words, the Young's modulus is the stress, below the proportional limit, divided by the corresponding strain. The stress and the strain introduced above are sometimes called "engineering stress and strain." They are not true stress and strain. The true strain is the natural logarithm of the ratio of the length at any instant to the original length, that is: $\ln(l/l_0)$. Below the elastic limit, the engineering stress and the true stress are almost identical.

In the tensile test, a gradually increasing load of tension is applied at one end of a sample, and the other end is anchored in a rigid support so that the sample is slowly pulled apart. Magnitude of the load applied on the sample throughout the test is recorded by machine. At the same time, measurements are made of the increasing length of a selected portion of the sample, which is usually located in the middle of the sample, called the gage length. Measurements of load and elongation will stop shortly after the plastic deformation begins; however, the maximum load reached is always recorded.

The tensile test mainly gives three factors about a material: the load at which the plastic deformation or “yielding” begins, the maximum tensile strength or the maximum load that can be carried by the sample, and the percent of extension or the strain.

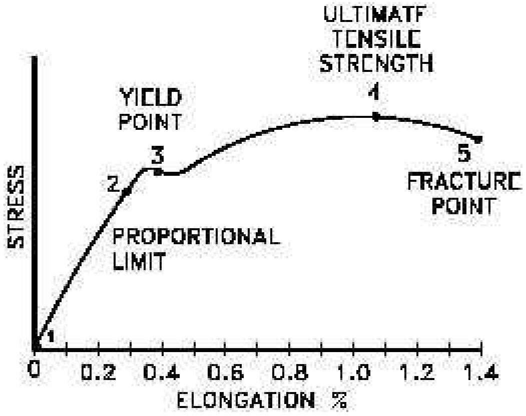


Fig. 5.3.1: Typical stress strain diagram

Figure shows the Stress/extension curve. The area between points 1 and 2 is called the elastic region. If the load is removed, the material will return to its original length. Point 2 is the elastic limit, and point 3 is the yield point. The area between the points 2 and 5 is the plastic region where the sample will not be able to return to its original length. Point 4 is the point of ultimate strength, and the point 5 is the fracture point at which the failure of the sample occurs.

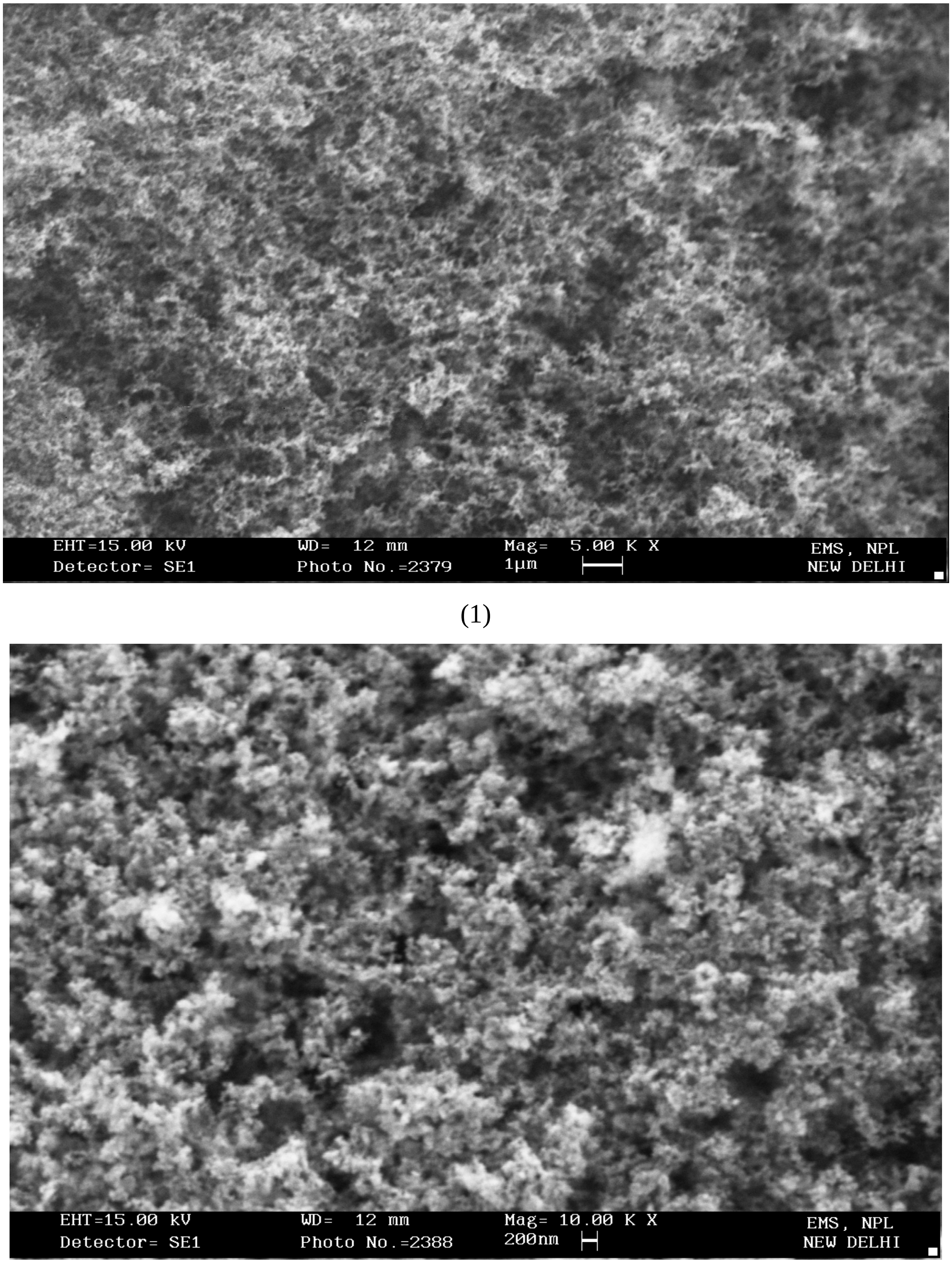
Chapter 6: Characterization of Nanotubes

6.1 SEM Analysis

Carbon nanotubes were synthesized by D.C. Arc discharge technique as mentioned in chapter 5.1.1. The synthesized material contain two types of material first one is chamber deposit with some impurities and second one is cathode deposit contains. Both type of materials were characterized by SEM as shown in figure 5.1.1, 5.1.2, 5.1.3, and 5.1.4.

Generally appearance of the carbon material deposited inside the chamber in each run of experiment was found to be quite similar. The material resembled sheets of soot like fibrous mat. SEM micrograph of such material is shown in figure 5.1.1, 5.1.2, 5.1.3, 5.1.4 which shows that these contained multitude of nanotubes or ropes. The highest amount of concentration of the nanotubes was found to form inside the core of the 'cathode deposit' which when crushed forms into straight needle like bunch of tubes. An overall yield of the nanotubes through SEM could be estimated as 50% by volume both in each sample when collectively taking amount of both wall and cathode deposit.

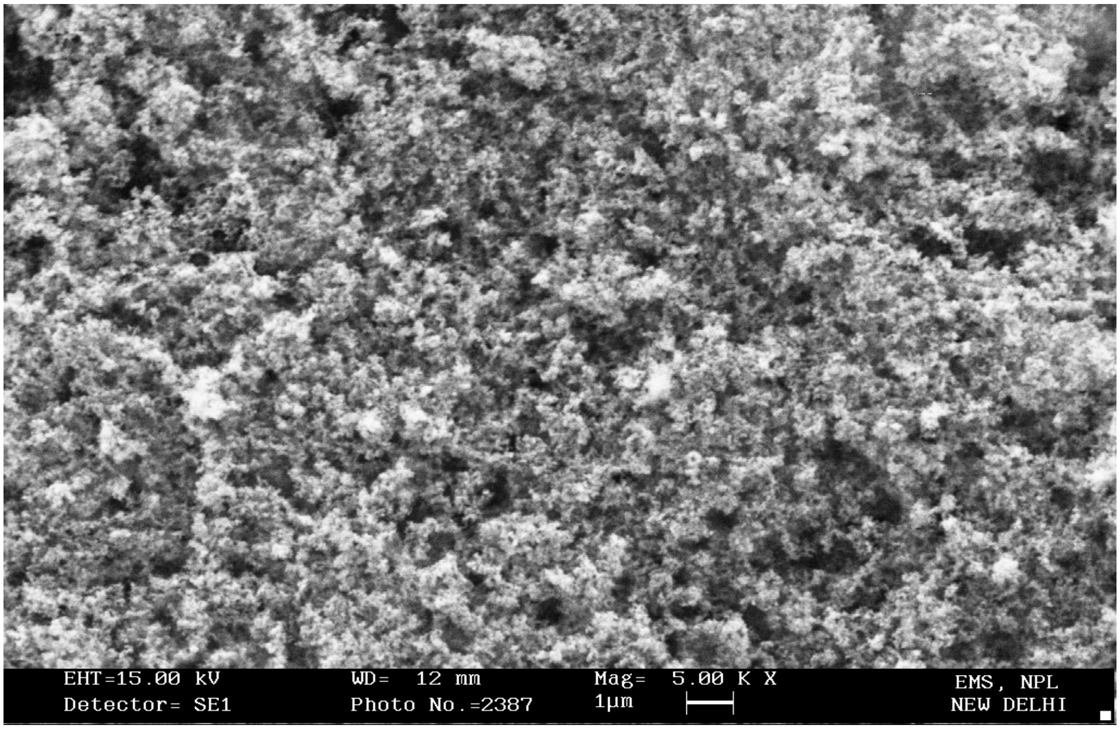
Several runs under he similar conditions were carried out to collect sufficient amount of carbon deposits. These were found to be of reproducible quality and the production rate of total deposits (a+b) per batch was estimated to be around 4-5 gms. The total time taken to consume about 60mm length of electrode was about 30 min.



(1)

(2)

Fig. 6.1.1SEM micrograph of as produced chamber deposit CNT's with 1% Fe as catalyst



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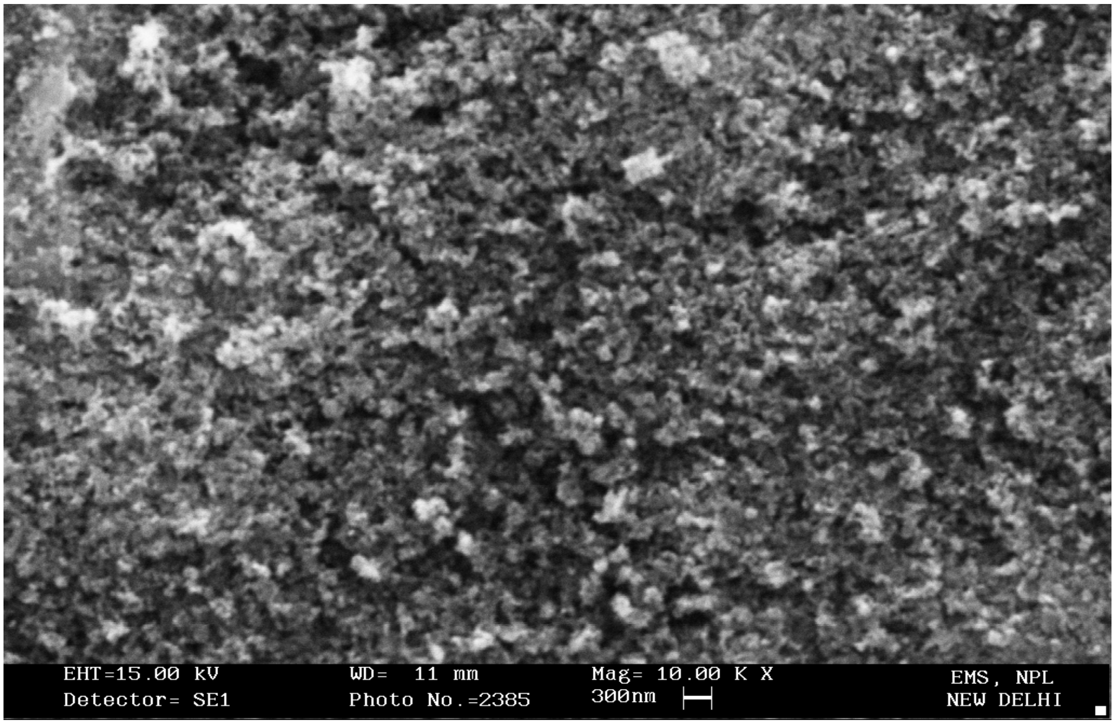
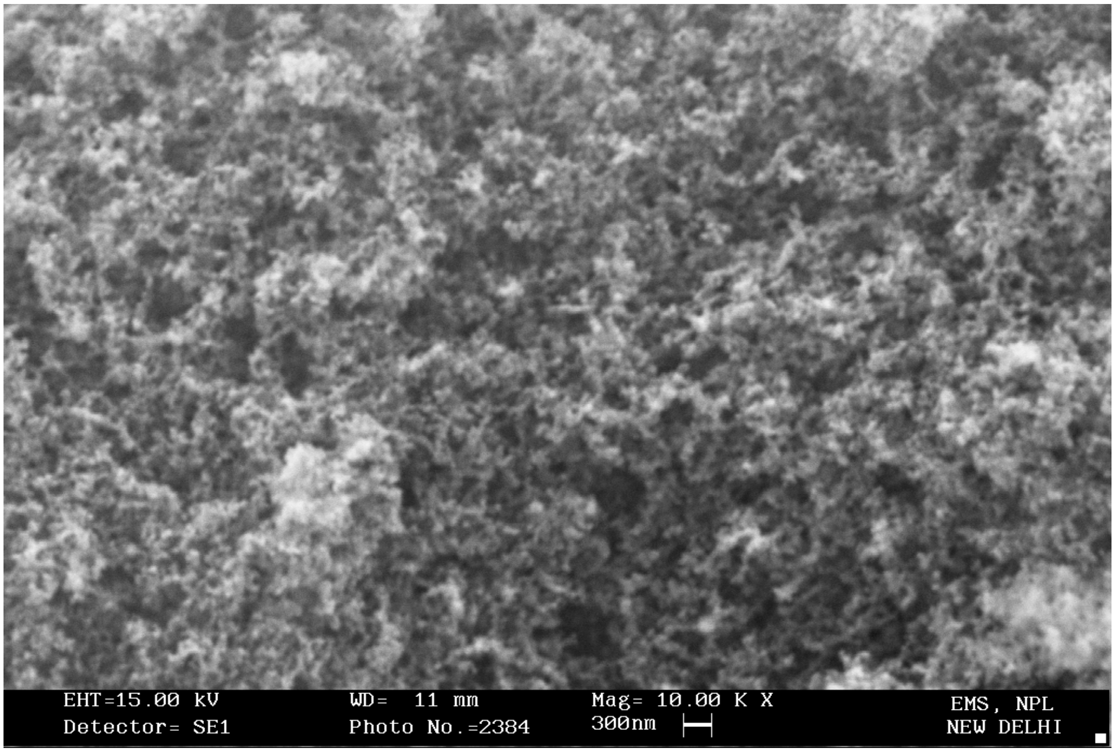
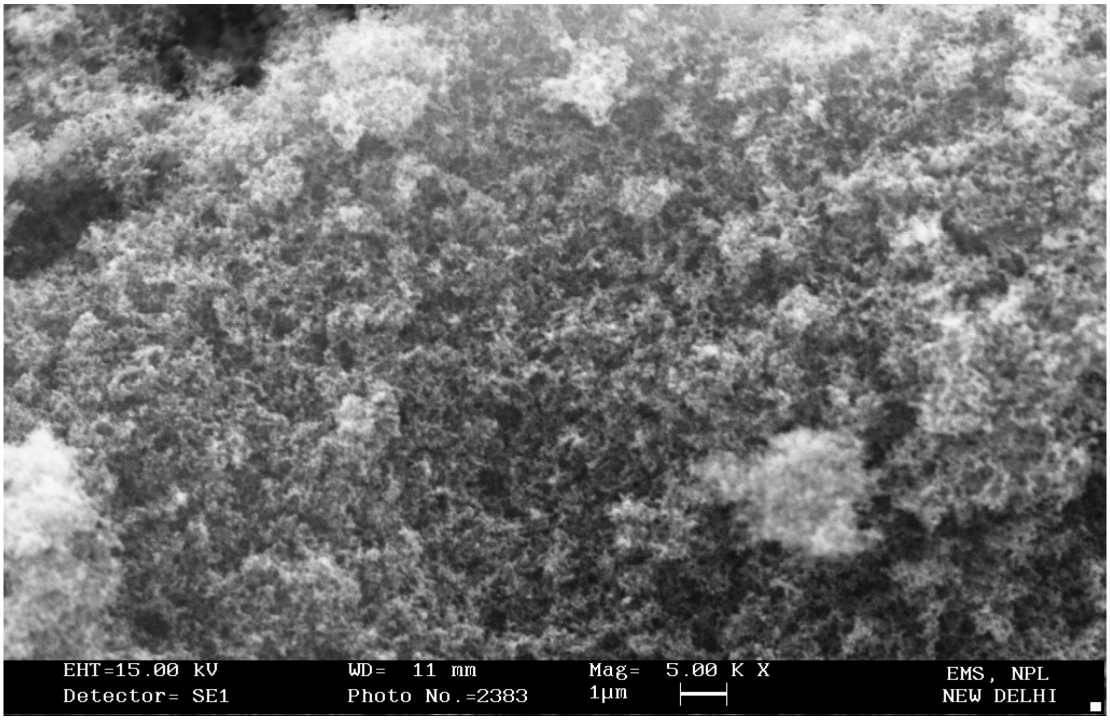


(2)

Fig.6.1.2 SEM micrograph of as produced chamber deposit CNT's with 2% Fe as catalyst

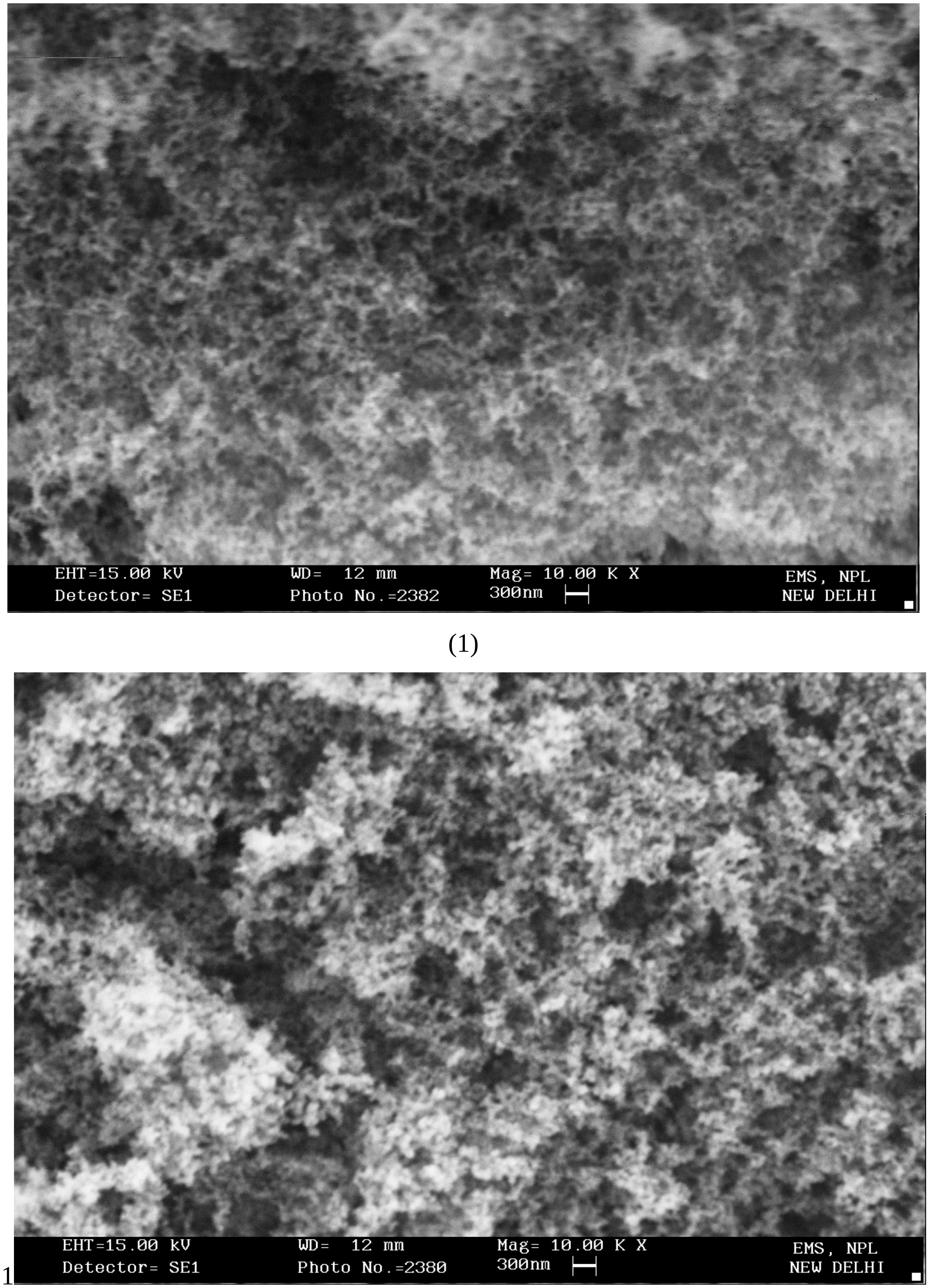


(1)



(2)

Fig.6.1.3 SEM micrograph of as produced chamber deposit CNT's with 3% Fe as catalyst



(1)

(2)

Fig.6.1.4 SEM micrograph of as produced chamber deposit CNT’s with 4% Fe as catalyst

6.2 X-ray diffraction

X-ray diffraction was done on X-ray diffractometer model D 500. Figure shows the X-ray diffractrogram of sample 1 which shows the peaks at 265^0 and 44.5 degrees. D002 value was found to be 3.3718^0 A which shows the presence of Carbon Nanotubes accompanies with SEM micrographs.

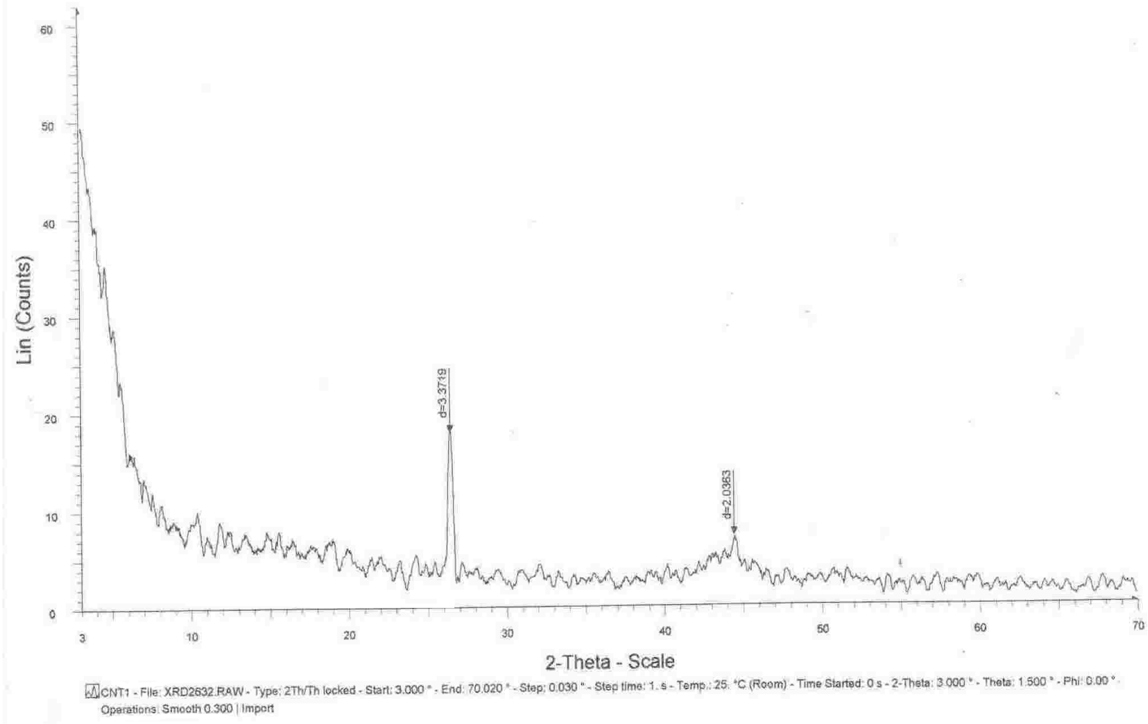


Fig 6.2.1 X-ray pattern of carbon nanotubes produced

6.3 Thermo gravimetric analysis

TGA is common technique used for estimation of the each species present in the carbon nanotubes deposits corresponding to their peak position and the area of DTG curve. The thermal gravimetry of the as produced sample chamber deposits and cathode deposit was carried out in a Mettler-Toledo, TGA/SDTA 851 thermal analysis system. Heating rate of 10^0C/min in flowing dry air was maintained and the maximum temperature was kept to 900^0C. Figure 5.3.1, 5.3.2, 5.3.3, 5.3.4 shows the weight loss behavior of the as produced sample a in presence of flowing dry air. The solid line corresponds to thermo-gravimetry (TG). There is no obvious weight loss up to 300^0C, which can be ascribed to start of oxidation of amorphous carbon.

In each experiment an isothermal time of 30 minutes shows that there is still residue left in the crucible. As practically up to 800^0C there are no nanotubes left in the residue, it could be concluded that the residue indicates to the amount of metal catalyst left. Percentage of catalysts as impurity in the sample was observed to be 16.70%, 18.73%, 21.08% and 31.13% with 1%, 2%, 3% and 4% Fe respectively. It can be easily concluded that at higher volume% of Fe in electrode results in higher metal residue in carbon nanotubes.

The weight loss behavior of this material is also shown in Figures below. These weight loss behavior show that there is no weight loss up to 300^0C, after which a gradual weight loss between 500^0C-850^0C. After which there is practically no weight loss. The residue left at the end is the Fe catalyst which ranges to 31.2%.

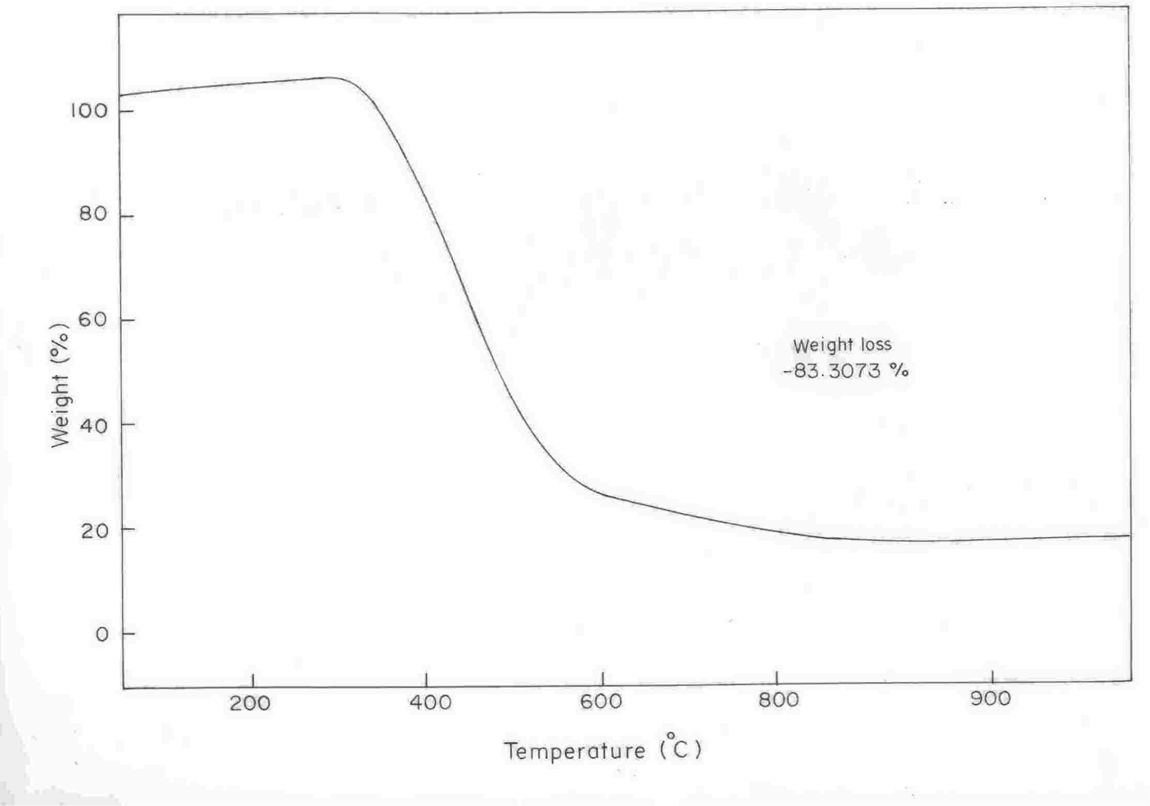


Fig. 6.3.1 TGA of CNT,s prepared by 1% Fe as a catalyst

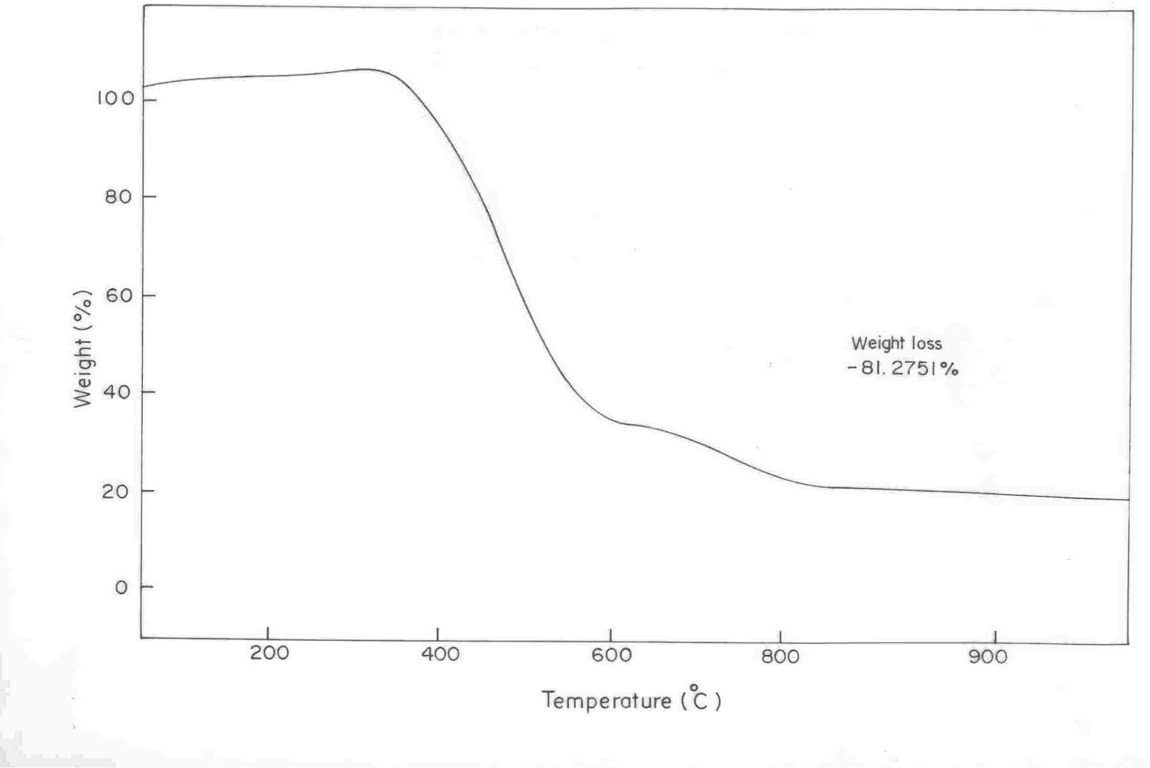


Fig. 6.3.2 TGA of CNT’s prepared by 2% Fe as a catalyast

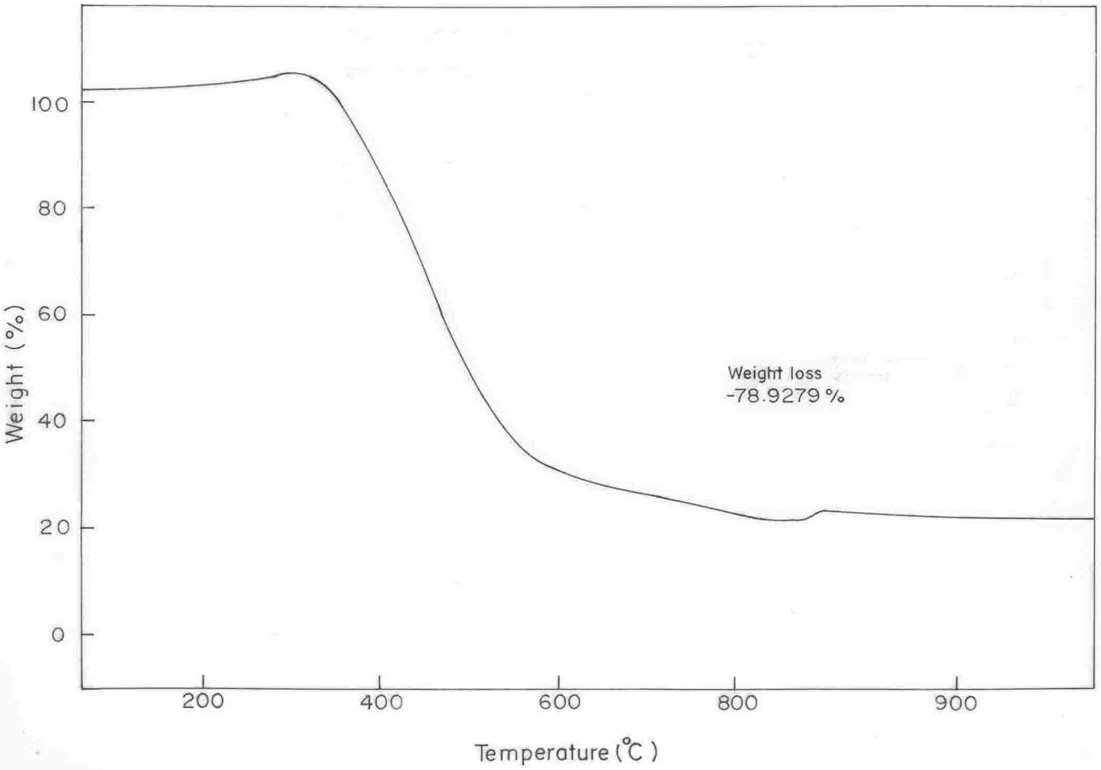


Fig. 6.3.3 TGA of CNT’s prepared by 3% Fe as a catalyst

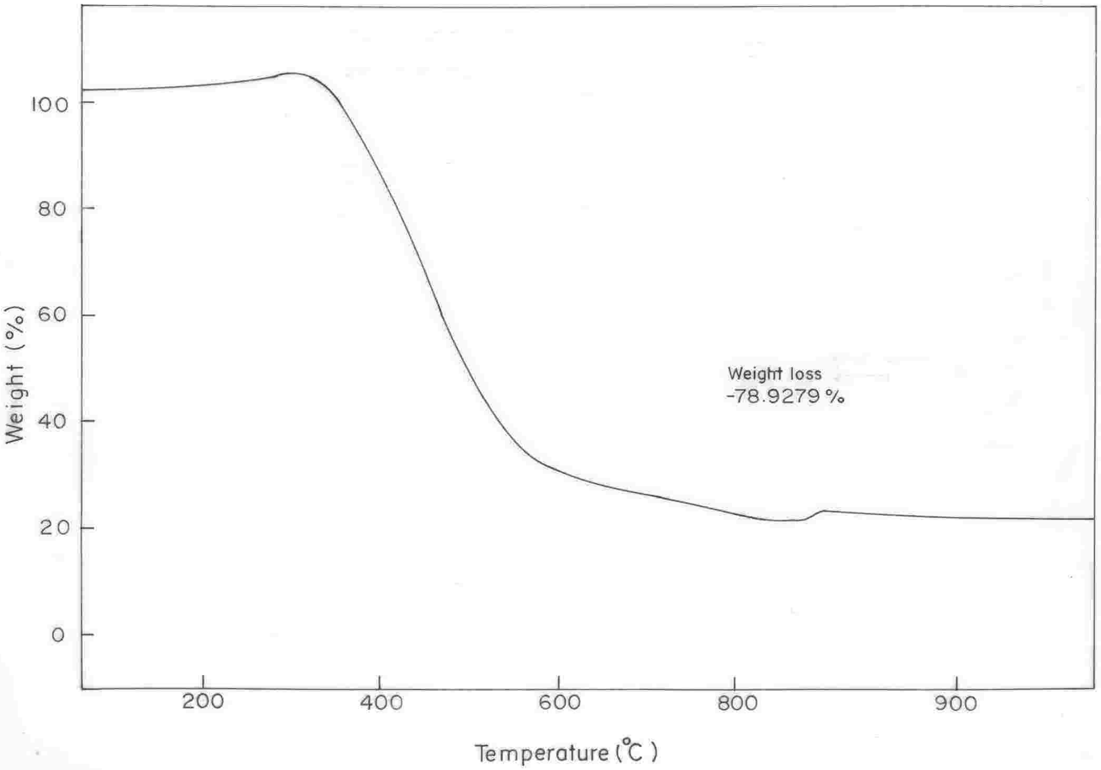


Fig. 6.3.4 TGA of CNT’s prepared by 4% Fe as a catalyst

Chapter 7: Results and discussion

Tensile strength and modulus values of the composite prepared by using 2 volume% of CNTs at the phenolic resin were determined. Strength of the composites was observed to change with changing volume percent of Fe. With reference to the neat phenolic sample the tensile modulus was found enhanced by 24-25%, which shows the increase to be about 12-15%. Tensile strength of the samples increased by 66-70% of the neat resin value except for 3 atomic weight percent Fe where the increase is found to be around 125% with respect to neat resin value. The maximum Tensile strength achieved is 35 Mpa.

The tensile strength and the modulus of the composites samples was measured on INSTRON Model-441, ASTM D 638. Composite samples prepared of dog bone shape with thickness 1.5mm and width 6mm with span length 30mm. Span to depth ratio for the test samples was kept as 20:1 and the crosshead speed was maintained at 0.5mm/min.

Figure no. 7.1 shows the influence of carbon nanotubes prepared with different concentration of Fe catalyst on the tensile strength of the composite. Neat phenolic resin samples were also prepared for the comparision with CNT reinforced composites. All of these samples were prepared with the reinforcement 2 volume% phenolic resin. As seen from the figure 7.1 the tensile strength of the comnposites shows a gradual increase in 1, 2 and 3 % Fe concentrated precursor material for CNT synthesis and the maximum value was achieved with 3% Fe concentrated precursor material. The improvement in the strength shows the effective and efficient load transfer between CNT network and polymer matrix. Basically the main criteria for effective reinforcement is high aspect ratio, good dispersion and good interfacial stress transfer. In our study we have used a special method for better dispersion of carbon nanotubes in resin matrix, which has been described in experimental. Carbon nanotubes have very high aspect ratio sufficient to provide proper interfacial area with the matrix. All these factors have resulted in better mechanical properties of the phenolic resin.

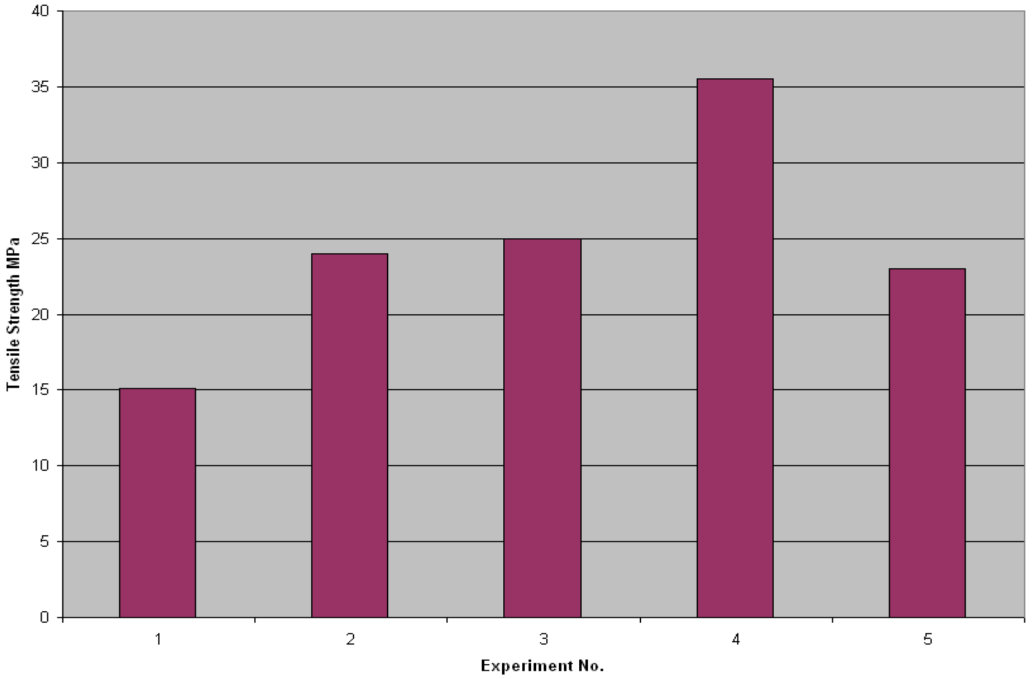


Fig. 7.1 Tensile strength vs. experiment no.

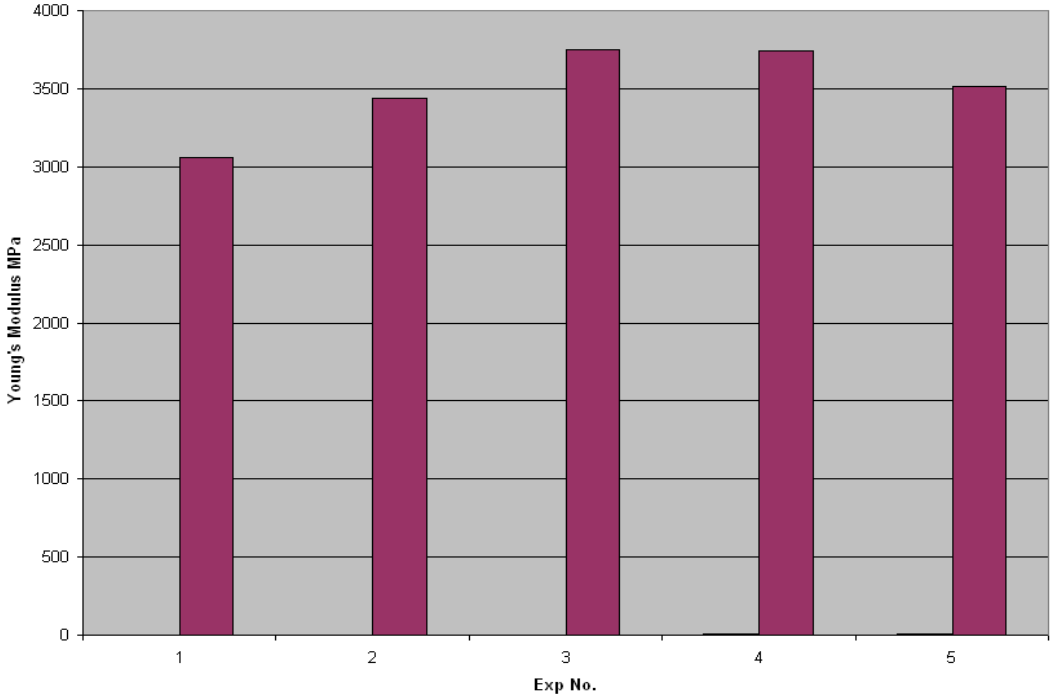


Fig. 7.2 Tensile modulus vs. experiment no.

Chapter 8 Future Scope

Nanotubes being produced by arc discharge method are in small amount, i.e. a few grams. Mass scale production of carbon nanotubes is in progress. The set up is to be scaled up for this purpose.

Further set up can also be improved for much automation process for precise data related to arching. With the help of this automation, relation between arching parameters can be optimized and predicted with accuracy.

Further in experimental nanotubes can be purified to remove the catalyst from them. For this they can be treated in a definite pattern. The catalyst present acts as impurity and better results can be obtained by elimination of Fe and using purified carbon nanotubes as reinforcement.

Carbon nanotubes can be purified as well functionalized. Processes are on the go to get functionalized carbon nanotubes. Functionalized nanotubes can give better bonding with matrix by chemical bonding with it. Thus higher strength composites can be obtained.

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