

Synthesis of Carbon Nanotubes by Electric Arc Discharge Method

A Major Report submitted towards partial fulfillment of the requirements for the degree of

MASTER OF ENGINEERING IN POLYMER TECHNOLOGY

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CERTIFICATE

This is to certify that the project entitled “**SYNTHESIS OF CARBON NANOTUBES BY ELECTRIC ARC DISCHARGE METHOD**” is being submitted by **Mr. NAND LAL RAJAK**, is a bonafide record of student’s own work carried by him under our guidance and supervision in partial fulfillment of requirement for the award of the Degree of **Master of Engineering in Polymer Technology, Department of Applied Chemistry and Polymer Technology, Delhi College of Engineering, Delhi, University of Delhi.**

During the entire project from Feb. 2005 to June 2006 I/we have found Mr. N.L. Rajak a very hard working, sincere and intelligent worker. I wish him success in his all future endeavors.

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During the entire project from Feb 2005 to June 2006 we have found Mr. Nand Lal Rajak a very hard working and sincere student. I wish him success in his all-future endeavors.

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.....

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ABSTRACT

Carbon nanotubes are a fascinating material having outstanding properties, which 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 combination of the catalysts Ni, Co and Y were tried to optimize to get higher yield. Single walled and multi-walled carbon nanotubes were obtained by the same technique on chamber deposits and cathode deposits respectively.

Secondly carbon nanotubes were synthesized by chemical vapor deposition technique with toluene as the carbon source and ferrocene as catalyst source in a two zone electric furnace. Up to 7.5 gm of carbon nanotubes were synthesized per batch by the same technique with ~ 90% of purity and ~ 30% conversion from given carbon source to Carbon nanotube based material.

Carbon nanotubes synthesized by both the above techniques have been characterized by scanning electron microscopy, transmission electron microscopy, thermogravimetry analysis and electron dispersive analysis.

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 different volume fractions that is 0, 0.5, 1, 2, 3, 4, 5 and 10 % respectively. Composite samples prepared in this study were of 50X5X3 mm³ size. The mechanical properties, flexural strength and flexural modulus of these samples were measured an 'INSTRON UNIVERSE TESTING MACHINE'.

CHAPTER 1: OBJECTIVE OF THE PROJECT

1. Synthesis of carbon nanotubes from electric arc discharge method and chemical vapor deposition method.
2. Characterization of produced carbon nanotubes by scanning electron microscopy, Transmission electron microscopy, Raman Spectroscopy & Thermo gravimetric analysis.
3. Preparation of Carbon nanotubes reinforced composite and to investigate their mechanical properties.

CHAPTER 2: INTRODUCTION

2. Introduction

2.1 General

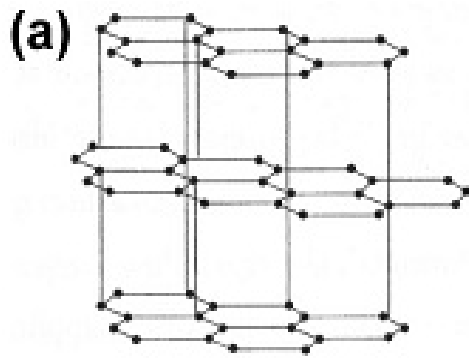
Carbon is a remarkable element, which possesses the exceptional ability of stable clusters in the vapor phase. Yet until recently we knew for certain of just two types of all carbon crystalline structure, the naturally occurring allotropes diamond and graphite. In August 1985, Kroto discovered the Fullerene,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

2.2 Discovery of fullerenes and Carbon Nanotubes

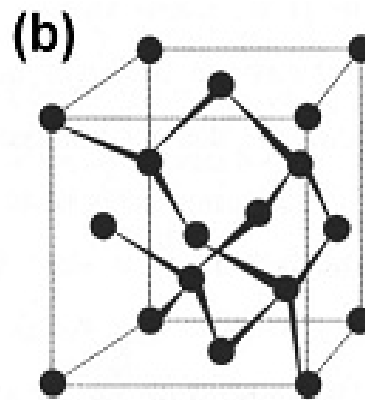
Fullerenes are large, closed-cage, carbon clusters and have several special properties that were not found in any other compound before. Therefore, fullerenes in general form an interesting class of compounds that surely will be used in future technologies and applications. Before the first synthesis 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.

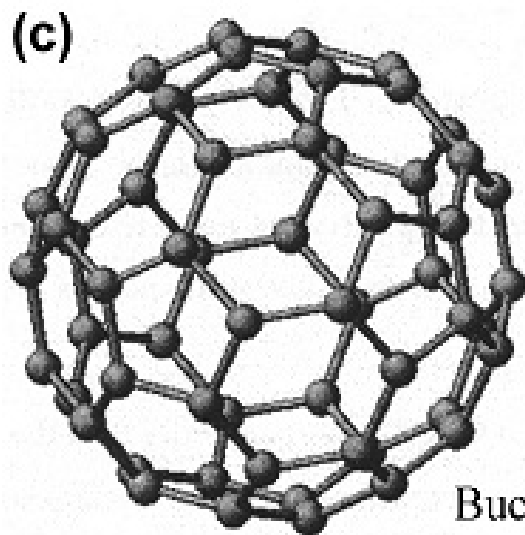
Carbon Nanotubes were discovered by Iijima and Coworkers in 1991, while examining fullerenes and containing carbon soot. Carbon nanotubes have been investigated by many researchers all over the world. Their large length (up to several microns) and small diameter.



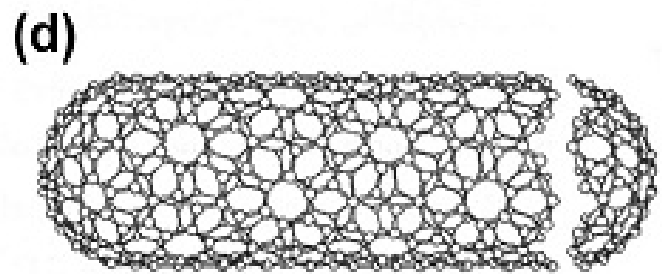
Graphite



Diamond



Bucky ball



Nanotube

Figure 2.1- Allotropes of carbon

(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.

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 discovered in 1991, and single-walled carbon nanotubes were discovered 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 1 and 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 0.34nm (about 3-5% larger than single crystal graphite spacing) as shown in figure 2.2 (b). The outer diameter MWNTs range between 2 and 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.

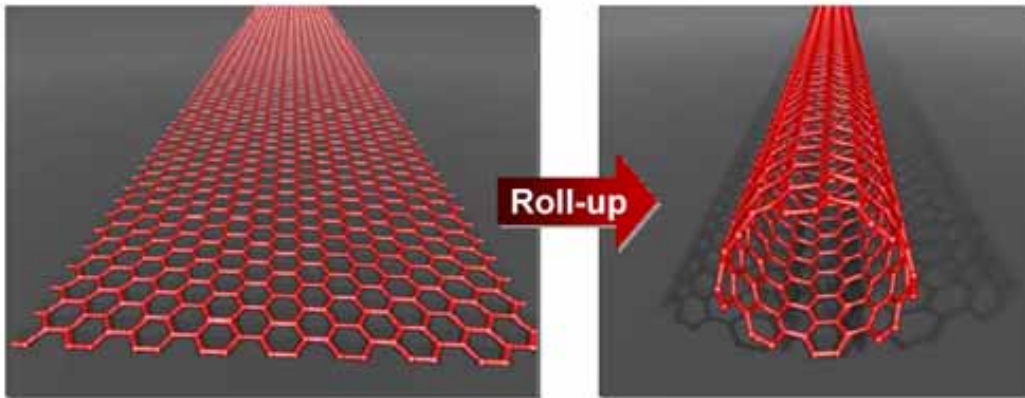


Figure 2.2 (a): A graphene layer folded into the single walled carbon nanotube

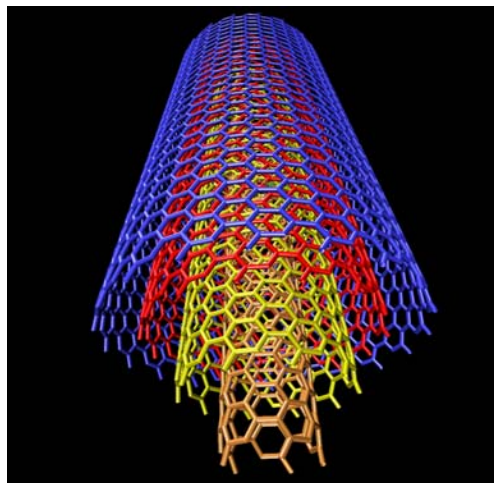


Figure 2.2 (b): Multi-walled nanotube

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 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.

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

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.

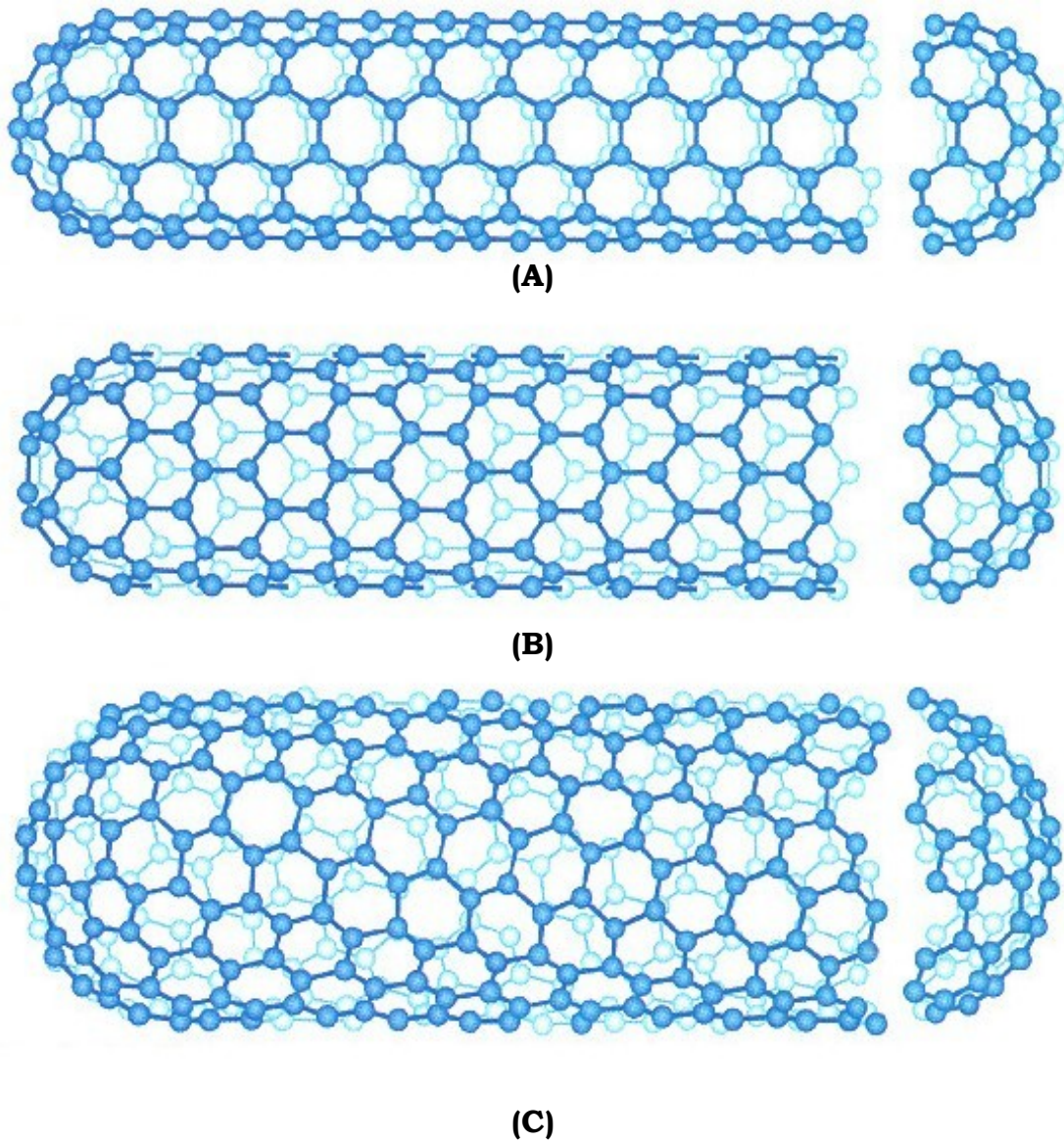


Figure 2.3: Structure of Single Walled Carbon Nanotube (A) Armchair (B) Zig zag (C) Chiral

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 idea 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 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 particle situation would be further affected by propensity for individual graphene cylinders to slide with respect to each other.

There are no direct 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 was measured by 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 vibrational 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 estimate. 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 involved 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 mode of structure like Nanotubes is also intriguing, e.g. it could happen via the collapse of the inside hollow providing absorption of energy and increased toughness. The high value of 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 hollows number of the layer on the nanotube wall and nanotubes size. It is generally seen that the single wall nanotubes are, more flexible and less prone to buckling compared with their multi-wall nanotubes 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 (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 severe structural distortions. This flexibility is related to the ability of the

carbon atoms to the rehybridize, the degree of sp^2 – sp^3 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/cc for SWNTs up to 1.8g/cc for MWNTs, compared to 2.26g/cc 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 graphite carbon, they have good resistance to chemical attack and have high thermal stability. Oxidation studies have shown that the onset of oxidation shifts 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 into 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.⁸ 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,

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 : 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 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 (1996) using a laser ablation method.

The optimization of SWNT growth by arc-discharge was achieved by Journet and coworkers (1997) 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 (1998 & 1999). by using methane as carbon feedstock and reaction temperatures in the range 850-1000°C.

Smalley and coworkers (1998) who used ethylene as carbon feedstock and growth temperatures around 800°C reported another CVD approach to SWNTs.

Liu (2000) made a significant progress and coworkers (2000) 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.

Rao and coworkers (1999) used a catalyst based on mixed oxide spinels to grow SWNTs.

Dresselhaus et al (1996) found that good quality yield of nanotubes were obtainable with Fe Co alloy nanoparticles.

Colomer and coworkers (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.

Cheng and coworkers (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.

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 800-1200°C.

Xie group (1996 & 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 600°C.

Ren (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 660° C.

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

Sandler et al (1999). reported dispersive of as produced 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 (2000). 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 (1998) obtained uniform film of MWNTs and poly (p-phenylene vinylene)(PPV) widely studied was prepared by spin –coating highly concentrated MWNT dispersion.

Zeng et al (2004). 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 (2002).found two to three times improvement in Young's modulus and yield strength resp. when 1 wt% MWNTs were added to the epoxy matrix.

Tai et al (2002 & 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.

Zhi Wang et al (2004). 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 4: EXPERIMENTAL

4.1 Synthesis of Carbon Nanotubes

4.1.1 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 30 mm in depth and was filled with Fe, Ni and Co mixtures or individual element in certain ratio. The mixed powders include Fe/Ni, Fe/Co, and Co/Ni. 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 varied from 0.1 bar to 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.



Figure 4.1.1a: Set-up for producing carbon nanotubes by dc electric arc discharge

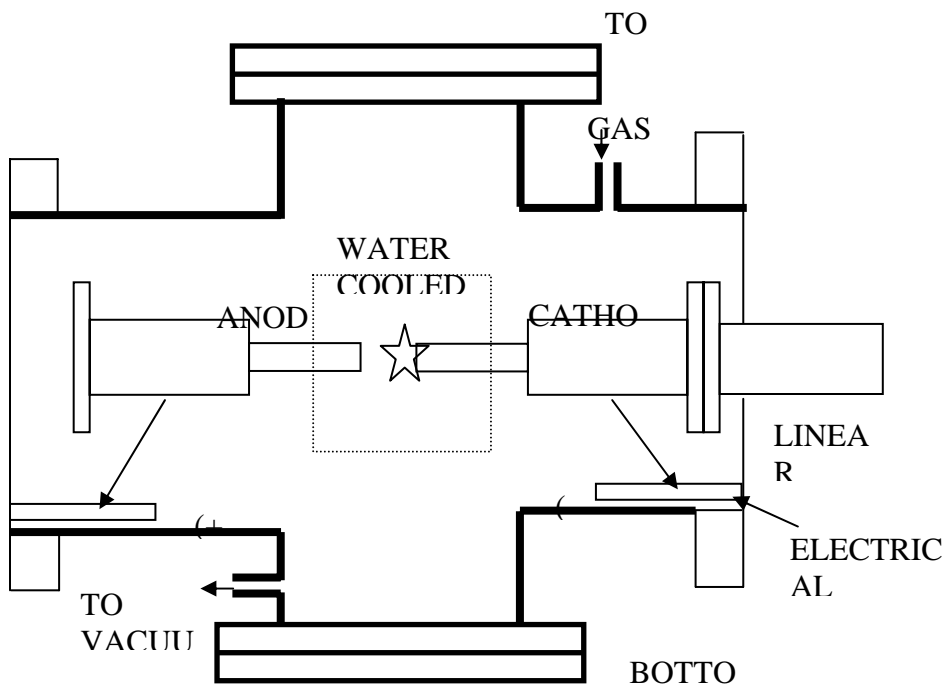


Figure 4.1.1b: Block Diagram of Arc Discharge Method

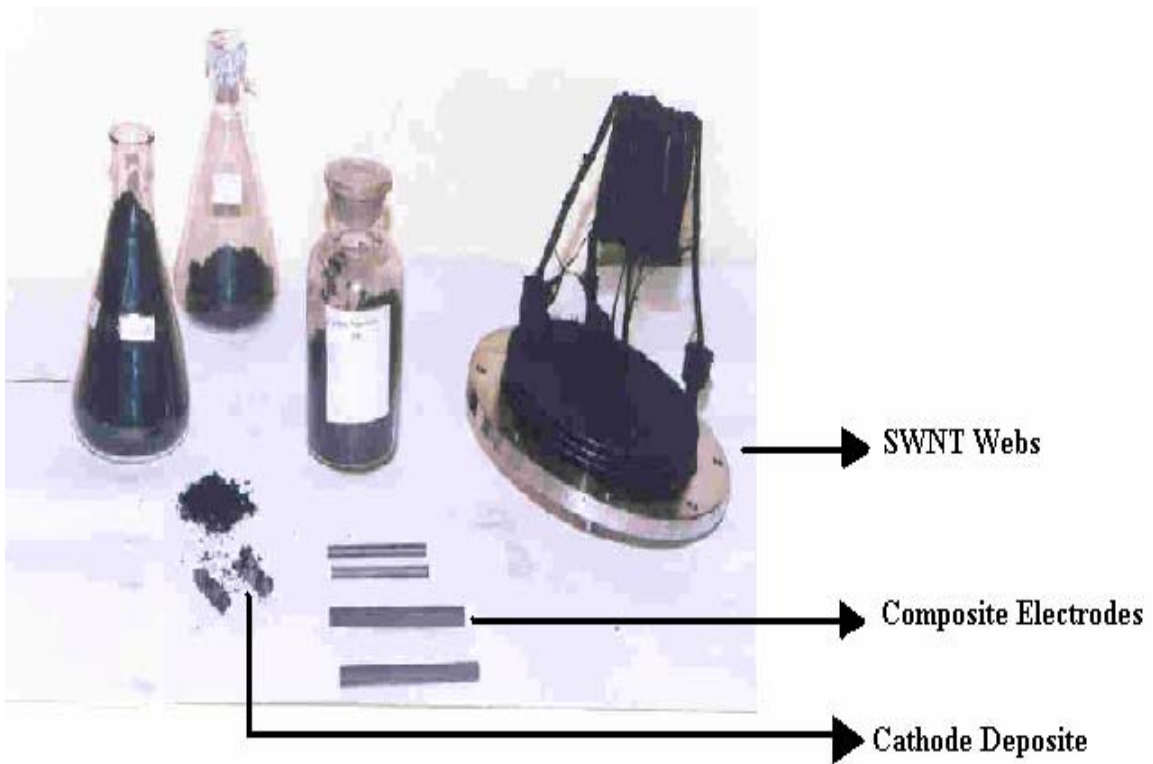


Figure 4.1.1c: Produce carbon nanotubes by arc discharge method

Experiment-1

3mm diameter hole was drilled in one of the graphite electrodes of diameter 8mm and length 60mm. The hole was filled with 2at% Ni and 2at%Co powder, purity 99.9%. This electrode was arced against a cathode of diameter 10mm. A current of 80A and 24 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 small amount of SWNTs, whereas the cathode deposit comprised of almost 90% of the total evaporated carbon and contained mostly MWNTs.

Experiment-2

3mm diameter hole was drilled in one of the graphite electrodes of diameter 8mm and length 60mm. The hole was filled with 1at% Ni and 2at%Co powder, purity 99.9%. This electrode was arced against a cathode of diameter 10mm. A current of 100A and 25 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 20% more of SWNTs, compared to previous experiment, whereas the cathode deposit comprised of almost 70% of the total evaporated carbon and contained mostly MWNTs.

Experiment-3

3mm diameter hole was drilled in one of the graphite electrodes of diameter 8mm and length 60mm. The hole was filled with 4at% Ni and 4at%Co powder, purity 99.9%. This electrode was arced against a

cathode of diameter 10mm. A current of 150A and 25 volts was maintained during arcing. Helium pressure was maintained at 400 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 doubled as compared to the soot in experiment-1. The amount of the catalyst in the soot as measured by EDX was also found to be 30%by weight of the total soot deposits. Additionally, the soot was also found to contain amorphous carbon and confirmed by Thermal Gravimetric Analysis. The cathode deposit weighs about 60% of the total carbon evaporated during the arcing.

Experiment-4

3mm diameter hole was drilled in one of the graphite electrodes of diameter 8mm and length 60mm. The hole was filled with the catalyst comprising of 1%Y + 1%Ni +1%Co, 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 catalysts in the soot as measured by EDX was also found to be >26%of the total soot deposits. Additionally, the soot was also found to contain

amorphous carbon and confirmed by Thermal Gravimetric Analysis. The cathode deposit weighs about 80% of the total carbon evaporated during the arcing.

4.1.2 Chemical Vapor Deposition Method

In the present study CNTs have been synthesized by using toluene as the carbon source and the ferrocene as the catalyst. The hydrocarbons 8 – 20 grams were mixed with 8% of ferrocene by wt., which was sonicated for a period of 30 minutes to achieve uniform dispersion. Ferrocene is a good precursor for producing Fe particles used for nanotube growth and is soluble in this hydrocarbon. The precursor raw material with approximately 6 ml/hr of flow rate was injected into the quartz reactor kept in the two-zone reaction furnace through the fine capillary shown in the figure 4.1. The temperature of both zones preheating and reaction zone of furnace is maintained at following experimental conditions. The main furnace zone temperature was kept 750°C. An inert atmosphere was maintained inside the quartz reactor by flowing the inert gas. Inert gas used also as a carrier gas was flown by 2 liter/min. The liquid feed (toluene + ferrocene) when pressed into the preheating zone of the furnace volatilizes off at 200°C. The two components, catalyst and the hydrocarbon are transported into the main zone of the furnace with the help of carrier gas Ar. After completing the reaction, the furnace is cooled down up to room temperature and the inert gas is continued to flow. A blackish carbon material is deposited inside the wall of quartz reactor. This material is scraped out from the reactor wall with the help of brush and weighed. These as produced CNTs are characterized by SEM, TEM, RAMAN, and TGA.

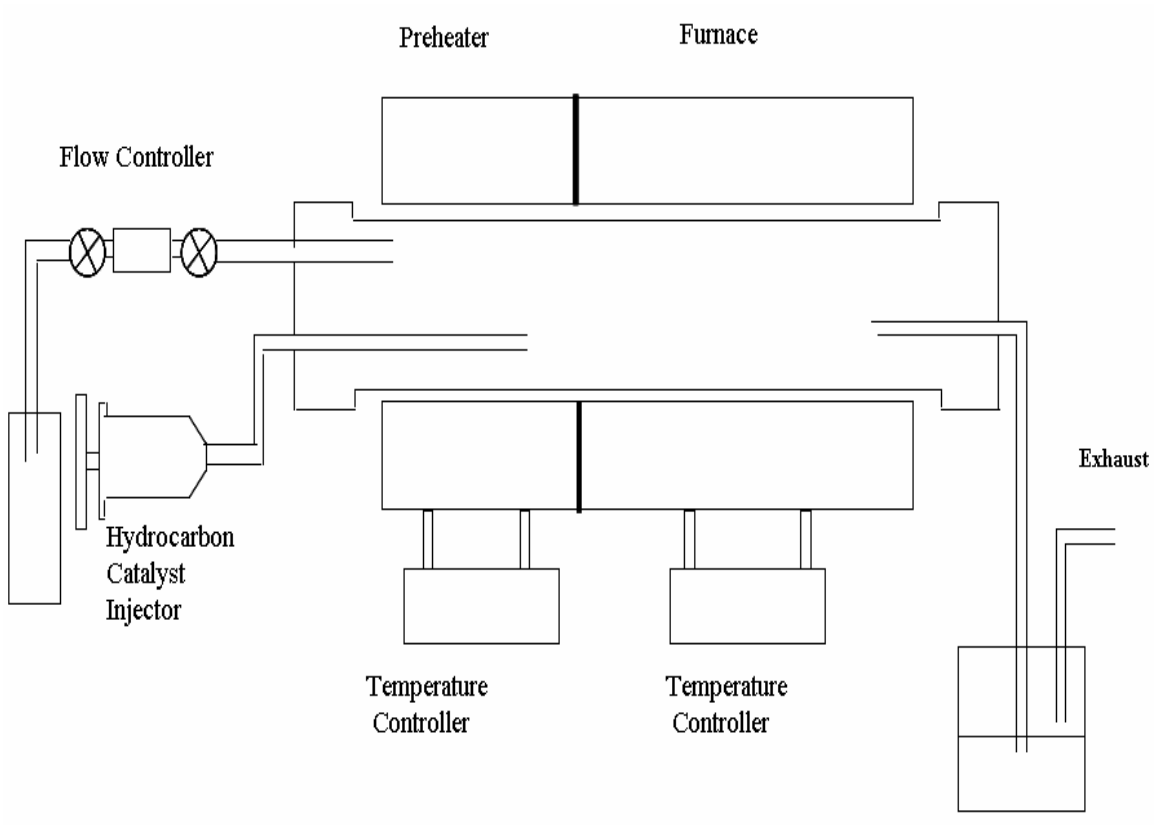


Figure 4.1.2: Schematic diagram of CVD experimental set up

4.2 Composite

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 size 50X5X3 mm³.

4.2.1 Procedure

Composites of CNTs and phenolic resin (phenol formaldehyde) have been prepared with different 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.

Dispersion was done through the dry mixing: CNTs are mixed with solid phenolic resin by a mortar and until a homogeneous powder is obtained.

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°C and when same temp reaches the sample material was pressed. After pressing these samples were cured at 180°C for two hr. For comparison 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, 0.5, 1, 2, 3, 4, 5, and 10 % with same resin.

The composite samples have been characterized for their mechanical properties (flexural strength and flexural modulus) on Instron Universal Testing machine as per the ASTM standard (ASTM D-790). Block diagram for determining the flexural strength of the sample is shown in figure below. The three points bending test provide values for the modules of elasticity in bending E_B , flexural stress σ_f , flexural strain ε_f and the flexural stress-strain response of the preparation and testing. However, this method has some disadvantages also: the results of the testing method are sensitive to specimen and loading geometry and the strain rate. Flexural strength of the composite samples are calculated as follows:

$$\sigma_f = \frac{3PL}{2bd^2}$$

Calculation of the flexural strain ε_f

$$\varepsilon_f = \frac{6Dd}{L^2}$$

Where P = load at a given point on the load deflection curve, [N]

L = support span, [mm]

b = width of the testing sample, [mm]

d= depth of the test sample, [mm]

D = maximum deflection of the center of the beam,[mm]

Flexural modulus is determined from the slope of the stress-strain line developed during the three point bending test.

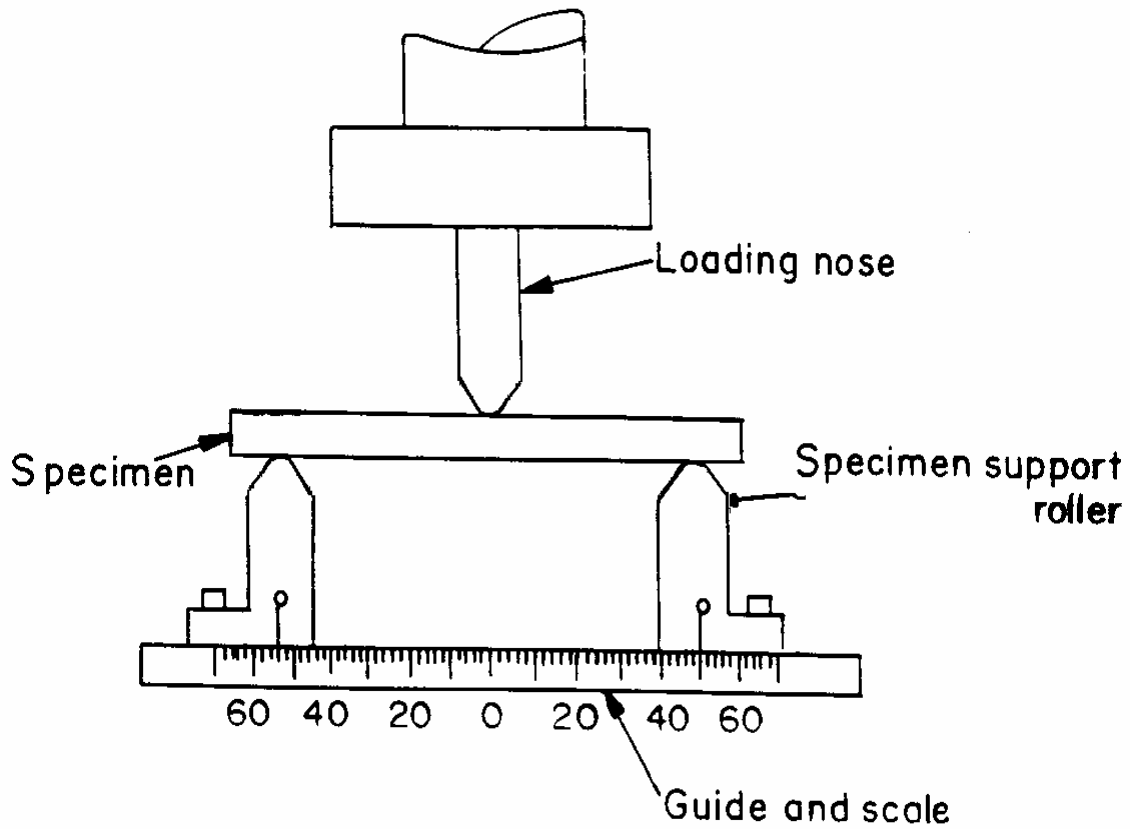


Figure 4.2 Block diagram of flexural testing instrument

CHAPTER 5: APPLICATION OF CARBON NANOTUBES

5. Application Of 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 the carbon nanotubes, but other applications of carbon nanotubes rarely need the 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 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 chemicals, such as gold or zinc oxide. These nanowires in turn can be used to cast nanotubes of other chemicals, 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 field 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.

5.1 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 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 con

Tender, 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. The

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 in 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.

5.2 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 grow out of the catalyst. Another way for the self-assembly of the carbon nanotubes 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.

5.3 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 lightning 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 10^{13} A/cm². 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.

5.4 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 larger ones 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.

5.5 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 ($\sim 1000 \text{ m}^2/\text{g}$), 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

5.6 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).

5.7 Molecular Electronics

The idea of building electronic circuits out of the essential building blocks of materials - molecules - has seen a revival 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.

5.8 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°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.

5.9 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.

5.10 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.

5.11 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.

5.12 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.

5.13 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.

5.14 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.

5.15 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 supporting 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 tubules, which would guarantee uniform emission

5.16 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.

5.17 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, the 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.

Lithium 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 uptake. If an optimum nanotube diameter can be found, the hydrogen uptake is high and can be compared to the best presently available material (metal hydrides) for hydrogen storage. 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

supporting 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 milli 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 tubules, which would guarantee uniform emission.

5.18 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.

5.19 Electrode Applications

The potential of nanotubes Torr electrode applications is being explored especially because carbon-based have been used for decades in important electrode application 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.

5.20 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 in high and can be compared to the best presently available material (metal hydrides) for 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.

5.21 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-phenylenevinylene-co 2, 5 dioctoxy-p-phenylenevinylene) (PYC) filled with MWNTs and SWNTs [69] Compared to the pristine polymer.

Nanotube/PPY composites have shown a large increase in electrical conductivity of nearly 8 orders of magnitude, with little in photoluminescence/ electroluminescence yield

5.22 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 6 : RESULT AND DISCUSSION

6 Results and Discussion

Carbon nanotubes were synthesized by D.C. Arc discharge technique. The synthesized material contain two type of material first one is chamber deposit which is SWCNT with some impurities and second one is cathode deposit contains MWCNT. Both type of materials were characterized by SEM as shown in figure [6.1(a) & 6.1(b)]

Generally appearance of the carbon material deposited inside the chamber [figure (6.1a)] and one deposited on the cathode [figure (6.1b)] was found to be quite different. The material (a), resembled sheets of soot like fibrous mat, SEM micrograph of such material figure [6.1(a) & 6.1(b)] Shows that these contained multitude of nanotubes or ropes. These ultra fine tubes were filled with amorphous soot and metal particle of metals or metal carbide, holding the material together. 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. These short and straight bundles actually contained multitude of nanotubes of outer diameter ~25nm aligned preferentially along the length of the electrode or electric field. An overall yield of the nanotubes through SEM could be estimated as 50% by volume both in sample 'a' and 'b' combined together.

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 5-8gms. The total time taken to consume about 60mm length of electrode was about 30 min.

Table 6.1 EDS analysis of deposits containing carbon nanotubes produced inside the arc discharge reactor

Sample Description	Element	As-Produced Sample (% By weight)
Chamber Deposit	C	69.00
	O	3.00
	Ni	10.00
	Co	18.00
Cathode Deposit	C	95.00
	O	5.00
	Ni	----
	Co	----

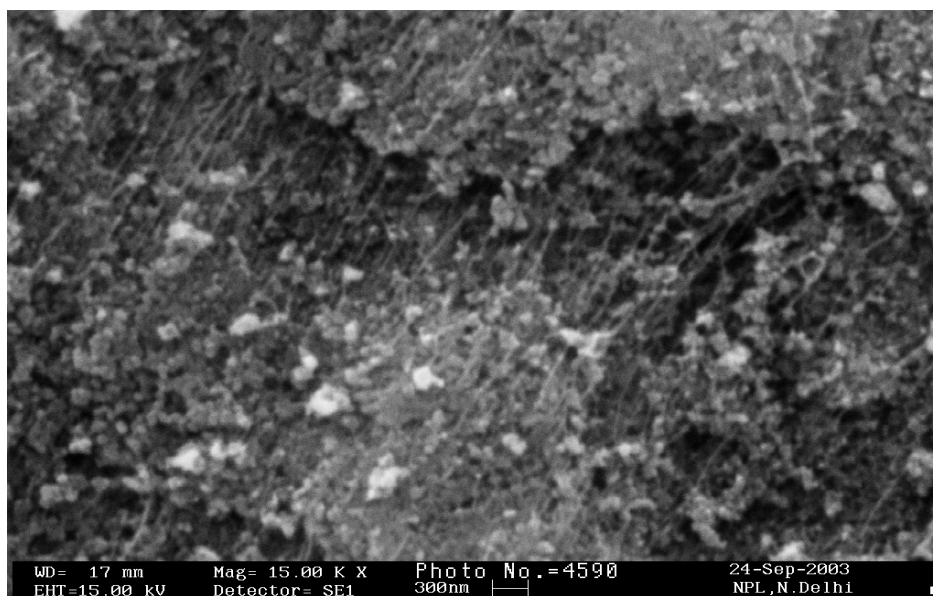


Figure 6.1(a): SEM photograph of CNTs on Chamber deposit produced by arc discharge technique

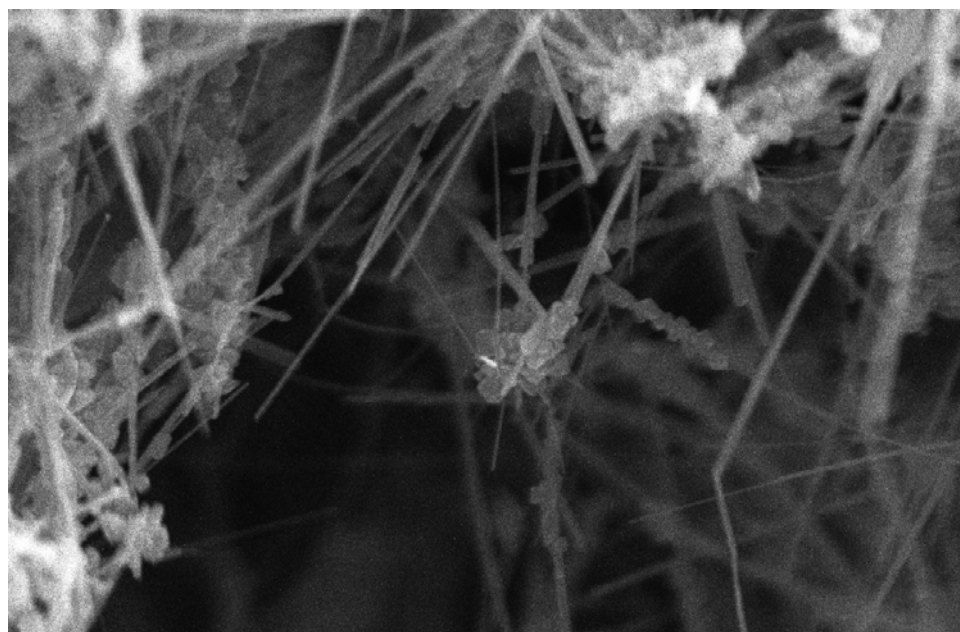


Figure 6.1 (b): SEM photograph of CNTs on cathode deposit produced by dc arc discharge technique

6.1 Thermo gravimetric analysis

TGA/DTG is common method for estimation of the each species present in the carbon nanotubes deposits corresponding to their peak position and the area in DTG curve. The thermal gravimetry of the as produce samples chamber deposits material and cathode deposit material respectively, was carried out in a Mettler-Toledo, TGA/SDTA 851 thermal analysis system. A heating rate of $10^{\circ}\text{C}/\text{min}$ in flowing dry was maintained and the maximum temperature was kept to 900°C . Figure 6.2(a) shows the weight loss behavior of the as produced sample a in presence of flowing dry air. The solid line corresponds to thermogravimetry (TG) and the dashed line to differential thermogravimetry(DTG). There is no obvious weight loss up to 300°C after which there is an abrupt weight loss a sudden weight loss around 300°C , with sharp DTG peak around 340°C can be ascribed to oxidation of amorphous carbon. An isothermal time of 30 minutes shows that there is still 36% residue, remaining in the crucible. Assuming that up to 800°C there are no nanotubes left in the residue, it could be concluded that the percentage of catalysts as impurity in the sample was about 36%. The weight loss behavior of this material is shown in Figure 6.2(b). The curve shows that there is no weight loss up to 600°C , after which a sharp weigh loss is observed with the DTG peak at 730°C with almost no residue left beyond 800°C . Absence of any weight loss in the low temperature region that is between $300\text{-}400^{\circ}\text{C}$ suggests the absence of amorphous carbon in sample. Since there is no residue left beyond 800°C .

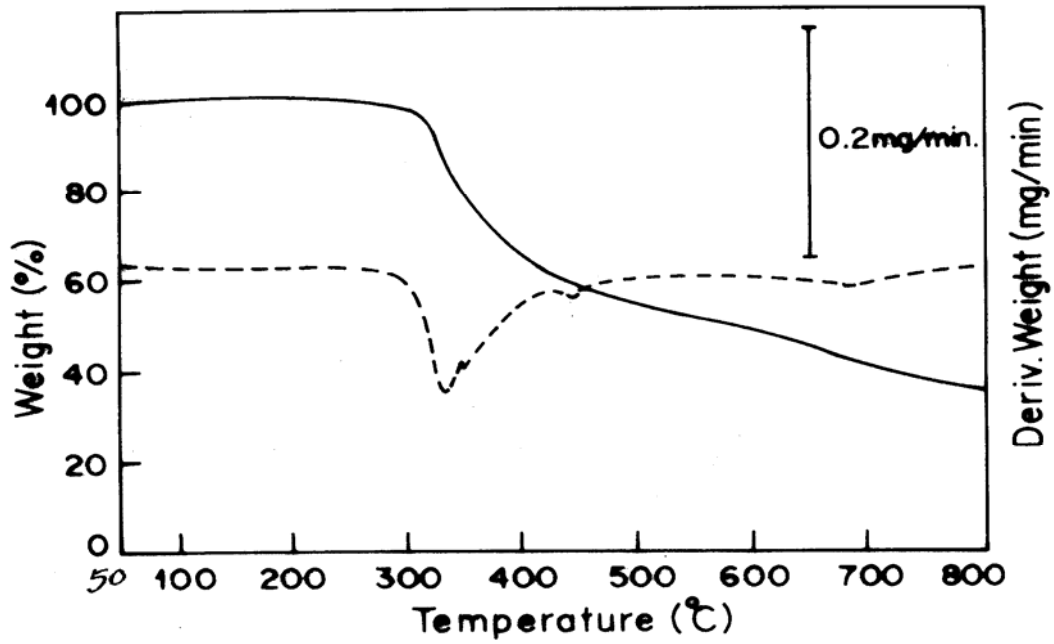


Figure 6.2(a): TGA and DTG data for the as produced chamber deposit

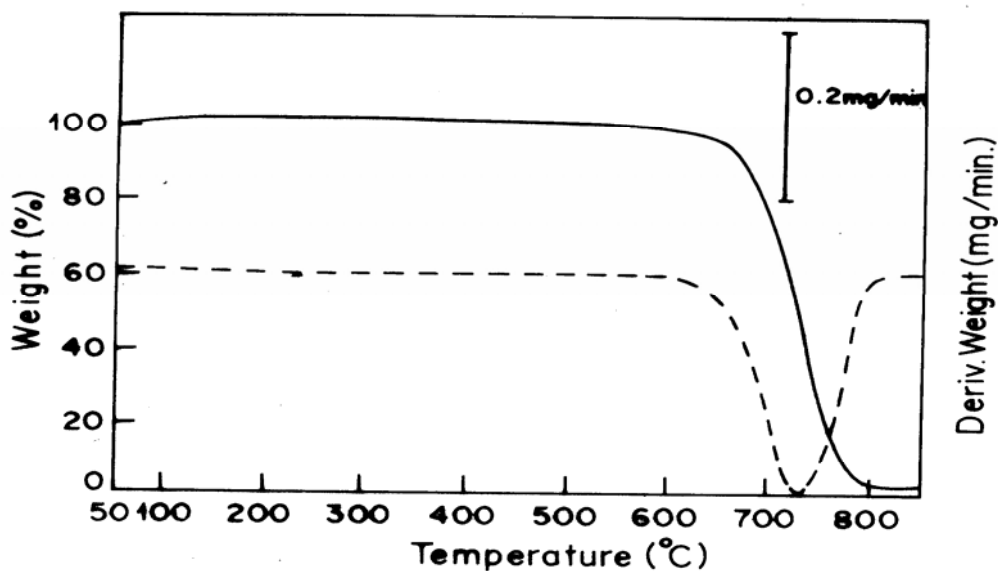


Figure 6.2(b): TGA and DTG data for the as produced cathode deposit

6.2 Raman spectroscopy

It is well known that SWNTs have two groups of characteristic mode. The one at the low frequency (~ 180) is called the radial breathing mode and the other at high frequency around 1590 is called the tangential stretching mode. When the sample contained amorphous or disordered carbon, the D mode at 1350 was observed. The relative intensity between C-C stretching and D mode can be taken as indicator of the purity of the nanotubes. The Raman spectra shown in figure suggests an important observation that while the chamber deposit show predominantly single wall carbon nanotubes, the cathode deposit show mostly multi-walled carbon nanotubes. The observation has been reported for the first time. This is further confirmed by the low frequency peaks at 164 and 187 respectively, corresponding to the presence of two different diameter SWNTs. The D-mode was also observed at 1350 cm^{-1} corresponding to amorphous or disordered carbons. The high frequency

peak for MWNTs appears at 1580 cm^{-1} . As shown in Figure 6.3, it is quite evident that while the chamber deposit shows presences of predominantly SWNTs, the cathode deposit shows the presence of MWNTs only. This is a very interesting finding. The presence of D-band in sample cathode deposit material shows the presence of disordered carbons, different from the amorphous carbons as in the case of sample chamber web.

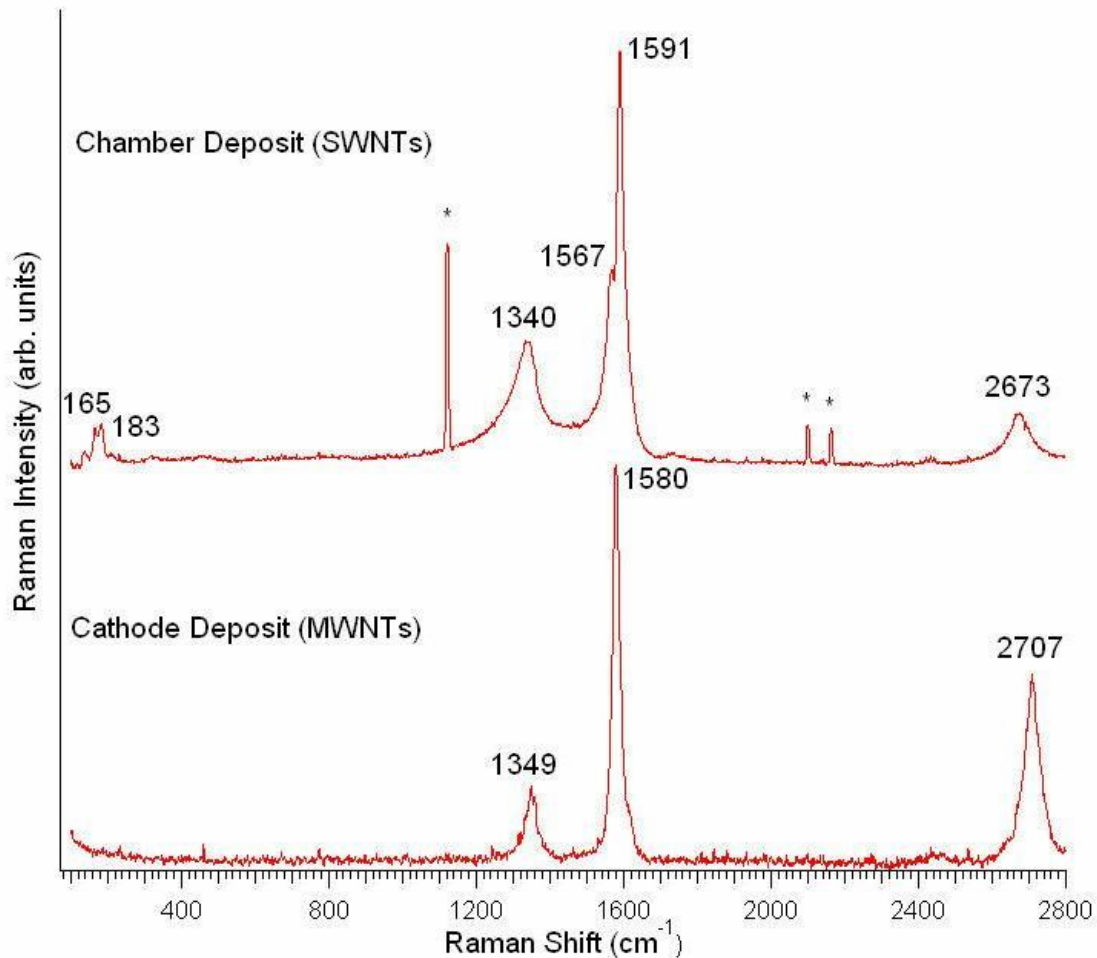


Figure 6.3: Raman Spectra of the chamber deposit, showing presence of SWCNTs and the cathode deposit showing the presence of MWNTs

The amount of carbon nanotubes synthesized by catalytic chemical vapor deposition (CCVD) at 750°C from toluene as the hydrocarbon with iron as catalyst, which made available from the decomposition of ferrocene, is given in Table 6.2. Toluene was processed in 42 mm diameter reactor in 8, 12, 16, 20 and 24 -gram batches. The maximum amount 7.0 gram of pristine carbon nanotubes was synthesized amounting to 29.17 % conversion from toluene.

Table 6.2: Percentage conversion of different hydrocarbons with ferrocene at 750 ° C

Name of hydrocarbon	Diameter of reactor (mm)	Amount of hydrocarbons (grams)	Amount of ferrocene (grams)	Amount of as produced CNTs (grams)	Percentage conversion of hydrocarbons*
Toluene	42	8.00	0.7000	1.76	22.00
Toluene	42	12.00	1.0500	2.70	22.50
Toluene	42	16.00	1.4000	4.20	26.25
Toluene	42	20.00	1.7500	5.50	27.50
Toluene	42	24.00	2.1000	7.50	29.17

6.3 Scanning electron microscopy

These synthesized CNTs have been characterized by scanning electron microscopy (SEM). The SEM photomicrographs of pristine carbon nanotubes synthesized from toluene at 750°C are shown in the Figures 6.4, 6.5, 6.6, and 6.7. As such scraped material from the reactor

was seen in SEM at low magnification, shown in figure 6.4. This figure is showing logs of carbon nanotubes. This log of CNTs contains many bundles. Figure 6.5 shows very long bundles of CNTs with length approximately $\sim 200 \mu\text{m}$. The magnified view of these bundles of tubes is shown in Figure. Where individual tube can be seen Figure 6.6 these synthesized were found to be uniform in diameter and very dense growth. Figure 6.7 shows very high dense growth of CNTs, which got entangled with each other. SEM photomicrographs are not showing the presence of amorphous carbon or any other type of impurities in these synthesized tubes.

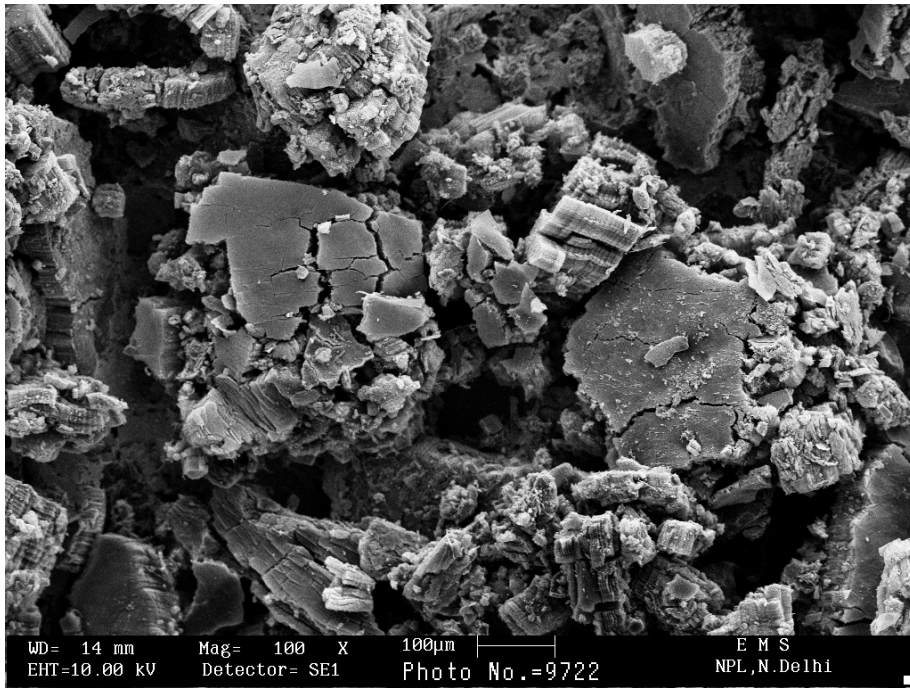


Figure 6.4: SEM photograph of as such carbon nanotubes at low magnification

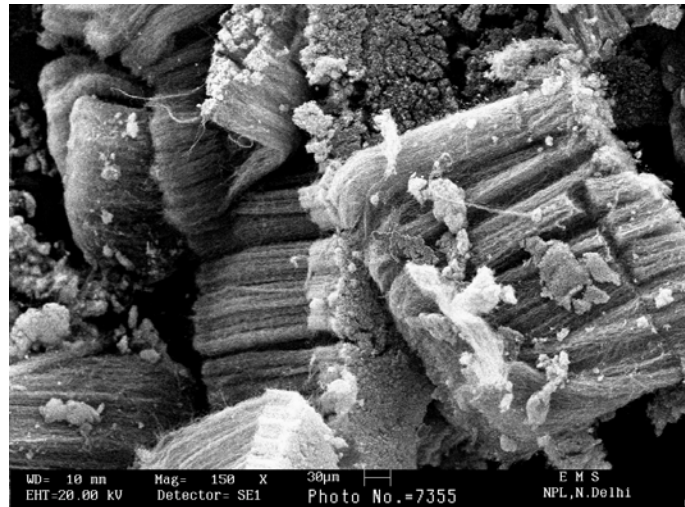


Figure 6.5: SEM micrograph of as produced carbon nanotubes by CVD technique

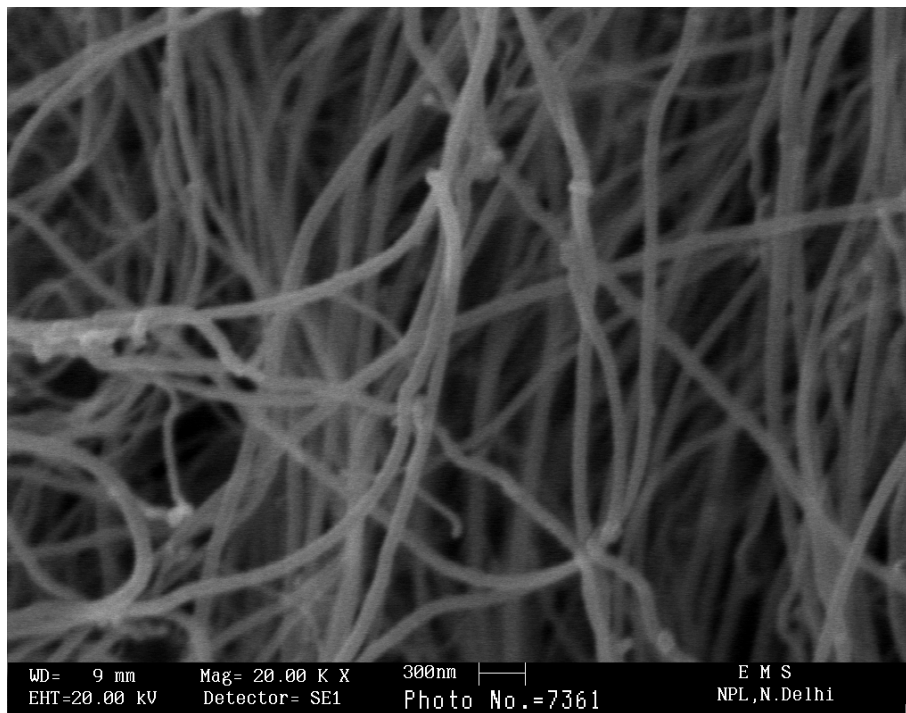


Figure 6.6: SEM photograph of as such carbon nanotubes at higher magnification

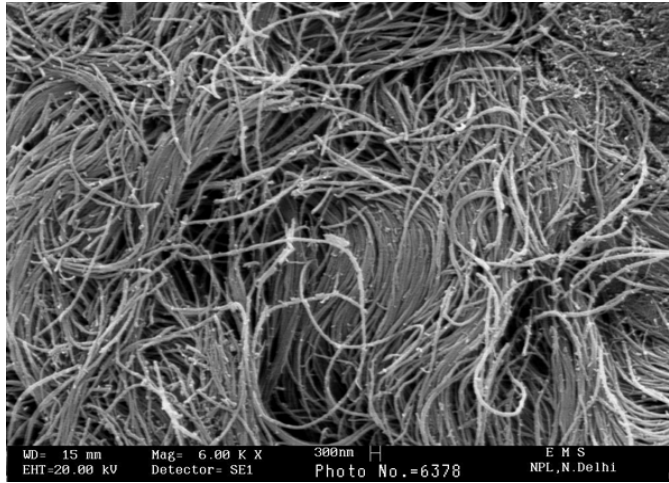


Figure 6.7: SEM micrograph of as produced carbon nanotubes by CVD technique

6.4 Transmission electron microscopy

These synthesized tubes were also characterized by transmission electron microscopy (TEM) and the micrographs are shown in Figure 6.8 these micrographs are of as produced CNTs at 750°C using toluene as the feed source. Figure shows a single CNT with a narrow cavity surrounded by many layers, which clearly shows that these tubes are multi walled. It is observed that the tubes are without any kind of impurities except catalyst. These TEM observations indicate that the tubes are multi walled carbon nanotubes. Figure 6.9 shows the TEM micrograph showing the presence of large amount of MWCNTs appears to be pure in nature along with the catalyst.

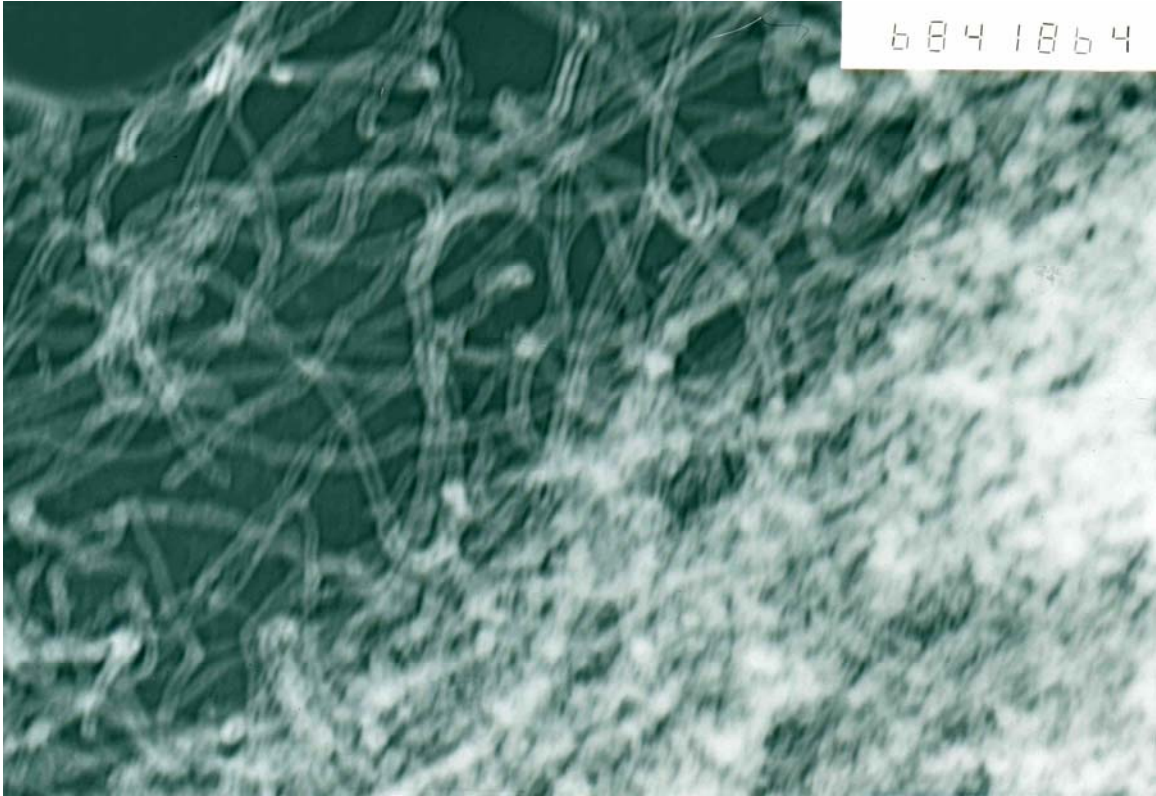


Figure 6.8: TEM micrograph of CNTs showing the large amount of tubes is present without any impurity except catalyst

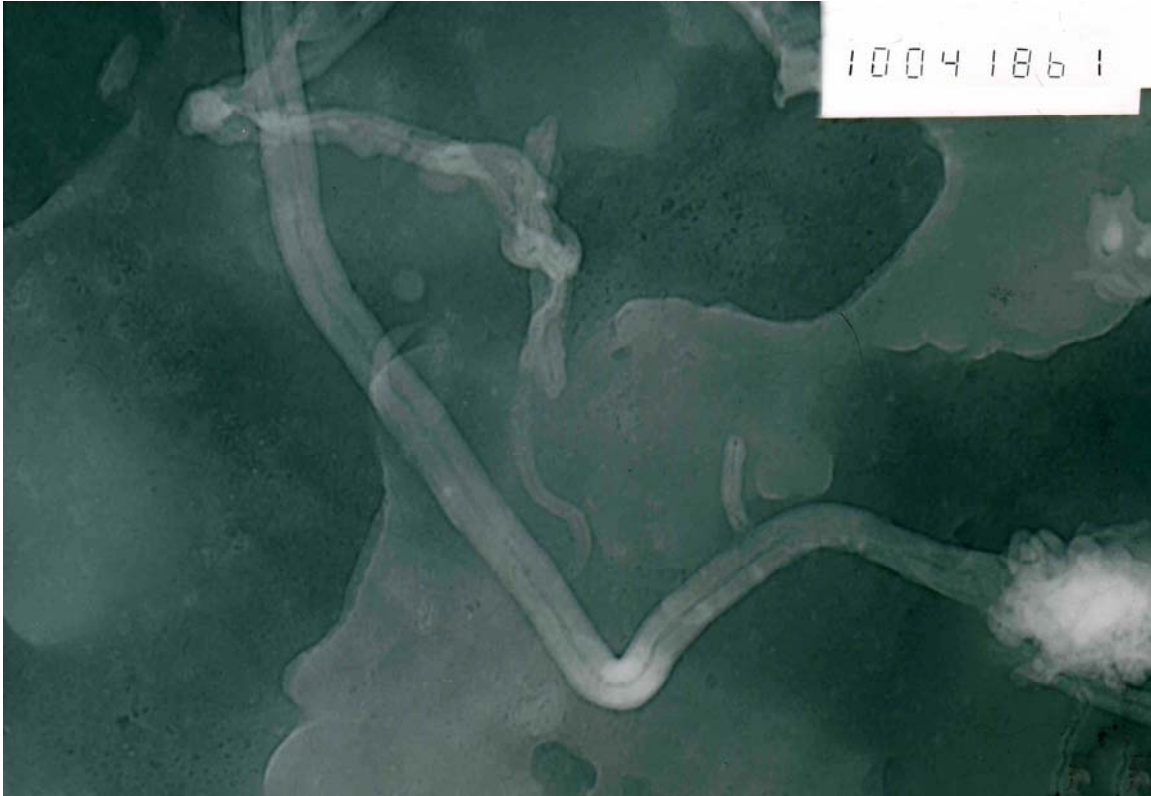


Figure 6.9: TEM micrograph of single CNTs showing the tube cavity surrounded by multi-layers

6.5 Raman spectroscopy

The Raman spectrum showing a very high intense peak at 1580 cm^{-1} shows the presence of multi-walled carbon nanotubes (MWCNTs). There are two peaks as 1580 cm^{-1} the G band and 1352 cm^{-1} the d band generally appear for disorder carbon. But in the SEM photographs no amorphous carbon has been seen. So this d band appears for presence of some defects in the tubes.

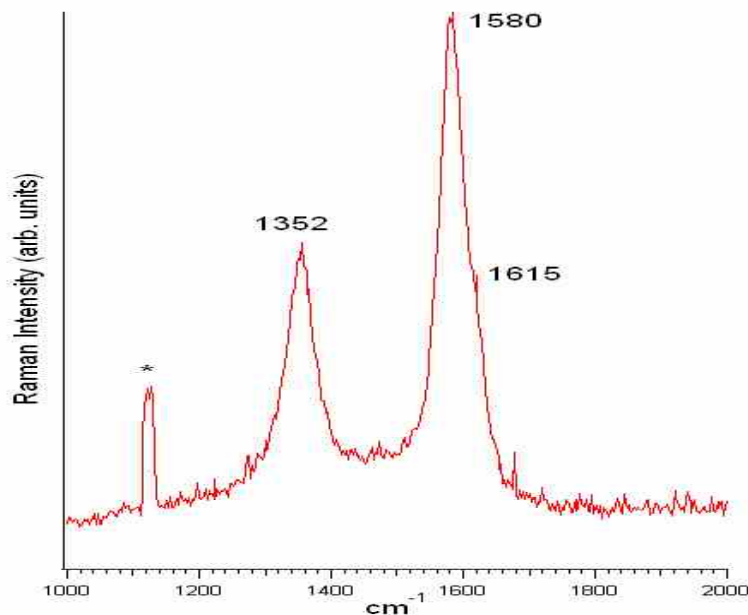


Figure 6.10: Raman spectra of the carbon nanotubes produce CVD sing presence of multi-walled carbon nanotubes

6.6 Thermo gravimetric analysis

The presence of metallic impurities is calculated through the TGA. Figure 6.11 Present the TGA of as such CNTs synthesized at 750°C with the toluene as carbonaceous feed source. It shows ~90% wt loss at 700°C in the presence of air, which showing only ~ 10% catalyst is present in the as produced CNTs.

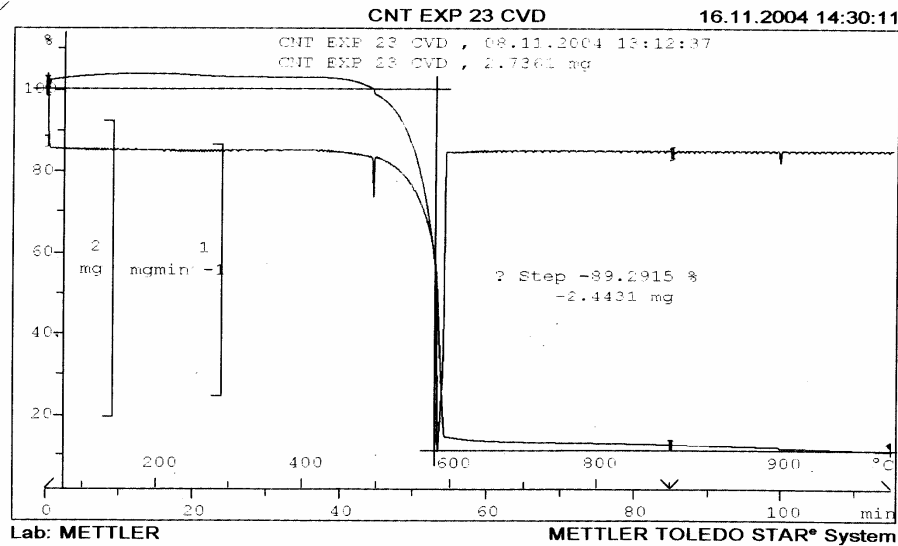


Figure 6.11: TGA curve for the carbon nanotubes containing soot produced by CVD. The curve shows that the purity of the nanotubes ~ 90%

6.7 Composite

Flexural strength and modulus values of the composite prepared by using different fraction of CNTs at the phenolic resin are produced in table 6.3. Strength as well as modulus of the resulting composite register an increase of ~100% with merely 4% by volume addition of CNTs in the composites, the highest value of flexural strength achieved are 120 MPa. Further experiments are in progress to use surface modified tubes for improving the properties of phenolic resin based composite.

Table 6.3: Mechanical properties of Carbon Nanotubes composites

S.No.	By Volume %	Strength MPa	Modulus MPa
1	0%	62	3750
2	0.5%	101	5349
3	1%	118	5222
4	2%	96	5239
5	3%	110	5473
6	4%	120	6796
7	5%	93	5882
8	10%	93	3850

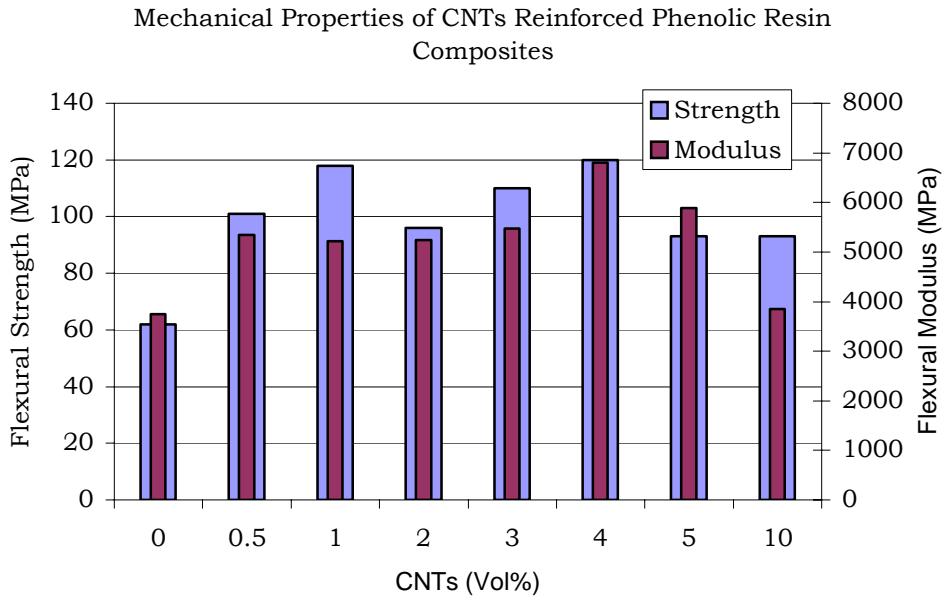


Figure 6.12: Mechanical Properties of CNTs Reinforced composite

CHAPTER7: CONCLUSION

Conclusion

In the present study single wall as well as multi-walled carbon nanotubes have been synthesized by dc arc discharge technique. Cathode deposit material contains multi-walled carbon nanotubes and chamber soot contains single wall carbon nanotube with some impurities like amorphous carbon, graphite particle and catalyst.

Carbon nanotubes were also synthesized successfully by chemical vapor deposition technique. By the same method up to 7.0 gm of multi-walled carbon nanotubes with ~ 90% of purity were produced. Percentage conversion of given hydrocarbon to carbon nanotube based material was ~30%. A useful insight was obtained for characterization of CNTs by SEM, TEM, Raman and TGA.

Due to extraordinary mechanical properties of carbon nanotubes, it was used for reinforcement with phenolic resin. Different volume fraction of CNTs was added into the polymer for composite formation and flexural strength of composite was found to be doubled at merely 4-volume% loading of CNT's w.r.t. that for neat resin. The flexural modulus of the same sample was also enhanced significantly by including merely 4% by vol. of carbon nanotubes.

Chapter8: Future Scope

The Nanotubes produced in our laboratory, during each experiment, are only about a few grams. Mass scale production of Nanotubes is being aimed by upgrading the present experimental setup. This can be done by building a bigger setup of the experiment and using a continuous process of injection of reaction mixture and expulsion of the undesired product. Arrangements can also be made for recycling the exhaust gases by extracting the Carbon in them. Better substrates, carrier gas and hydrocarbon + catalyst mixtures can also be explored that can increase the total yield.

Regarding the Polymer-CNT composites, constant endeavors are being made for obtaining greater adhesion through Functionalization of, that is adding functional groups to the surface of the CNTs which would make them chemically active and increase their affinity for bonding with the polymer. Strong binding would result into better composite performance.

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