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A REVIEW ON CARBON NANOTUBES

Omkar S. Yadav
BE Student, Mechanical Engineering Department
Indira College of Engineering and Management, Pune, India
Bhushan Mahajan
Asst. Prof, Mechanical Engineering Department
Indira College of Engineering and Management, Pune, India

Abstract – **Carbon nanotubes (CNTs) are one of the most exciting discoveries and are studied from the past two decades. This paper discusses the different allotropes of carbon. A brief survey of history of CNTs, different types of CNTs its geometry, structure and different shapes of CNTs was carried out. Various properties of CNTs such as electronic, mechanical and thermal are explained in detail. The different methods for the production of CNTs are explained outlining their capabilities, efficiencies and possible exploitation for large scale production.**

Keywords- CNTs, Graphene, CNT synthesis

1. Introduction

Carbon Nanotubes (CNTs) are cylindrical shells made by rolling graphene sheets into seamless cylinder. CNTs are of two types, single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). A single graphene sheet, which is a planar array of benzene molecules, involving only hexagonal rings with single and double C-C bonding is rolled to form a SWNT. The choice of rolling axis and the radius of closing cylinder allows different types of SWNTs. The concept of SWNTs was developed in 1993 a work by Iijima and another by Bethune. An article published much earlier by Oberlin in 1976.[1]

Marcio R. Loos et al. [1] published a book which relatively explains the reader CNT-reinforced composites. The book creates a solid background in basic themes such as theimportance of size, and why the properties of materials change at the nanoscale.

Mei Zhang and Jian Li et al. [2] this article reviews CNTs in different shapes such as formed duringgrowth, their morphologies and their possible applications.

H.Qui, J.Yang et al [3] published a chapter in a bookwhichaims to give an overview of the recent progress on CNTs in the areas of synthesis, property, and application, with a focus on the practical applications that areavailable or will appear soon. Chapter discusses the structure and property of CNT.

N.M. Mubarak, E.C. Abdullah, N.S. Jayakumar, J.N. Sahu et al. [4] published a paper in which a brief survey of experimental worktowards the synthesis of CNTs has been discussed. The various methods of production of CNTs are explained outlining their capabilities, efficiencies and possible exploitation as economic large scale production.

KhurshedA.Shah, Bilal A.Tali et al. [5] inthispapertheaspects such ascarbonsources, catalystsandsubstrateswithregardtoCVDsynthesisofcarbonnanotubesarereviewed to understand latest devlopments in the field. From this literature review it is found that carbon diffusibility and carbon solubility of any catalyst are two important factors in determining CNT nucleation and growth.

ZdenkoSpitalsky, DimitriosTasis, KonstantinosPapagelis, Costas Galiotis et al. [6] have reviewed the present state of polymer nanocompositesresearch.The various manufacturing methods for polymer nanocomposites are also listed.

Nanda GopalSahoo, SravendraRana, Jae Whan Cho, Lin Li, SiewHwa Chan et al. [7] have discussed the method and preperation of high performance CNT polymer composites in this review with a comparision of CNT functionalization methods.

] Garima Mittal, VivekDhand, KyongYop Rhee, Soo-Jin Park, Wi Ro Lee et al. [8] have focussed on the issue related to the processing, dispersion and alignment of CNT within nanocomposites. The various CNT synthesis and properties are also reviewd by the authors.

Kenan Song, Yiying Zhang, JiangshaMeng, Emily C. Green, NavidTajaddod, Heng Li and Marilyn L. Minus et al. [9] have discussed the current state of the art polymer/CNT high performance composite fibers regarding to processing, structure and performance. Future prospects and challenges for processing polymer/CNT composites are also discussed.

Kin-tak Lau, Chong Gu, David Hui et al. [10] have reviewed on recent research in nanotube/polymer composites.The growth of nanotubes from nanoclay substrates to form exfoliated nanotube/nanoclay polymer composites is also introduced in detail. Potential applications relating to nanotube/polymer composites are also listed.

This paper discuss about the different alotropes of carbon, different types of CNTs with their geometry and structure. The various properties of CNTs and the various methods for production of CNTs will be studied. An introduction to CNT/polymer composites their synthesis techniques and challenges involved. Furthermore, few applications of CNTs will be discussed.

2. Allotropes of carbon

Life would not exist without carbon atoms. Carbon is one of the most important element found in living organisms. Carbon is one the most abundant element about 0.5 ppm in the universe. Carbon has the ability to form bonds with various elements in different ways. The energy of a single C-C bond is 348 kJ/mol. Organic carbon in the form of plants and animals is transformed into oil which is a major energy source. Inorganic carbon is found in pencils, lubricant, diamond, carbon filters etc.

The most stable thermodynamic allotrope of carbon under normal condition of temperature and pressure is graphite. The structure of graphite consists of layers of atoms in hexagonal array. Covalent bonds and van der Waals bonds joins the atoms of each layer and atoms in different layers respectively. Graphite is a soft material and is used as lubricant. Graphite is a good conductor of electricity. It is optically dense in nature and the structure is anisotropic. Graphite as a whole has low thermal conductivity and hence a poor conductor of heat.

Diamond the second allotrope of carbon has two configurations, cubic and hexagonal. The C-C length in diamond is 1544 A°i.e. approx. 10% more than graphite. In a cubic diamond, tetrahedral arrangement of atoms is present. Diamond is one the hardest material. Diamond is used as a abrasive and an insulator. It is optically transparent and has a isotropic structure. It is a good conductor of heat.

Fullerenes the third allotrope of carbon were discovered in 1985. The molecular form of fullerene consists of a hollow cluster containing 60 carbon atoms (C_{60}) or more arranged in pentagons and hexagons. There are also C_{70}, C_{100} molecules etc. The average diameter of fullerene is 1.1 nm. C_{60} with 20 hexagones and 12 pentagones like a football. Fullerenes are formed under conditions of high temperature and pressure. It is used as insulator in pure form. Impure fullerene can be a conductor or semiconductor. Major synthesis method of fullerene is arc discharge. Elongated form of fullerenes forms carbon nanotubes (CNTs) [1].

3. Carbon nanotubes

CNTs are a kind of tubular structure having diameter in nanometer scale and length in micrometers. A CNT can be considered as a graphene sheet rolled to obtain a cylinder. The two types of CNTs as shown in Fig 3 single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

3.1 Carbon nanotubes in different shapes

I. Straight carbon nanotubes

The diameter of CNT is in nanometers while its length is in millimeters. Long CNTs remain straight when they are in oriented structures. Vertical alignment means CNTs are oriented perpendicular to substrate. There are two major breakthroughs in thesynthesis of CNT arrays. Porous silicon substrates with a catalyst patterned by electron-beam evaporation through shadow masks toproduce MWNT blocks that grew perpendicular to the substrate. A millimeter high SWNT array using water assisted CVD [2].

Scanning electron microscope (SEM) image of SWNT cylindrical pillars with 150 µm radius, 250 µm pitch, and ~1 mm height. Insert, SEN image of aroot of a pillar. (b) SEM images of SWNT sheets 10 µm thick. (c) High-resolutionTEM image of the SWNTs. (d) TEM image of a bundle consists of collapsedsingle-wall, double-wall, and triple-wall nanotubes with big diameters. (e) and (f) SEMimages of arrays of almost exclusivelysemiconducting SWNTs at different magnifications. [2]

II. Waved carbon nanotube.

During growth if no external forces exists single nanotube naturally curves. CNT bending can originate from a pentagon- heptagon topological defect pair or a local mechanical deformation in a uniform nanotube. A nanotube elastically deforms under a small bending stress, and buckles if the local curvature exceeds a critical value. Bending stress can come from interaction with neighbor molecules, own weight, or limited growing space [2].

The ~100 µm height sheets were grown from 0.2 µm wide and 40 µm long catalyst thin films. (c) CNTs in the thin sheet. (d) and (e) super-aligned MWNT array. (f) Straight and waved MWNTs in an array. (g) to (i) SEM images of a MWNT array with wavy structure at different magnifications. [2]

III. Coiled carbon nanotube

Coiled carbon nanotubes are created when paired pentagon-heptagon atomic rings arrange themselves periodically within the heaxgonal carbon network.Theoreticalcalculation also predicted that various forms of helically coiled structuresare possible and those structures are energetically and thermodynamicallystable.Morethan 95% of CNTs are in helical structures having various diameters and pitches.They grow out of the substrate and maintain their self-organization well duringgrowth. It is interesting to note that each coil grows with its own pitchand diameter [2].

large amount of helically coiled CNTs. Each coil grows with its own diameter and pitch. (b) The tip of a coil. (c)TEM image of a coil formed by two tubules with the same pitch but differentdiameters and a slight shift in phase. (d) TEM image of typical coiled CNTs. [2]

IV. Regularly bent carbon nanotubes

CNTs can be alligned during growth with an external force originated from an electric field, the gas flow or interactions with the substrate surface. Proper combination of these external forces is a way to make regularly bent CNTs [2].

a self-organized SWNT serpentines formed due to thecombined alignment effects from the quartz substrate and gas flow. (b) Arrayof CNTs grown with zigzag morphology using a three-stage growth process.Sample tilted 45° forSEM analysis. (c) A small group of MWNTs forms a coil-like structure by self assembly. [2]

V. Branched carbon nanotube

The first structural modelsfor CNT Y-junctions are based on theinsertion of non-hexagonal rings in the hexagonal network in theregion where the three branches of the Y are joined together. Branched nanotubes with T, Y, L, and more complex junctions were initially observed in arc-discharge produced nanotubes. Branched SWNTs are believed to have a profound impact on nextgenerationelectronic devices since they have a potential to be usedinnano-electronic devices as nano-diode, nano-transistor etc [2].

CNTs with beads were observed from different processes. Beadsappear in various patterns and their structures are either amorphous orpolycrystalline graphite. The beads form either with or after CNTformation during synthesis.The beads are carbon glass (amorphous phase). They are formed on nanotube because carboncoated on the nanotube was a viscous liquid and cooling caused theviscosity to increase to a degree that the beading process stagnated. Beaded CNTs in composites enhance the electrical conductivity of the matrix materials [2].

3.2. Properties of CNTs

CNTs are intrinsically coomposed of pure carbon atoms that arrange and interact with each other by stong sp^2C-C bonds and form a unique structure which gives CNTs its properties such as mechanical, electrical and thermal properties [3]. Due to these properties CNTs have wide applications.

I. Mechanical properties

Experimental and theoretical results show that CNTs are one of the strongest materials and are formed by carbon bonds: the strongest in nature. Due to C bonds the force required to break a CNT must be enormus. This covalent bonding underlies the high mechanical strength of a CNT. It has been known for a long time that graphite has a modulus of 1.06 TPa in the plane and,due to sp2 bonds, CNTs show similar properties. The specific resistance of nanotubes is in the order of $48.5 * 10^3$kN m/kg. This combination of high strength and low density makes nanotube one of the most attractive materials for applications requiring low weight and high strength, such as airplanes, space shuttles, wind turbines, boats, etc. Expirement conducted by Yu in 2000 reported a maximum strength of 13 to 52 GPa and modulus between 320 to 1470 GPa for SWNTs and resistance of outer wall 11 to 63 GPa, the modulus 270 -950 GPa and elongation at break of 12% was obtained for MWNTs [1].

Table 1 Mechanical properties of materials. [1]

Material	Density(g/cm3)	E (GPa)	Max resistance (GPa)	Elongation (%)
SWNTs	1.33	1054	150	12
MWNT	2.6	1200	150	12
Carbon fibre M60JB	1.93	588	3.82	0.7
S- Glass	2.48	86	4.58	5.4
Kevlar 49	1.44	112	3	2.4
Al 2219	2.83	73	0.46	10
Steel 17 – PH RH950	7.65	204	1.38	6
Epoxy	1.25	3.5	0.005	4

II. Electrical conductivity

The electrical properties of CNTs are largely due to its one-dimensionalstructure (1D) and the peculiar electronic structure of graphite. Graphite is a semi-metal, but depending on the chiral vector related to integers(n, m), CNTs can be metallic or semiconductors. A nanotube is metallic either when n = m or when m - n or n - m are multiples of 3, or mand n take values that satisfy the relation m - n = 3i (where i is an integer). Hence all chiral are metallic

As n-m = 0. For all other cases they are semiconductors. On average, one-third of SWNTs are metallic and two-thirds are semiconductors. MWNTs behave as one-dimensional conductors with high electrical conductivity. Their metallic properties come from themulti-layer structure consisting of tubes with different electrical properties, whereelectronic coupling between layers occurs [1].

Table 2 Electrical Conductivity of Material [1]

Material	Conductivity (S/m)
CNT	10^6-10^7

I. Thermal conductivity

The thermal conductivity of CNTs is almost double the conductivity of diamond. Specific heat and thermal conductivity are determined by phonons in CNTs. Theoretical studies suggest that the thermal conductivity of individual SWNTs can reach 6000W/m K in the axial direction but is very low in the radial direction. Values up to 3000 W/m K have been experimentally obtained for MWNTs [1].

Table 3 Thermal conductivity of materials [1]

Material	K (W/m K)
SWNT	>3000

3.3 Synthesis of CNTs

Few techniques employed to produce CNTs are electric arc discharge, laser ablation and chemical vapour deposition.

I. Electric – arc discharge

It is one of the most common technique and an oldest way of CNT production.By using this method, the electric arc vaporizes a hollow graphite anode packed with a mixture of transition metals (such as Fe, Co or Ni) and graphite powder. The inert gas flow is maintained at 50–600 Torr. Variation of process parameters like gas pressure, flow rate and metal concentration is needed for high yield of CNTs. SWNTs with diameters ranging from 0.6 to 1.4 nm and 10 nm diameter MWNTs. This method is easy to implement and 30% yeild will be obtained. Impurity content in CNTs is higher in this method compared to others. Two carbon electrodes are used in the carbon arc discharge technique to produce an arc by digital current (DC). Fig. shows schematic of arc-discharge to produce CNTs. Initially, the two electrodes are kept independent. The electrodes are kept in a vacuum chamber and an inert gas is supplied to the chamber. The inert gas increases the speed of carbon deposition. Once thepressure is stabilized, the power supply is turned on (about 20 V). The positive electrode is then gradually brought closer to the negative one to strike the electric arc. The electrodes become red hot and a plasma forms. Once the arc stabilizes, the rods are kept about a millimeter apart while the CNT deposits on the negative electrode. Once the specific length is reached, the power supply is cut off and the machine is left for cooling [4].

II. Laser ablation

It is a newer method currently being used to create nanotubes. This method vapourizes the carbon and later deposits it onto a substrate. In this method, a piece of graphite target is vaporized by laser irradiation under high temperature in an inert atmosphere.The quality and yield of these products have been found to depend on the reaction temperature. The best quality is obtained at 1200ºC reaction temperature. At lower temperatures, the structure quality decreases and the CNTs start presenting many defects. The setup of the laser furnace consists of a furnace, a quartz tube with a window, a target carbon composite doped with catalytic metals, a water-cooled trap, and flow systems for the buffer gas to maintain constant pressures and flow rates. A laser beam (typically a YAG or CO2 laser) is introduced through the window and focused on to the target located in the center of the furnace. The target is vaporized in high-temperatureAr buffer gas and forms SWNTs. The Ar flow rate and pressure are typically 1 cm s^{-1} and 500 Torr, respectively. The SWNTs produced are conveyed by the buffer gas to the trap, where they are collected. The vaporization surface is kept as fresh as possible by changing the focus point or moving the target [4].

III. Chemical vapour deposition (CVD)

Among these above techniques the CVD based methods appears to be most suitable for large scale CNT production because of their scalability. However laser ablation and arc discharge suffer many disadvantages for being uneconomical and expensive for large scale production despite their high quality and yield of CNTs.

Advantages of CVD

- It is simple, economical and scalable technique for mass production.
- Utilizes plenty of hydrocarbons in any form.
- Can be used to grow CNTs in different forms like coiled, straight, entangled etc [5].

4. CNT/Polymer Composites

To maximize the advantage of CNTs as effective reinforcement for high strength polymer composites, the CNTs should not form aggregates, and must be well dispersed to enhance the interfacial interaction with the matrix. Several processing methods available for fabricating CNT/polymer composites based on either thermoplastic or thermosetting matrices have been described are mainly solution mixing, in situ polymerization, melt blending and chemical modification processes. Although inherently different processing routes have been attempted, they all address important issues that affect composite properties, such as exfoliation of CNT bundles and ropes, homogeneous dispersion of the individual tubes into the matrix, alignment and interfacial bonding. The effective utilization of CNT material in composite applications depends strongly on their ability to be dispersed individually and homogeneously within a matrix. An optimized interfacial interaction between the CNT sidewalls and the matrix should result in an efficient load transfer to the hard component of the composite. All processing methods known thus far for CNT-based composites are described below. [6]

4.1 CNT functionalization

Since CNTs agglomerate due to Van der Waalsforce, they are extremely difficult to align and disperseina polymer matrix. Thus, a significant challenge in developinghigh performance CNT/polymer composites is tointroduce the individual CNTs in a polymer matrix in orderto achieve better dispersion and alignment and stronginterfacial interactions, to improve the load transfer acrossthepolymer/CNT matrix interface. The functionalization ofCNT is an effective way to prevent nanotube aggregation,which helps to better disperse and stabilize the CNTs withina polymer matrix. There are several approaches for functionalizationof CNTs including defect functionalization,covalent functionalization and non-covalent functionalization. [7]

4.2 CNT/Polymer synthesis

I. Solution mixing

This is the simplest and most widely used method for processing CNT/polymer nanocomposites in which CNT and polymer are mixed with a suitable solvent which evaporates in a controlled condition after forming nanocomposite films on the surface of the substrate. A large range of polymers like PMMA, PVA, polystyrene has been processed by this method. To achieve better dispersion of CNTs many variations has been demonstrated by researchers in further sections. Safadi et al. used ultrasonic agitation method for the dispersion of MWNTs into the polystyrene matrix. A number of studies show that surface modification of CNTs has been done by adding functional groups for proper dispersion]. But sometimes compatibility issue of functional group with the polymer matrix arises. To elude thisproblem another method of CNT dispersion by surfactants addition is used. In this way the structure of CNT also remains intact.

II. Melt processing

Limiting factor of solution mixing approach is the solubility of the polymers into the solvent. To alleviate this problem an alternative method melt processing is used which usually deals with thermoplastic polymers i.e. polypropylene, polystyrene, polycarbonate, poly (ethylene-2, 6-naphthalate), etc. This method involves melting of polymer to form viscous liquid followed by blending with CNTs. The dispersion of CNTs can be improved by shear mixing which can be achieved by extrusion and injection molding techniques. This technique is considered as less efficient than the solution mixing because high viscosity of thermoplastic polymers leads to hindrance in achieving uniform dispersion of CNTs. In a number of studies fiber-spinning is also used which produces elongated fiber samples.

4.3 Potential applications of nanotube related composites

The application of nanotubes for the composite industry is huge, ranging from the improvement of mechanical properties to the alternations of thermal and electrical properties of traditional polymeric-based composite materials. Each application only needs a small amount of nanotubes to be added into the polymer based materials. Numerous researches have been conducted in these areas, and several excellent results have been reported in the past few years. Apart from the improvement of the mechanical properties of the composites, it has also been proved that the electrical conductivity increased with the amount of nanotubes used in epoxy-based materials. By combining with conductive polymer, such as Polyaniline (PANI), nanotubes can be used to design sensitive electrochemical sensors. It was observed that with an increase of the nanotube concentration, the conductivity of PANI/nanotube films and the current level in the metal-semiconductor devices increase, even at an elevating temperature condition. Besides, the fire behaviour of polyamide 6 was also improved by adding a small amount of nanotubes into it, due to the increase of the melt viscosity thatprevent dripping and flowing but hinder the decomposition of volatiles feeding the flame. It was reported that nanotubes can also be used for power applications, such as proton exchange membrane (PEM) fuel cells, polymeric solar cells, LiC batteries, and thermionic emitters. However, besides those positive responses from many previous literatures, it was also found that the nanotubes would be more toxic than other carbon particles or quartz dust when being absorbed into the lung tissue. Without any constraint, the application of these nanocomposites in real life for mass production in harsh manufacturing environments would be another big challenge in the future. Besides, the control of the dispersion properties and the alignment of nanotubes are still major problems that have not been solved in producing macroscale polymer-based composites. [10]

5. Conclusion

This paper reports the various allotropes of carbon atom. The history of CNTs is explained in detail along with its types and structures. The recent research on the CNTs of different shapes is illustrated. Various properties possesed by the CNTs and the various synthesis techniques developed for CNT preparation is noted. Further CNT/polymer composites along with its synthesis techniques and potential application of nanotube composites is illustrated.

6. References

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