A Brief Review on Carbon Nano Tubes & Its Application in Composites

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Abstract— **Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibers known, with Young's moduli as high as 1 TPa and tensile strengths of up to 63 GPa. They also have remarkable electronic properties and can be metallic or semiconducting depending on their structure and diameter. There is currently great interest in exploiting these properties by incorporating carbon nanotubes into some form of matrix. A wide range of polymer matrices have been employed, and there is growing interest in nanotube/ceramic and nanotube/metal composites. This review outlines the properties of carbon nanotubes and describes the preparation and properties of carbon nanotube composites. The prospects for commercial exploitation of these materials are discussed.**

Index Terms— **Composite materials, Nanotubes, Nanotube/polymer composites**

I. INTRODUCTION

The current interest in carbon nanotubes is a direct consequence of the synthesis of buckminsterfullerene, C60, in 1985 and its derivatives thereafter. The discovery that carbon could form stable, ordered structures other than graphite and diamond stimulated many researchers in the world to search for other allotropes of carbon. This further led to another key finding in 1990 that C60 could be produced in a simple arc-evaporation apparatus readily available in most laboratories. Sumio Iijima discovered fullerene-related carbon nanotubes in 1991 using a similar evaporator. The word nanotube is derived from their size, because the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair) and can be up to several micrometers in length. A nanotube (also known as a Bucky tube) is a member of the fullerene structural family. Nanotubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist). To make things more interesting, besides having a single cylindrical wall (SWNTs), Nanotubes can have multiple walls (MWNTs)--cylinders inside the other cylinders.

II. TYPES OF CNTs

Single-walled carbon nanotube structure Single-walled carbon nanotubes can be formed in three different designs: Armchair, Chiral, and Zigzag. The design depends on the way the graphene is wrapped into a cylinder. For example, imagine rolling a sheet of paper from its corner, which can be considered one design, and a different design can be formed by rolling the paper from its edge. A single-walled nanotube's structure is represented by a pair of indices (n, m) called the chiral vector. Tube diameter of between 0.6 and -5 nm is found. Well characterized structure and properties are found. In multi-walled carbon nanotube structure, there are two structural models of multi-walled nanotubes. In the Russian Doll model, a carbon nanotube contains another nanotube inside it (the inner nanotube has a smaller diameter than the outer nanotube). In the Parchment model, a single graphene sheet is rolled around itself multiple times, resembling a rolled up scroll of paper. Multi-walled carbon nanotubes have similar properties to single-walled nanotubes, yet the outer walls on multi-walled nanotubes can protect the inner carbon nanotubes from chemical interactions with outside materials. Multi-walled nanotubes also have a higher tensile strength than single-walled nanotubes. Inner diameter: 1.5 – 15 nm, Outer diameter: 2.5 – 50 nm ~50 layers. Many structural defects are found.

III. SPECIAL PROPERTIES OF CARBON NANOTUBES

Some of the unique properties of carbon nanotubes include:
Strength- Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 gigapascals (GPa). This translates into the ability to endure tension of a weight equivalent to 6422 kg on a cable with cross-section of 1 mm2.

Hardness- Diamond is considered to be the hardest material, and it is well known that graphite transforms into diamond under conditions of high temperature and high pressure. One study succeeded in the synthesis of a super-hard material by compressing SWNTs to above 24 GPa at room temperature. The hardness of this material was measured with a Nano indenter as 62–152 GPa. The hardness of reference diamond and boron nitride samples was 150 and 62 GPa, respectively.

Kinetic- Multi-walled nanotubes, multiple concentric nanotubes precisely nested within one another, exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell thus creating an atomically perfect linear or rotational bearing. This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already this property has been utilized to create the world's smallest rotational motor.
Electrical- Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. They function as semiconductors. Multiwalled carbon nanotubes with interconnected inner shells show superconductivity with a relatively high transition temperature T_c = 12 K. In contrast, the T_c value is an order of magnitude lower for ropes of

single-walled carbon nanotubes or for MWNTs with usual, non-interconnected shells.

Thermal- All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction", but good insulators laterally to the tube axis. Measurements show that a SWNT has a room-temperature thermal conductivity along its axis of about 3500 W·m−1·K−1; compare this to copper, a metal well-known for its good thermal conductivity, which transmits 385 W·m−1·K−1.

PREPARATION AND PURIFICATION Techniques like carbon arc-discharge, laser ablation, high pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD) are being employed to synthesize CNTs of sizeable quantities. Of these, the CVD method has shown the most promise in terms of its price/unit ratio. The arc-evaporation method, which produces the best quality nanotubes, involves applying a current of about 50 A between two graphite electrodes in a helium atmosphere. This results in graphite evaporation, part of which condenses on the walls of the reactor vessel and part on the cathode. Deposit on the cathode usually contains the CNTs. In laser-ablation technique, intense laser pulses are used to ablate a carbon target. The pulsed laser-ablation of graphite in the presence of an inert gas and catalyst yields CNTs8 in the form of ropes or bundles of 5 to 20 nm diameter and tens to hundreds of micrometers long.

IV. Arc Discharge Method

A chamber containing a graphite cathode and anode contains evaporated carbon molecules in a buffer gas such as helium. The chamber also contains some amount of metal catalyst particles (such as cobalt, nickel, and/or iron). DC current is passed through the chamber while the chamber is also pressurized and heated to ~4000K. In the course of this procedure, about half of the evaporated carbon solidifies on the cathode tip into a "cylindrical hard deposit." The remaining carbon condenses into "chamber soot" around the walls of the chamber and "cathode soot" on the cathode. The cathode soot and chamber soot yield either single-walled or multi-walled carbon nanotubes. The cylindrical hard deposit doesn't yield anything particularly interesting. The choice of buffer gas, the pressure of the chamber, and the metallic catalyst added to the chamber. Apparently the nanotubes grow from the surfaces of the metallic catalyst particles. These choices determine the shape and whether they are single- or multi-walled. The advantage of this method is that it produces a large quantity of nanotubes. But the main disadvantage is that there is relatively little control over the alignment (i.e. chirality) of the produced nanotubes, which is critical to their characterization and role. Furthermore, due to the metallic catalyst included in the reaction, the products need to be purified afterwards. Methods such as oxidation, centrifugation, filtration, and acid treatment have been used.

Laser Ablation Method

A quartz tube containing a block of graphite is heated in a furnace. A flow of argon gas is maintained throughout the reaction. A laser is used to vaporize the graphite within the quartz. The carbon vaporizes, is carried away by the argon, and condenses downstream on the cooler walls of the quartz. This condensation is SWNT and metallic particles. Thereafter, purification methods are applied to this mixture. . The key to the proper formation of the condensed nanotubes is that the location where the carbon atoms begin to condense should be set up as a curved sheet of graphene with a catalyst metallic atom nearby. As carbon atoms begin to attach and form rings, the metallic atom, if it has the proper electronegativity properties, will preserve the open edge of the tube and prevent it from drawing to a close. The authors of the paper describe this phenomenon as the “scooter” effect, because the metallic atom “scoots” around the open edge, preventing it from closing.

Advantages of this technique include a relatively high yield and relatively low metallic impurities, since the metallic atoms involved tend to evaporate from the end of the tube once it is closed. One disadvantage is that the nanotubes produced from this method are not necessarily uniformly straight, but instead do contain some branching.

Chemical Vapor Deposition

The CVD approach allows CNTs to grow on a variety of materials, which makes it more viable to integrate into already existent processes for synthesizing electronics. This process involves the chemical breakdown of a hydrocarbon on a substrate. It's already been shown in previous methods, such as the arc discharge method, that a main way to grow carbon nanotubes is by exciting carbon atoms that are in contact with metallic catalyst particles.

The CVD method extends this idea by embedding these metallic particles (iron, in the case of the seminal paper) in properly aligned holes in a substrate (silicon, in this case). Essentially, tubes are drilled into silicon and implanted with iron nanoparticles at the bottom. Then, a hydrocarbon such as acetylene is heated and decomposed onto the substrate. The carbon comes into contact with the metal particles embedded in the holes and start to form nanotubes that are "templated" from the shape of the tunnel. It turns out that the carbon nanotubes grow very long and very well aligned, in the angle of the tunnel.

The advantages of this method are that the yield is very high, the alignment of the nanotubes is consistent (which is crucial for creating particular types of nanotubes, e.g. semiconductor or metallic), and the size of the growth area is theoretically arbitrary. The main disadvantage is that, though the size of the growth area is basically arbitrary, large sized areas (several millimeters) tend to crack, shrink, and otherwise warp. The substrates need to be dried very thoroughly to prevent against this. N-hexane Pyrolysis Researchers developed a method to synthesize large, long single walled nanotube bundles in a vertical furnace by pyrolyzing hexane molecules. These n-hexane molecules are mixed with certain other chemicals that have been shown independently to help with growth of nanotubes. These are burned (pyrolyzed) at a very high temperature in a flow of hydrogen and other optional gases. According to the paper, using a different hydrocarbon or using a different gas prevented the formation of long nanotubes. The primary advantage of this method is that it produces macroscopic nanotube bundles ("microtubes"): their diameters are typically larger than that of human hair, and their length is several centimeters. The disadvantage is that the alignment is not as produced from other methods, making it viable for creating "microcables", but not nanotubes with precise electrical properties. Another disadvantage is that from the researchers' measurements, the elasticity of these nanotube bundles is not as great as hoped (i.e. they are more brittle).

V. APPLICATIONS

The properties of *carbon nanotubes* have caused researchers and companies to consider using them in several fields. The following survey of carbon nanotube applications introduces many of these uses.

Carbon Nanotubes and Energy

Researchers at North Carolina State University have demonstrated the use of silicon coated carbon nanotubes in anodes for Li-ion batteries. They are predicting that the use of silicon can increase the capacity of Li-ion batteries by up to 10 times. However silicon expands during a batteries discharge cycle, which can damage silicon based anodes. By depositing silicon on nanotubes aligned parallel to each other the researchers hope to prevent damage to the anode when the silicon expands.

Researchers at Los Alamos National Laboratory have demonstrated a catalyst made from nitrogen-doped carbon-nanotubes, instead of platinum. The researchers believe this type of catalyst could be used in Lithium-air batteries, which can store up to 10 times as much energy as lithium-ion batteries.

Researchers at Rice University have developed electrodes made from carbon nanotubes grown on graphene with very high surface area and very low electrical resistance. The researchers first grow graphene on a metal substrate then grow carbon nanotubes on the graphene sheet. Because the base of each nanotube is bonded, atom to atom, to the graphene sheet the nanotube-graphene structure is essentially one molecule with a huge surface area.

Using carbon nanotubes in the cathode layer of a battery that can be produced on almost any surface. The battery can be formed by simply spraying layers of paint containing the components needed for each part of the battery.

Carbon nanotubes can perform as a catalyst in a fuel cell, avoiding the use of expensive platinum on which most catalysts are based. Researchers have found that incorporating nitrogen and iron atoms into the carbon lattice of nanotubes results in nanotubes with catalytic properties.

Carbon Nanotubes in Healthcare

Researchers are improving dental implants by adding nanotubes to the surface of the implant material. They have shown that bone adheres better to titanium dioxide nanotubes than to the surface of standard titanium implants. As well they have demonstrated to the ability to load the nanotubes with anti-inflammatory drugs that can be applied directly to the area around the implant.

Researchers at MIT have developed a sensor using carbon nanotubes embedded in a gel that can be injected under the skin to monitor the level of nitric oxide in the bloodstream. The level of nitric oxide is important because it indicates inflammation, allowing easy monitoring of inflammatory diseases. In tests with laboratory mice the sensor remained functional for over a year.

Researchers have demonstrated artificial muscles composed of yarn woven with carbon nanotubes and filled with wax. Tests have shown that the artificial muscles can lift weights that are 200 times heavier than natural muscles of the same size.

Nanotubes bound to an antibody that is produced by chickens have been shown to be useful in lab tests to destroy breast cancer tumors. The antibody-carrying nanotubes are attracted to proteins produced by one type of breast cancer cell. Once attached to these cells, the nanotubes absorb light from an infrared laser, incinerating the nanotubes and the attached tumor.

Researchers at the University of Connecticut have developed a sensor that uses nanotubes and gold nanoparticles to detect proteins that indicate the presence of oral cancer. Tests have shown this sensor to be accurate and it provides results in less than an hour.

Carbon Nanotubes and the Environment

Carbon nanotubes are being developed to clean up oil spills. Researchers have found that adding boron atoms during the growth of carbon nanotubes causes the nanotubes to grow into a sponge like material that can absorb many times its weight in oil. These nanotube sponges are made to be magnetic, which should make retrieval of them easier once they are filled with oil.

Carbon nanotubes can be used as the pores in membranes to run reverse osmosis desalination plants. Water molecules pass through the smoother walls of carbon nanotubes more easily than through other types of nanopores, which requires less power. Other researchers are using carbon nanotubes to develope small, inexpensive water purification devices needed in developing countries.

Sensors using carbon nanotube detection elements are capable of detecting a range of chemical vapors. These sensors work by reacting to the changes in the resistance of a carbon nanotube in the presence of a chemical vapor.

Researchers at the Technische Universität München have demonstrated a method of spraying carbon nanotubes onto flexible plastic surfaces to produce sensors. The researchers believe that this method could produce low cost sensors on surfaces such as the plastic film wrapping food, so that the sensor could detect spoiled food.

An inexpensive nanotube-based sensor can detect bacteria in drinking water. Antibodies sensitive to a particular bacteria are bound to the nanotubes, which are then deposited onto a paper strip. When the bacteria is present it attaches to the antibodies, changing the spacing between the nanotubes and the resistance of the paper strip containing the nanotubes.

Carbon nanotubes tipped with gold nanoparticles can be used to trap oil drops polluting water. Since the gold end is attracted to water while the carbon end is attracted to oil.

Therefore the nanotubes form spheres surrounding oil droplets with the carbon end pointed in, toward the oil, and the gold end pointing out, toward the water.

Carbon Nanotubes Effecting Materials

Researchers are developing materials, such as a carbon nanotube-based composite developed by NASA that bends when a voltage is applied. Applications include the application of an electrical voltage to change the shape (morph) of aircraft wings and other structures.

Researchers have found that carbon nanotubes can fill the voids that occur in conventional concrete. These voids allow water to penetrate concrete causing cracks, but including nanotubes in the mix stops the cracks from forming.

Researchers at MIT have developed a method to add carbon nanotubes aligned perpendicular to the carbon fibers, called nanostiching. They believe that having the nanotubes perpendicular to the carbon fibers help hold the fibers together, rather than depending upon epoxy, and significanly improve the properties of the composite.

Avalon Aviation incorporated carbon nanotubes in a carbon fiber composite engine cowling on an aerobatic aircraft to increase the strength to weight ratio. The engine cowling is highly stressed components in this aircraft, adding carbon nanotubes to the composite allowed them to reduce the weight without weakening the component.

Carbon Nanotubes and Electronics

Building transistors from carbon nanotubes enables minimum transistor dimensions of a few nanometers and the development of techniques to manufacture integrated circuits built with nanotube transistors.

Other applications in this area include:

Carbon nanotubes used to direct electrons to illuminate pixels, resulting in a lightweight, millimeter thick "nanoemissive" display panel.

Printable electronic devices using nanotube "ink" in inkjet printers

Transparent, flexible electronic devices using arrays of nanotubes.

Filled Composites

The mechanical behavior of carbon nanotubes is exciting since nanotubes are seen as the “ultimate” carbon fiber ever made. The traditional carbon fibers have about *fifty times* the specific strength (strength/density) of steel and are excellent load-bearing reinforcements in composites. Nanotubes should then be ideal candidates for structural applications. Carbon fibers have been used as reinforcements in high strength, light weight, high performance composites; one can typically find these in a range of products ranging from expensive tennis rackets to spacecraft and aircraft body parts.

NASA has recently invested large amounts of money in developing carbon nanotube-based composites for applications such as the futuristic Mars mission. Early theoretical work and recent experiments on individual nanotubes (mostly MWNTs) have confirmed that nanotubes are one of the stiffest structures ever made. Since carbon–carbon covalent bonds are one of the strongest in nature, a structure based on a perfect arrangement of these bonds oriented along the axis of nanotubes would produce an exceedingly strong material.

Theoretical studies have suggested that SWNTs could have a Young’s modulus as high as 1TPa, which is basically the in-plane value of defect free graphite. For MWNTs, the actual strength in practical situations would be further affected by the sliding of individual graphene cylinders with respect to each other. In fact, very recent experiments have evaluated the tensile strength of individual MWNTs using nano-stressing stage located within a scanning electron microscope. The observed tensile strength of individual MWNTs corresponded to <60GPa.

Experiments on individual SWNT ropes are in progress and although a Sword-in-sheath failure mode cannot occur in SWNT ropes, failure could occur in a very similar fashion. The individual tubes in a rope could pull out by shearing along the rope axis, resulting in the final breakup of the rope, at stresses much below the tensile strength of individual nanotubes. Although testing of individual nanotubes is challenging, and requires specially designed stages and nanosize loading devices, some clever experiments have provided valuable insights into the mechanical behavior of nanotubes and have provided values for their modulus and strength.

Recent experiments have also used atomic force microscopy to bend nanotubes attached to substrates and thus obtain quantitative information about their mechanical properties. Simulations on SWNTs have suggested very interesting deformation behavior; highly deformed nanotubes were seen to switch reversibly into different morphological patterns with abrupt releases of energy. Nanotubes gets flattened, twisted and buckled as they deform. They sustain large strains (40%) in tension without showing signs of fracture.

The most important application of nanotubes based on their mechanical properties will be as reinforcements in composite materials. Although nanotube-filled polymer composites are an obvious materials application area, there have not been many successful experiments, which show the advantage of using nanotubes as fillers over traditional carbon fibers. The main problem is in creating a good interface between nanotubes and the polymer matrix and attaining good load transfer from the matrix to the nanotubes, during loading.

The reason for this is essentially two-fold. First, nanotubes are atomically smooth and have nearly the same diameters and aspect ratios (length/diameter) as polymer chains. Second, nanotubes are almost always organized into aggregates which behave differently in response to a load, as compared to individual nanotubes. There have been conflicting reports on the interface strength in nanotube-polymer composites.

Depending on the polymer used and processing conditions, the measured strength seems to vary. In some cases, fragmentation of the tubes has been observed, which an indication of a strong interface bonding is. In some cases, the effect of sliding of layers of MWNTs and easy pull-out are seen, suggesting poor interface bonding. Micro-Raman spectroscopy has validated the latter, suggesting that sliding of individual layers in MWNTs and *shearing* of individual tubes in SWNT ropes could be limiting factors for good load transfer, which is essential for making high strength composites. To maximize the advantage of nanotubes as reinforcing structures in high strength composites, the aggregates needs to be broken up and dispersed or cross-linked to prevent slippage. In addition, the surfaces of nanotubes have to be chemically modified (functionalized) to achieve strong interfaces between the surrounding polymer chains.

There are certain advantages that have been realized in using carbon nanotubes for structural polymer (e.g., epoxy) composites. Nanotube reinforcements will increase the toughness of the composites by absorbing energy during their highly flexible elastic behavior. This will be especially important for nanotube-based ceramic matrix composites. An increase in fracture toughness on the order of 25% has been seen in nano-crystalline alumina nanotube (5% weight fraction) composites, without compromising on hardness.

Other interesting applications of nanotube-filled polymer films will be in adhesives where a decoration of nanotubes on the surface of the polymer films could alter the characteristics of the polymer chains due to interactions between the nanotubes and the polymer chains; the high surface area of the nanotube structures and their dimensions being nearly that of the linear dimensions of the polymer chains could give such nanocomposites new surface properties. The low density of the nanotubes will clearly be an advantage for nanotube-based polymer composites, in comparison to short carbon fiber reinforced (random) composites. Nanotubes would also offer multifunctionality, such as increased electrical conduction. Nanotubes will also offer better performance during compressive loading in comparison to traditional carbon fibers due to their flexibility and low propensity for carbon nanotubes to fracture under compressive loads.

Applications of Carbon Nanotubes 411 Other than for structural composite applications, some of the unique properties of carbon nanotubes are being pursued by filling photo-active polymers with nanotubes. Recently, such a scheme has been demonstrated in a conjugated luminescent polymer, poly (m-phenylenevinylene-co-2, 5-dioctoxyp-phenylenevinylene) (PPV), filled with MWNTs and SWNTs. Nanotube/

PPV composites have shown large increases in electrical conductivity by nearly eight orders of magnitude) compared to the pristine polymer, with little loss in photoluminescence/electro-luminescence yield.

In addition, the composite is far more robust than the pure polymer regarding mechanical strength and photo-bleaching properties (breakdown of the polymer structure due to thermal effects). Preliminary studies indicate that the host polymer interacts weakly with the embedded nanotubes, but that the nanotubes act as nano-metric heat sinks, which prevent the buildup of large local heating effects within the polymer matrix.

Use of the nonlinear optical and optical limiting properties of nanotubes has been reported for designing nanotube-polymer systems for optical applications, including photo-voltaic applications. Functionalization of nanotubes and the doping of chemically modified nanotubes in low concentrations into photo-active polymers, such as PPV, have been shown to provide a means to alter the hole transport mechanism and hence the optical properties of the polymer.

Small loadings of nanotubes are used in these polymer systems to tune the color of emission when used in organic light emitting devices. The interesting optical properties of nanotube-based composite systems arise from the low dimensionality and unique electronic band structure of nanotubes; such applications cannot be realized using larger micron-size carbon fibers.

DRAWBACKS of using CNT composites

There are challenges to be overcome when processing nanotube composites.

One of the biggest problems is dispersion. It is extremely difficult to separate individual nanotubes during mixing with polymers or ceramic materials and this creates poor dispersion and clumping together of nanotubes, resulting in a drastic decrease in the strength of composites. By using high power ultrasound mixers and using surfactants with nanotubes during processing, good nanotube dispersion may be achieved, although the strengths of nanotube composites reported to date have not seen any drastic improvements over high modulus carbon fiber composites.

Another problem is the difficulty in fabricating high weight fraction nanotube composites, considering the high surface area for nanotubes which results in a very high viscosity for nanotube-polymer mixtures. Notwithstanding all these drawbacks, it needs to be said that the presence of nanotubes stiffens the matrix (the role is especially crucial at higher temperatures) and could be very useful as a matrix modifier, particularly for fabricating improved matrices useful for carbon fiber composites. The real role of nanotubes as an efficient reinforcing fiber will have to wait until we know how to manipulate the nanotube surfaces chemically to make strong interfaces between individual nanotubes (which are really the strongest material ever made) and the matrix materials. In the meanwhile, novel and unconventional uses of nanotubes will have to take the center stage.

VI. CONCLUSION

There is much about carbon nanotubes that is still unknown. More research needs to be done regarding the environmental and health impacts of producing large quantities of them. There is also work to be done towards cheaper mass-production and incorporation with other materials before many of the current applications being researched can be commercialized. There is no doubt however that carbon nanotubes will play a significant role in a wide range of commercial applications in the near future. Not only will they help create some very cool tech gadgets, they may also help solve the world’s energy problems.

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