Technical Inquiry

Nanotube Ropes and Applications

Developed by:

HDIAC
104 Union Valley Rd.
Oak Ridge, TN 37830
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Technical Inquiry Summary. HDIAC received a technical inquiry regarding composite nanotube rope applications, manufacturing, availability and information on who is creating it and who is using the technology.

Background Information: Carbon Nanotubes (CNTs) come in a variety of diameters, lengths and functional group content. CNTs are available for industrial applications in bulk quantities up to metric ton quantities from Cheap Tubes. Several CNT manufacturers have greater than 100 ton per year production capacity for multi-walled nanotubes.

CNTs may consist of one tube of graphite, a one-atom thick single-walled nanotubes (SWNTs) a two atom thick double-walled carbon nanotubes (DWNTs) or a number of concentric tubes called multi-walled nanotubes (MWNTs). When viewed with a transmission electron microscope these tubes appear as planes. Whereas SWNTs appear as two planes, in MWNTs more than two planes are observed, and can be seen as a series of parallel lines. There are different types of CNTs, because the graphitic sheets can be rolled in different ways. The three types of CNT structures are Zigzag, Armchair and Chiral. It is possible to recognize Zigzag, Armchair, and Chiral CNTs just by following the pattern across the diameter of the tubes, and analyzing their cross-sectional structure.

MWNTs consist of multiple rolled layers (concentric tubes) of graphene. There are two models that can be used to describe the structures of MWNTs. In the Russian Doll model, sheets of graphite are arranged in concentric cylinders, (e.g., a 0.8 SWNT within a larger 0.17 single-walled nanotube). In the Parchment model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled newspaper. The interlayer distance in MWNTs is close to the distance between graphene layers in graphite, approximately 3.4 Å. The Russian Doll structure is observed more commonly. Its individual shells can be described as SWNTs, which can be metallic or semiconducting. Because of statistical probability and restrictions on the relative diameters of the individual tubes, one of the shells, and thus the whole MWNT, is usually a zero-gap metal.

DWNTs form a special class of nanotubes because their morphology and properties are similar to those of SWNTs but their resistance to chemicals is significantly improved. This is especially important when functionalization, grafting of chemical functions at the surface of the nanotube, is required to add new properties to the CNT. In the case of SWNTs, covalent functionalization will break some C=C double bonds, leaving "holes" in the structure on the nanotube and, thus, modifying both its mechanical and electrical properties. In the case of DWNTs, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 by the Combustion Chemical Vapor Deposition CCVD technique, from the selective reduction of oxide solutions in methane and hydrogen.

The telescopic motion ability of inner shells and their unique mechanical properties will permit the use of MWNTs as main movable arms in coming nanomechanical devices. Retraction force that occurs to telescopic motion caused by the Lennard-Jones interaction between shells and its value is about 1.5 nN.

Key Findings:

- The most common composite nanotube rope is of carbon and graphene
- Rice University is leading the research on nanotube fibers with funding from the National Science Foundation (NSF), Department of Energy (DOE), industry (Teijin), Air Force and the Department of Defense (DoD).
- Nanotube rope technology have diverse applications, including:
    - Biological (antibacterial activity/antimicrobial applications)
    - Wearable and portable electronics/energy storage devices
    - Liquid precursor derived A-CMNC architectures
    - Structural applications (confinement of concrete)
    - Reinforcement for multifunctional composites
    - Reconstructive surgery (ceramic bone grafts/bone electrotherapy purposes)
    - Artificial muscles
    - Tracking of implanted cells
    - Cancer therapy
    - Biological sensors
    - Cyclic loading stress relaxation
    - Applications where electrical conductivity and mechanical properties are of primary importance (data exchange/communication sectors)
    - Lightweight conductors in the aviation industry
    - Human bionics
    - Personal Protective Equipment (PPE)

Analysis: The special nature of carbon combines with the molecular perfection of SWNTs to endow them with exceptional material properties, such as very high 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 delocalized pi-electron donated by each atom is free to move about the entire structure, rather than remain with its donor atom, giving rise to the first known molecule with metallic-type electrical conductivity. Furthermore, 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 substantially by the occurrence of defects in their structure. For example, high-strength steel typically fails at only about 1 percent of its theoretical breaking strength. CNTs, however, achieve values very close to their theoretical limits because of their molecular perfection of structure. This aspect is part of the unique story of CNTs. CNTs are an example of true nanotechnology: they are only about a nanometer in diameter, but are molecules that can be manipulated chemically and physically in very useful ways. They open an incredible range of applications in materials science, electronics, chemical processing, energy management, and many other fields.

CNTs 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 well-known and tremendously rich chemistry of carbon.

This provides opportunity to modify their structure, and to optimize their solubility and dispersion. It is significant to note CNTs are molecularly perfect, which means they are normally free of property-degrading flaws in the nanotube structure. Their material properties can therefore approach closely the very high levels intrinsic to them. These extraordinary characteristics give CNTs potential in numerous applications.

CNTs are the best known field emitters of any material. This is understandable, given their high electrical conductivity, and the incredible sharpness of their tip (because the smaller the tip's radius of curvature, the more concentrated will be an electric field, leading to increased 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 low-power electrical devices that utilize this feature. CNTs can carry an astonishingly high current density, possibly as high as 10^{13} A/cm^2. Furthermore, the current is extremely stable. An immediate application of this behavior receiving considerable interest is in field-emission flat-panel displays. Instead of a single electron gun, as in a traditional cathode ray tube display, in CNT-based displays there is a separate electron gun (or even many of them) for each individual pixel in the display. Their high current density; low turn-on and operating voltages; and steady, long-lived behavior make CNTs very attractive field emitters in this application. Other applications utilizing the field-emission characteristics of CNTs include general types of low-voltage cold-cathode lighting sources, lightning arrestors, and electron microscope sources.

Much of the history of plastics over the last half-century has involved their use as a replacement for metals. For structural applications, plastics have made tremendous headway, but not where electrical conductivity is required, because plastics are very good electrical insulators. This deficiency is overcome by loading plastics up with conductive fillers, such as carbon black and larger graphite fibers (such as the ones used to make golf clubs and tennis rackets). The loading required to provide the necessary conductivity using conventional fillers 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 the aspect ratio of filler particles, the lower the loading required needed to achieve a given level of conductivity. CNTs are ideal in this sense, since they have the highest aspect ratio of any carbon fiber. In addition, their natural tendency to form ropes provides inherently very long conductive pathways even at ultra-low loadings.

Applications that exploit this behavior of CNTs include EMI/RFI shielding composites; coatings for enclosures, gaskets and other uses; electrostatic dissipation (ESD); antistatic materials and (even transparent!) conductive coatings; and radar-absorbing materials for low-observable (stealth) applications.

CNTs have the intrinsic characteristics desired in material used as electrodes in batteries and capacitors, two technologies of rapidly increasing importance. CNTs have a tremendously high surface area (~1000 m^2/g), good electrical conductivity, and very importantly, their linear geometry makes their surface highly accessible to the electrolyte. Research has shown that CNTs have the highest reversible capacity of any carbon material for use in lithium-ion batteries. In addition, CNTs are outstanding materials for supercapacitor electrodes and are now being marketed for this application.

CNTs also have applications in a variety of fuel cell components. They have a number of properties, including high surface area and thermal conductivity, which 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. CNTs' 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.

The same properties that make CNTs attractive as conductive fillers for use in electromagnetic shielding, ESD materials, etc., make them attractive for electronics packaging and interconnection applications, such as adhesives, potting compounds, and coaxial cables and other types of connectors.

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 nanoscale, the interconnections between switches and other active devices become increasingly important. Their geometry, electrical conductivity and ability to be precisely derived, make CNTs the ideal candidates for the connections in molecular electronics. In addition, they have been demonstrated as switches themselves.

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

The technology for creating aligned structures and ribbons of CNTs is a step toward realizing incredibly efficient heat conduits. In addition, composites with CNTs have been shown to dramatically increase their bulk thermal conductivity, even at very small loadings.

The superior properties of CNTs 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 of one or more of these properties.

Fibers spun of pure CNTs have recently been demonstrated and are undergoing rapid development, along with CNT composite fibers. Such super strong fibers will have many applications including body and vehicle armor, transmission line cables, woven fabrics and textiles. CNTs are also being used to make textiles stain resistant.

CNTs intrinsically have an enormously high surface area; in fact, for SWNTs every atom is not just on one surface, each atom is on two surfaces, the inside *and* outside of the nanotube! Combined with the ability to attach essentially any chemical species to their sidewalls (functionalization) provides an opportunity for unique catalyst supports. Their electrical conductivity may also be exploited in the search for new catalysts and catalytic behavior.

The exploration of CNTs in biomedical applications is just underway, but has significant potential. Since a large part of the human body consists of carbon, it is generally thought of as a very biocompatible material. Cells have been shown to grow on CNTs, so they appear to have no toxic effect. The cells also do not adhere to the CNTs, potentially giving rise to applications such as coatings for prosthetics, as well as anti-fouling coatings for ships.

The ability to functionalize, or chemically modify, the sidewalls of CNTs also leads to biomedical applications such as vascular stents and neuron growth and regeneration. It has also been shown that a single strand of DNA can be bonded to a nanotube, which can then be successfully inserted into a cell.

Many researchers and corporations have already developed CNT-based air and water filtration devices. It has been reported that these filters can not only block the smallest particles but also kill most bacteria. This is another area in which CNTs have already been commercialized and products are on the market.

A ceramic material reinforced with carbon nanotubes has been made by materials scientists at University of California Davis. The new material is far tougher than conventional ceramics, conducts electricity and can both conduct heat and act as a thermal barrier, depending on the orientation of the nanotubes.

Ceramic materials are very hard and resistant to heat and chemical attack, making them useful for applications such as coating turbine blades, but they are also very brittle. The researchers mixed powdered alumina (aluminum oxide) with 5 to 10 percent carbon nanotubes and a further 5 percent finely milled niobium. The researchers treated the mixture with an electrical pulse in a process called spark-plasma sintering. This process consolidates ceramic powders more quickly and at lower temperatures than conventional processes.

The new material has up to five times the fracture toughness—resistance to cracking under stress—of conventional alumina. The material shows electrical conductivity seven times that of previous ceramics made with nanotubes. It also has interesting thermal properties, conducting heat in one direction, along the alignment of the nanotubes, but reflecting heat at right angles to the nanotubes, making it an attractive material for thermal barrier coatings

There is a wealth of other potential applications for CNTs, such as solar collection; nanoporous 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 ones of all. Many researchers are looking into conductive and or water proof paper made with CNTs. CNTs have also been shown to absorb Infrared light and may have applications in the I/R Optics Industry.

Sources: Resources used are attached in an Excel file with several worksheets.