Carbon nanotubes and their composites

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Carbon nanotubes have been the focus of considerable research since their observation from 1991 onwards. The extensive basic studies performed by physicists and chemists in the processing of carbon nanotubes during the past decade have established a sound foundation for exploring their technological application. The exceptional mechanical properties of carbon nanotubes can be exploited in the development of nanotube-based composite materials that may far exceed the properties of existing fiber-reinforced composites. Nanocomposites of carbon tubes that have extraordinary specific stiffness and specific strength represent tremendous opportunity for application in the 21st century. This paper provides a concise review of the recent advancement in carbon nanotubes and their composites. We examine the research work reported in the literature on the structure and processing of carbon nanotubes, as well as the characterization and modeling of the properties of carbon nanotubes and their composites.

Keywords: Nanocomposites, Carbon Nanotubes, Polymer Composites and Alumunium

Introduction

Carbon nanotubes are a relatively new form of carbon and exhibit exceptional material properties. Single-walled nanotubes have diameters in the range of 0.6-18 nm and densities of 1.33-1.40 g/cm^3, about one-half of that of aluminum. Many researchers have reported mechanical properties of carbon nanotubes that exceed any current materials. Although there are varying reports in the literature on the exact properties of carbon nanotubes, their strength is more than twenty times of that of high-strength steel alloy and they can sustain large elastic deformation without breaking. In addition, exceptional elastic stiffness, greater than 1 TPa (the elastic modulus of diamond is 1.2 TPa), has been reported. Indeed, if the reported mechanical properties are accurate, carbon nanotubes may result in an entire new class of advanced materials. To unlock the potential of carbon nanotubes for application in polymer nanocomposites, a comprehensive understanding of the thermo-mechanical behavior of these composites is required. Like traditional fiber composites, the properties of these new nanocomposites depend on the elastic and fracture properties of the reinforcement and matrix as well as the interaction at the reinforcement/matrix interface [1] [2]. In addition to the exceptional mechanical properties associated with carbon nanotubes, they also posses superior thermal and electric properties: thermally stable up to 2800ºC in vacuum and 750ºC in air, thermal conductivity about twice as high as diamond, electric current carrying capacity 1000 times higher than copper wires. These exceptional properties of carbon

nanotubes have been investigated for devices such as field-emission displays [3], scanning probe microscopy tips [4], and microelectronic devices [5, 6]. In this paper we provide an overview of the recent advancements in processing, characterization, and modeling of carbon nanotubes and their composites.

CNT Structure

The unique properties reported for carbon nanotubes are a consequence of the atomic and nano-structure of the tubes. In this section, we review the fundamentals of carbon nanotube structure and the influence on nanotube properties. Carbon nanotubes can be viewed as a sheet of graphite that has been rolled into a tube. Unlike diamond, where a 3-D diamond cubic crystal structure is formed with each carbon having four nearest neighbors arranged in a tetrahedron, graphite is formed as a 2-D sheet of carbon atoms arranged in a hexagonal array. In this case, each carbon atom has three nearest neighbors. "Rolling" sheets of graphite into cylinders forms carbon nanotubes. The properties of nanotubes depend on atomic arrangement (how sheets of graphite are "rolled") and the morphology, or nano-structure. The atomic structure of nanotubes is described in terms of the tube chirality, which is defined by the chiral vector, C_h, and the chiral angle. In Figure 1, we can isualize cutting the graphite sheet along the dotted lines and rolling the tube so that the tip of the chiral vector touches its tail. The chiral angle determines the amount of "twist" in the tube. The two limiting cases for chirality exist where the chiral angle is at 0º and 30º. These limiting cases

are referred to as ziz-zag (0º) and armchair (30º) based on the geometry of the carbon bonds.

The chirality of the carbon nanotube has significant implications on the material properties. The tube chirality has a strong impact on the electronic properties of carbon nanotubes. It has been shown that nanotubes can be either metallic or semiconducting, depending on tube chirality. Investigations on the influence of chirality on the mechanical properties have also been reported. The analytical work of Yakobson et al. [7, 8] examined the instability of carbon nanotubes beyond linear response. Their simulations show that carbon nanotubes are remarkably resilient, sustaining extreme strain with no signs of brittleness or plasticity. Although the chirality has a relatively small influence on the elastic stiffness, they concluded that the Stone-Wales transformation, a reversible diatomic interchange where the resulting structure is two pentagons and two heptagons in pairs, plays a key role in the nanotube deformation under tension. The Stone-Wales transformation occurs when a nanotube having armchair chirality is stressed in the axial direction. Nardelli et al. [9] theorized that the Stone-Wales transformation results in ductile fracture for armchair nanotubes.
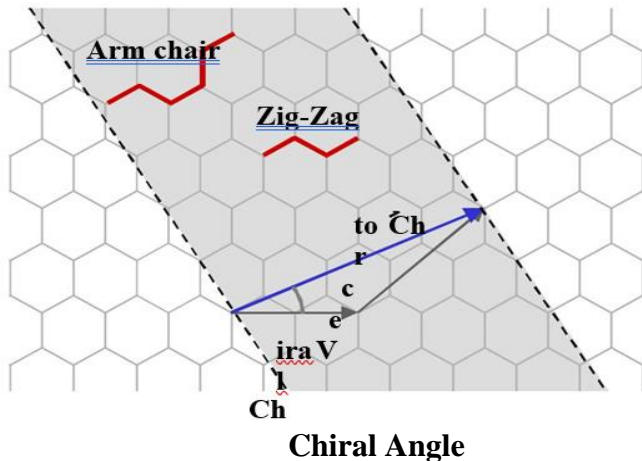

Chiral Angle

Fig. 1 An illustration of how carbon nanotubes are formed via "rolling" sheets of graphite to form a tube
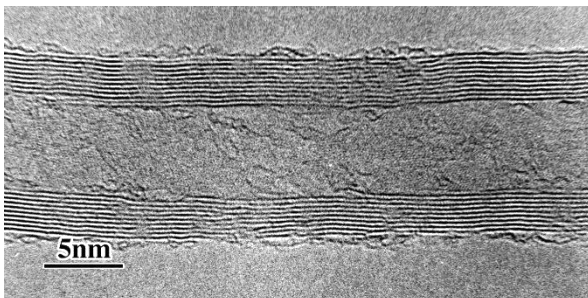

Fig. 2 TEM micrograph showing the structure of a multi-walled carbon nanotube [10].

Carbon nanotubes can be single walled or multi-walled structures. Figure 2 is a transmission electron microscope (TEM) image showing the nano-structure of a multi-walled carbon nanotube where several layers of graphitic carbon and a hollow core can be seen. Multi-walled carbon nanotubes are essentially concentric single walled tubes, where each individual tube can have different chirality. The concentric tubes are held together through secondary, Van der Waals bonding.

Processing of CNT for Composites

Since carbon nanotubes were discovered nearly a decade ago, there have been a variety of techniques developed for producing nanotubes. Primary synthesis methods for single and multi-walled carbon nanotubes include arc-discharge [1, 11], laser ablation [12], gas-phase catalytic growth from carbon monoxide [13], and chemical vapor deposition (CVD) [14-16] methods. For application of carbon nanotubes in polymer composites, large quantities of nanotubes are required, and the scale-up limitations of the arc discharge and laser ablation techniques would make the cost of nanotube-based composites prohibitive. Gas-phase growth from carbon monoxide and CVD offers the greatest potential for scale-up of nanotube production for processing of composites. Here, we discuss the CVD technique for producing high-purity multi-walled carbon nanotubes with varying diameter and structure. One unique aspect of CVD techniques is the ability to synthesize aligned arrays of carbon nanotubes with controlled diameter and length. The synthesis of well-aligned, straight carbon nanotubes on a variety of substrates has been accomplished using plasma-enhanced chemical vapor deposition (PECVD) [15, 16]. Figures 3a and 3b shows the ability to grow straight carbon nanotubes over a large area with excellent uniformity in diameter, length, straightness, and site density. Adjusting the thickness of the catalyst layer controls the diameter of the tubes when they are grown, shown in Figures 4a and 4b.
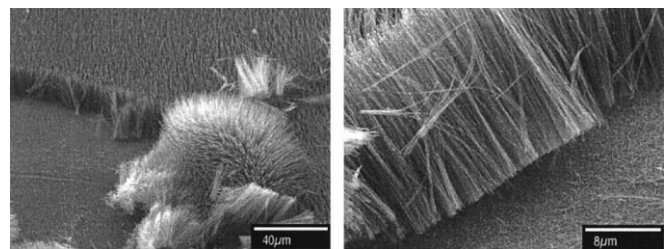

Fig. 3 SEM micrographs showing (a) excellent alignment and uniformity of carbon nanotubes grown over a large area and an enlarged view of the nanotubes along the scratched edge to show uniformity in length, diameter, and site density [15].

Fig. 4 SEM micrographs showing control over nanotube diameter 40-50 nm (a) and 200-300 nm (b) aligned carbon nanotubes [15].
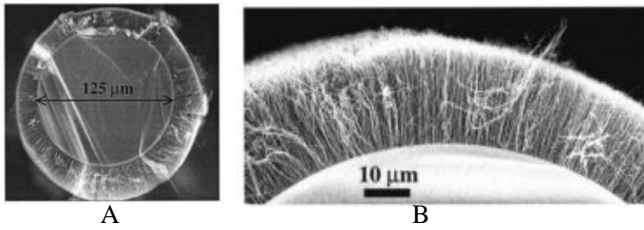

A   B

Fig. 5 SEM micrographs showing (a) the radially grown nanotubes on the surface of an optical fiber and (b) a close-up showing the perpendicular nature of nanotube growth [17].

In CVD growth of straight carbon nanotube arrays, a substrate is first coated with a layer of nickel catalyst. High purity ammonia (99.999%) is used as the catalytic gas and acetylene (99.6%) is used as the carbon source. A direct current power supply (1000V x 3A) is used to generate the required plasma, and a deeply carbonized tungsten filament assists the dissociation of the reactive gases and supplies heat to substrate. Control over the nanotube length and graphitization is accomplished by changing the growth time and temperature, respectively, and application of the DC plasma results in tube growth in the direction of the plasma. Using an alternating microwave frequency source to excite the plasma results in growth of carbon nanotubes that occur directly normal to the surface of the substrate. Bower et al. [17] showed that in microwave plasma-enhanced CVD (MPECVD) alignment of the carbon nanotubes result from the self-bias that is imposed on the surface of the substrate from the microwave plasma. Figures 5a and 5b show the alignment of carbon nanotubes grown normal to the surface of an optical glass fiber. In addition to highly aligned arrays of carbon nanotubes, large quantities of carbon nanotubes can be processed using conventional CVD techniques. Unlike PECVD, which requires the use of specialized plasma equipment, tangled carbon nanotubes are grown in a tube furnace. Figure 6 shows an SEM micrograph of the furnace-grown carbon nanotubes. The outer diameters of these tubes range from 10-50 nm. These tangled, spaghetti-like nanotubes can be produced at a larger quantity and lower cost than PECVD tubes, but there is less control over length, diameter, and structure.

Characterization of CNT and their Composites

The exceptional properties of carbon nanotubes give motivation to the development of nanotube-based composites. Comprehensive understanding of the thermo-mechanical behavior of nanotube composites requires knowledge of the elastic and fracture properties of the constituent materials as well as the interaction at the reinforcement/matrix interface [2]. Significant challenges exist in both micromechanical characterization of nanotubes and their composites as well as in modeling of the elastic and fracture behavior at the nano-scale. Challenges in characterization of nanotubes and their composites include (a) complete lack of micromechanical characterization techniques for direct property measurement, (b) tremendous limitations on specimen size, (c) uncertainty in data obtained from indirect measurements, and (d) inadequacy in test specimen preparation techniques and lack of control in nanotube alignment and distribution. To better understand the mechanical properties of carbon nanotubes, a number of investigators have attempted to characterize carbon nanotubes directly. Treacy et al. [18] first investigated the elastic modulus of isolated multi-walled nanotubes by measuring, in the transmission electron microscope, the amplitude of their intrinsic thermal vibration. The average value obtained over 11 samples was 1.8 TPa. Direct measurement of the stiffness and strength of individual, structurally isolated multi-wall carbon nanotubes has been made using an atomic force microscope. Wong and co-workers [19] were the first to perform direct measurement of the stiffness and strength of individual, structurally isolated multi-wall carbon nanotubes using an atomic force microscope (AFM). The nanotube was pinned at one end to molybdenum disulfide surfaces and load was applied to the tube using the AFM tip. The bending force versus displacement was measured along the unpinned length, and a value of 1.26 TPa was obtained for the elastic modulus. The average bending strength measured was 14.2 $\pm$ 8 GPa. Single-walled nanotubes tend to assemble in "ropes" of nanotubes. Selvetat and co-workers [20] measured the properties of these nanotube bundles with the AFM. As the diameter of the tube bundles increase, the axial and shear moduli decrease significantly. This suggests slipping of the nanotubes within the bundle. Because of the uncertainty associated with direct characterization of carbon nanotubes, attempts have been made to characterize nanotubes in reinforced composites. It is, however, difficult to obtain a uniform dispersion of carbon nanotubes in the polymer matrix. Even when obtaining a uniform dispersion, difficulty arises in characterization of these composites because the orientation of tubes within the matrix is random. Shaffer and Windle [21] characterized carbon nanotube/polyvinyl alcohol composite films fabricated from the formation of a stable colloidal intermediate. The elastic modulus and damping properties of the dry composite films,which varied in thickness from 53 to 44 m, were assessed in a dynamic mechanical thermal analyzer (DMTA) as a function of nanotube loading and temperature. A nanotube elastic modulus of 150 MPa was obtained from the experimental data for in-plane stiffness as a function of nanotube concentration. This value in a microscopic composite is well below the values reported for isolated nanotubes. It is not clear whether this result is a consequence of the imperfections in the graphite layers of the catalytically grown nanotubes used or

whether it relates to a fundamental difficulty in stress transfer between the shells of multi-walled nanotubes.

Because interaction of the nanotube at the nanotube/matrix interface is critical to understanding the mechanical behavior of nanotube-based composites, a number of researchers have investigated the efficiency of interfacial stress transfer. Wagner et al. [22] examined stress-induced fragmentation of multi-walled carbon nanotubes in polymer films. Their nanotube-containing film had a thickness of approximately 200 □m. The observed fragmentation phenomenon was attributed to either process-induced stress resulting from curing of the polymer or tensile stress generated by polymer deformation and transmitted to the nanotube. Based upon estimated values of nanotube axial normal stress and elastic modulus, Wagner and co-workers concluded that the nanotube/polymer interfacial shear stress is on the order of 500 MPa and up. This value, if reliable, is an order of magnitude higher than the stress transfer ability of current advanced composites and, therefore, such interfaces are more able than either the matrix or the nanotubes themselves to sustain shear. Stress transfer has also been investigated through the use of Raman spectroscopy. Cooper and co-workers [23] prepared composite specimens by applying an epoxy resin/nanotube mixture to the surface of an epoxy beam. After the specimens were cured, stress transfer between the polymer and the nanotubes was detected by a shift in the G' Raman band to a lower wavenumber. The shift in the G' Raman band corresponds to strain in the graphite, and the shift indicates that there is stress transfer, and hence reinforcement by the nanotubes. It was also concluded that the effective modulus of single walled nanotubes dispersed in a composite could be over 1 TPa and that of multi-walled nanotubes was about 0.3 TPa. In their investigation of single-walled nanotube composites, Ajayan et al. [24] suggest that their nearly constant value of the Raman peak in tension is related to tube sliding within the nanotube bundles and, hence, poor interfacial load transfer between the nanotubes.

THEORETICAL MODELING OF NANOTUBE MECHANICS

As discussed in the previous section, nanotube deformation has been examined experimentally. In these investigations, the notion of continuum mechanics has been used to infer that carbon nanotubes possess exceptionally high elastic modulus. Similar conclusions have also been reached by Overney et al. [25], who studied the low frequency vibrational modes and structural rigidity of long nanotubes consisting of 100, 200 and 400 atoms. The calculations were based upon an empirical Keating Hamiltonian with parameters determined from the first principles. A comparison of bending stiffness of single walled nanotubes and an Iridium beam was presented. The bending stiffness of the Iridium beam was deduced using the continuum Bernoulli-Euler theory of beam bending.

Overney and co-workers concluded that the beam bending rigidity of a nanotube exceeds the highest values found in any other presently available materials. Govindjee and Sackman [26] were the first to examine the use of continuum mechanics to estimate the properties of nanotubes. They investigated the validity of the continuum approach in using Bernoulli-Euler bending to infer the Young's modulus. They used a simple elastic sheet model and showed that at the nanotube scale the assumptions of continuum mechanics must be carefully respected in order to obtain reasonable results. They showed the explicit dependence of "material properties" on system size when a continuum cross-section assumption is used.

A relatively comprehensive study of the elastic properties of single and multi-walled nanotubes, reported by Lu [27], attempted to answer the following basic questions: (a) How do elastic properties of single walled nanotubes depend on the structural details, such as size and chirality? (b) How do interlayer interactions affect elastic properties? (c) How do elastic properties of nanotubes compare with those of graphite and diamond? Lu adopted an empirical lattice dynamics model, which has been successfully used in calculating the phonon spectrum and elastic properties of graphite. In the empirical lattice dynamics model, atomic interactions in a single carbon layer are approximated by a sum of pair-wise harmonic potentials between atoms. The local structure of a nanotube layer is constructed from conformal mapping of a graphite sheet on to a cylindrical surface. The interactions between the layers of a multi-walled nanotube, which are not as well registered as they are in the single crystal graphite, are modeled by the summation of all pair-wise radial harmonic potential up to a certain cutoff distance. Lu [27] has concluded that the elastic properties of nanotubes are the same for all nanotubes with a radius larger than 1 nm. The predicted Young's modulus (~1 TPa) and shear modulus (~0.45 TPa) are comparable to those of diamond and an order of magnitude larger than those of typical carbon fibers. The bulk modulus (~0.74 TPa) is almost twice as large as that of diamond, making the nanotubes the hardest of all known materials[27]. The inelastic behavior of fullerene nanotubes has also been studied from an analytical viewpoint. The analytical work of Yakobson et al. [7] examined the instability of carbon nanotubes beyond linear response. Their simulations show that carbon nanotubes are remarkably resilient, sustaining extreme strain with no signs of brittleness, plasticity or atomic rearrangements[28][29]. When subjected to large deformation, carbon nanotubes reversibly switch into different morphological patterns. Each shape change corresponds to an abrupt release of energy and a singularity in the stress-strain curve. A continuum shell model was used to explain these deformations [30] .

Conclusions

The exceptional mechanical properties and low density of carbon nanotubes gives motivation toward the development of nanotube-based composites. To fully understand the thermo-mechanical behavior of nanotube-based composites, further understanding of the elastic and fracture properties of carbon nanotubes as well as the interactions at the nanotube/matrix interface is required. Although this requirement is no different from that in conventional fiber composites [2], the scale of the reinforcement phase diameter has changed from micrometer (e.g. glass and carbon fibers) to nano-meter. Significant challenges exist in both the development of nanotube production at the scale required for producing macroscopic composites that are cost-effective and in the development of processing, characterization, and analysis techniques to optimize the structural and functional properties of this new class of nanocomposites.

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