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Advances in the science and technology of carbon nanotubes and their composites: a review

Erik T. Thostenson[a], Zhifeng Ren[b], Tsu-Wei Chou[a],*

[a]*Department of Mechanical Engineering and Center for Composite Materials, University of Delaware, Newark, DE 19716, USA*
[b]*Department of Physics, Boston College, Chestnut Hill, MA 02167, USA*

Abstract

Since their first observation nearly a decade ago by Iijima (Iijima S. Helical microtubules of graphitic carbon Nature. 1991; 354:56–8), carbon nanotubes have been the focus of considerable research. Numerous investigators have since reported remarkable physical and mechanical properties for this new form of carbon. From unique electronic properties and a thermal conductivity higher than diamond to mechanical properties where the stiffness, strength and resilience exceeds any current material, carbon nanotubes offer tremendous opportunities for the development of fundamentally new material systems. In particular, the exceptional mechanical properties of carbon nanotubes, combined with their low density, offer scope for the development of nanotube-reinforced composite materials. The potential for nanocomposites reinforced with carbon tubes having extraordinary specific stiffness and strength represent tremendous opportunity for application in the 21st century. This paper provides a concise review of recent advances 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 characterization and property modeling of carbon nanotubes and their composites. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

In the mid 1980s, Smalley and co-workers at Rice University developed the chemistry of fullerenes [2]. Fullerenes are geometric cage-like structures of carbon atoms that are composed of hexagonal and pentagonal faces. The first closed, convex structure formed was the C_{60} molecule. Named after the architect known for designing geodesic domes, R. Buckminster Fuller, buckminsterfullerene is a closed cage of 60 carbon atoms where each side of a pentagon is the adjacent side of a hexagon similar to a soccer ball (the C_{60} molecule is often referred to as a bucky ball) [2]. A few years later, their discovery led to the synthesis of carbon nanotubes. Nanotubes are long, slender fullerenes where the walls of the tubes are hexagonal carbon (graphite structure) and often capped at each end.

These cage-like forms of carbon have been shown to exhibit exceptional material properties that are a consequence of their symmetric structure. Many researchers have reported mechanical properties of carbon nanotubes that exceed those of any previously existing materials. Although there are varying reports in the literature on the exact properties of carbon nanotubes, theoretical and experimental results have shown extremely high elastic modulus, greater than 1 TPa (the elastic modulus of diamond is 1.2 TPa) and reported strengths 10–100 times higher than the strongest steel at a fraction of the weight. 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, one must fully understand the elastic and fracture properties of carbon nanotubes as well as the interactions at the nanotube/matrix interface. Although this requirement is no different from that for conventional fiber-reinforced composites [3], the scale of the reinforcement phase diameter has changed from micrometers (e.g. glass and carbon fibers) to nanometers.

In addition to the exceptional mechanical properties associated with carbon nanotubes, they also posses

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* Corresponding author. Tel.: +1-302-831-2421; fax: +1-302-831-3619.
E-mail address: chou@me.udel.edu (T.-W. Chou).

superior thermal and electric properties: thermally stable up to 2800 °C in vacuum, thermal conductivity about twice as high as diamond, electric-current-carrying capacity 1000 times higher than copper wires [4]. These exceptional properties of carbon nanotubes have been investigated for devices such as field-emission displays [5], scanning probe microscopy tips [6], and microelectronic devices [7,8]. In this paper we provide an overview of the recent advances in processing, characterization, and modeling of carbon nanotubes and their composites. This review is not intended to be comprehensive, as our focus is on exploiting the exceptional mechanical properties of carbon nanotubes toward the development of macroscopic structural materials. Indeed, the exceptional physical properties of carbon nanotubes also present the opportunity to develop multifunctional nanotube composites with tailored physical and mechanical properties.

2. Atomic structure and morphology of carbon nanotubes

Carbon nanotubes can be visualized 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 atom 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 the sheets of graphite are 'rolled'), the diameter and length of the tubes, and the morphology, or nano structure. Nanotubes exist as either single-walled or multi-walled structures, and multi-walled carbon nanotubes (MWCNTs) are simply composed of concentric single-walled carbon nanotubes (SWCNTs).

2.1. Nanotube structure

The atomic structure of nanotubes is described in terms of the tube chirality, or helicity, which is defined by the chiral vector, $\vec{C}_h$, and the chiral angle, θ. In Fig. 1, we can visualize 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 vector, often known as the roll-up vector, can be described by the following equation:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \qquad (1)$$

where the integers (n, m) are the number of steps along the ziz-zag carbon bonds of the hexagonal lattice and $\vec{a}_1$ and $\vec{a}_2$ are unit vectors, shown in Fig. 1. The chiral angle determines the amount of 'twist' in the tube. The
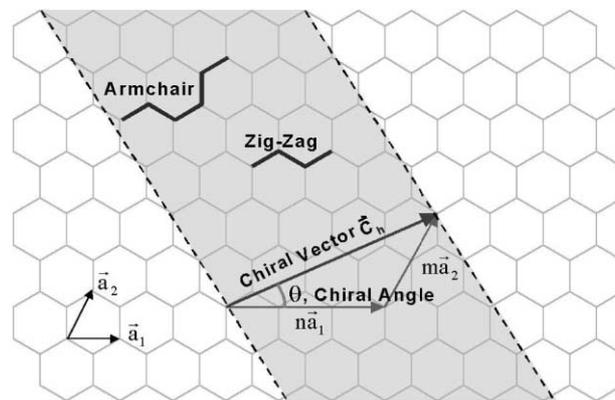

Fig. 1. Schematic diagram showing how a hexagonal sheet of graphite is 'rolled' to form a carbon nanotube.

two limiting cases exist where the chiral angle is at 0° and 30°. These limiting cases are referred to as ziz-zag (0°) and armchair (30°) based on the geometry of the carbon bonds around the circumference of the nanotube. The difference in armchair and zig-zag nanotube structures is shown in Fig. 2. In terms of the roll-up vector, the ziz-zag nanotube is $(n, 0)$ and the armchair nanotube is (n, n). The roll-up vector of the nanotube also defines the nanotube diameter since the inter-atomic spacing of the carbon atoms is known.

The chirality of the carbon nanotube has significant implications on the material properties. In particular, tube chirality is known to have a strong impact on the electronic properties of carbon nanotubes. Graphite is considered to be a semi-metal, but it has been shown that nanotubes can be either metallic or semiconducting, depending on tube chirality [9].

Investigations on the influence of chirality on the mechanical properties have also been reported. The analytical work of Yakobson et al. [10,11] examined the
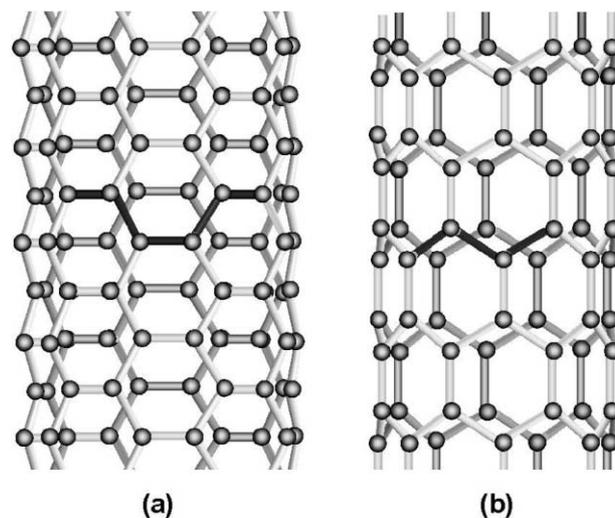

Fig. 2. Illustrations of the atomic structure of (a) an armchair and (b) a ziz-zag nanotube.

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 plastic deformation under tension. The Stone-Wales transformation, shown in Fig. 3, occurs when an armchair nanotube is stressed in the axial direction. Nardelli et al. [12] theorized that the Stone-Wales transformation results in ductile fracture for armchair nanotubes.

2.2. Nanotube morphology

As mentioned before, fullerenes are closed, convex cages that are composed of pentagons and hexagons. The Stone-Wales transformation introduces a new defect in the nanotube structure, the heptagon. Heptagons allow for concave areas within the nanotube. Thus, the heptagonal defects in nanotubes can result in many possible equilibrium shapes. Indeed, most nanotubes are not straight cylinders with hemispherical caps.

In addition to different tube morphologies resulting from defects, carbon nanotubes can be single walled or multi-walled structures. Fig. 4 shows a transmission electron microscope (TEM) image showing the nanostructure of a multi-walled carbon nanotube where several layers of graphitic carbon and a hollow core are evident. Multi-walled carbon nanotubes are essentially concentric single walled tubes, where each individual tube can have different chirality. These concentric nanotubes
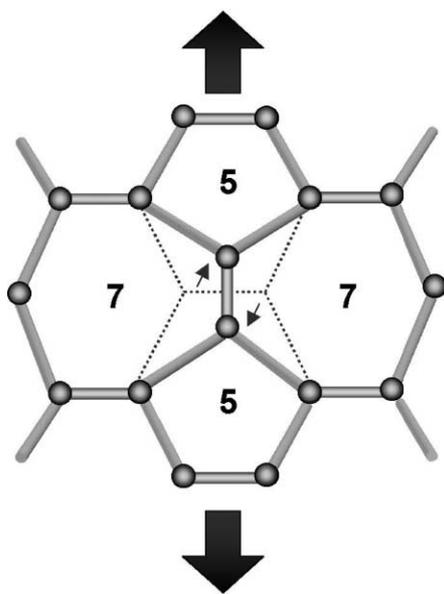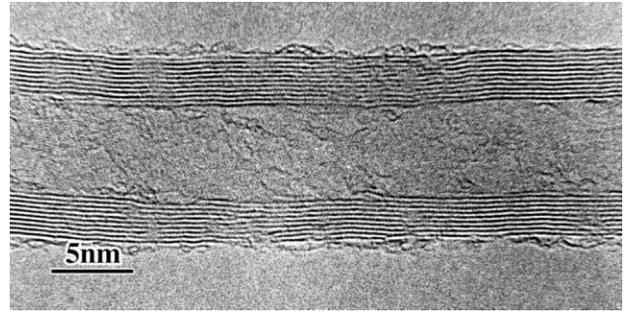

Fig. 4. TEM micrograph showing the layered structure of a multi-walled carbon nanotube.

are held together by secondary, van der Waals bonding. Single-walled nanotubes are most desired for fundamental investigations of the structure/property relationships in carbon nanotubes, since the intra-tube interactions further complicate the properties of carbon nanotubes. Indeed, both single and multi-walled nanotubes show unique properties that can be exploited for use in composite materials.

3. Processing of carbon nanotubes for composite materials

Since carbon nanotubes were discovered nearly a decade ago, there have been a variety of techniques developed for producing them. Iijima [1] first observed multi-walled nanotubes, and Iijima et al. [13] and Bethune et al. [14] independently reported the synthesis of single-walled nanotubes a few years later. Primary synthesis methods for single and multi-walled carbon nanotubes include arc-discharge [1,15], laser ablation [16], gas-phase catalytic growth from carbon monoxide [17], and chemical vapor deposition (CVD) from hydrocarbons [18–20] methods. For application of carbon nanotubes in 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. During nanotube synthesis, impurities in the form of catalyst particles, amorphous carbon, and non-tubular fullerenes are also produced. Thus, subsequent purification steps are required to separate the tubes. The gas-phase processes tend to produce nanotubes with fewer impurities and are more amenable to large-scale processing. It is the authors' belief that gas-phase techniques, such as CVD, for nanotube growth offer the greatest potential for the scaling-up of nanotube production for the processing of composites. In this section, we briefly review the primary techniques for producing carbon nanotubes and some of the benefits and drawbacks of each technique.

Iijima [1] first observed nanotubes synthesized from the electric-arc discharge technique. Shown schematically in Fig. 5, the arc discharge technique generally
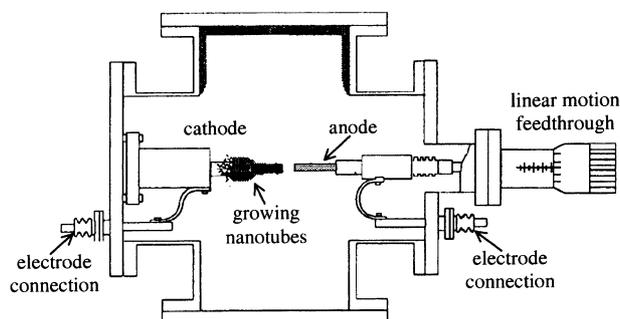

Fig. 3. The Stone-Wales transformation occurring in an armchair nanotube under axial tension.

Fig. 5. Schematic illustration of the arc-discharge technique (after Ref. [22]).

Fig. 6. Schematic of the laser ablation process (after Ref. [4]).

involves the use of two high-purity graphite rods as the anode and cathode. The rods are brought together under a helium atmosphere and a voltage is applied until a stable arc is achieved. The exact process variables depend on the size of the graphite rods. As the anode is consumed, a constant gap between the anode and cathode is maintained by adjusting the position of the anode. The material then deposits on the cathode to form a build-up consisting of an outside shell of fused material and a softer fibrous core containing nanotubes and other carbon particles. To achieve single walled nanotubes, the electrodes are doped with a small amount of metallic catalyst particles [13–15,21,22].

Laser ablation was first used for the initial synthesis of fullerenes. Over the years, the technique has been improved to allow the production of single-walled nanotubes [16,23,24]. In this technique, a laser is used to vaporize a graphite target held in a controlled atmosphere oven at temperatures near 1200 °C. The general set-up for laser ablation is shown in Fig. 6. To produce single-walled nanotubes, the graphite target was doped with cobalt and nickel catalyst [16]. The condensed material is then collected on a water-cooled target.

Both the arc-discharge and the laser-ablation techniques are limited in the volume of sample they can produce in relation to the size of the carbon source (the anode in arc-discharge and the target in laser ablation). In addition, subsequent purification steps are necessary to separate the tubes from undesirable by-products. These limitations have motivated the development of gas-phase techniques, such as chemical vapor deposition (CVD), where nanotubes are formed by the decomposition of a carbon-containing gas. The gas-phase techniques are amenable to continuous processes since the carbon source is continually replaced by flowing gas. In addition, the final purity of the as-produced nanotubes can be quite high, minimizing subsequent purification steps.

Nikolaev et al. [17] describe the gas-phase growth of single-walled carbon nanotubes with carbon monoxide as the carbon source. They reported the highest yields of single walled nanotubes occurred at the highest accessible temperature and pressure (1200 °C, 10 atm).
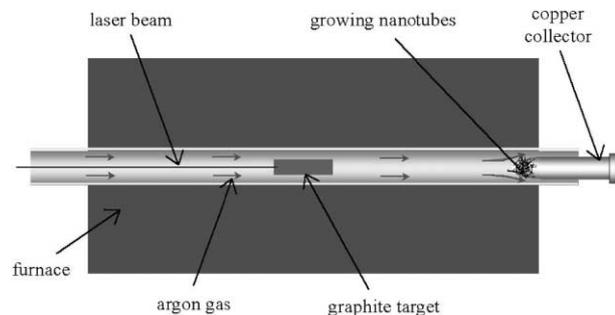
Smalley and his co-workers at Rice University have refined the process to produce large quantities of single-walled carbon nanotubes with remarkable purity. The so-called HiPco nanotubes (high-pressure conversion of carbon monoxide) have received considerable attention as the technology has been commercialized by Carbon Nanotechnologies Inc (Houston, TX) for large-scale production of high-purity single-walled carbon nanotubes.

Other gas-phase techniques utilize hydrocarbon gases as the carbon source for production of both single and multi-walled carbon nanotubes via CVD [25–28]. Nikolaev and co-workers [17] point out that hydrocarbons pyrolize readily on surfaces heated above 600–700 °C. As a consequence, nanotubes grown from hydrocarbons can have substantial amorphous carbon deposits on the surface of the tubes and will require further purification steps. Although the disassociation of hydrocarbons at low temperatures affects the purity of the as-processed nanotubes, the lower processing temperature enables the growth of carbon nanotubes on a wide variety of substrates, including glass.

One unique aspect of CVD techniques is its 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 by the use of plasma-enhanced chemical vapor deposition (PECVD) where the plasma is excited by a DC source [18–20] or a microwave source [29–33]. Fig. 7a and b 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, shown in Fig. 8a and b.

In CVD growth of straight carbon nanotube arrays, described by Ren et al. [19] a substrate is first coated with a layer of nickel catalyst. High-purity ammonia is then used as the catalytic gas and acetylene as the carbon source. A direct-current power generates the required plasma, and a deeply carbonized tungsten filament assists the dissociation of the reactive gases and supplies heat to the substrate. Control over the nanotube length
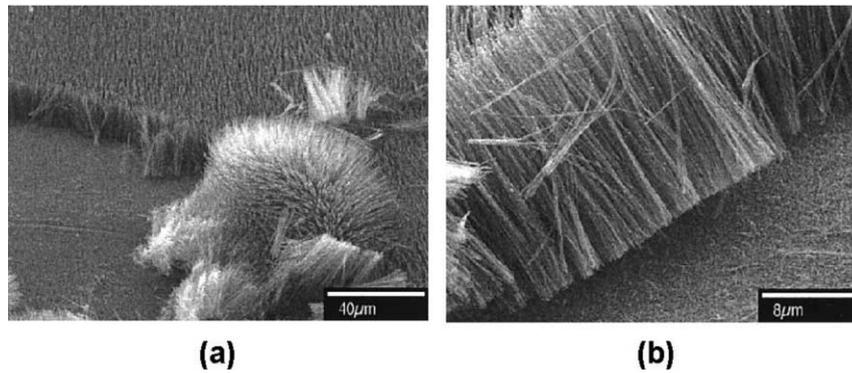
Fig. 7. Micrographs showing the straightness of MWCNTs grown via PECVD [19].
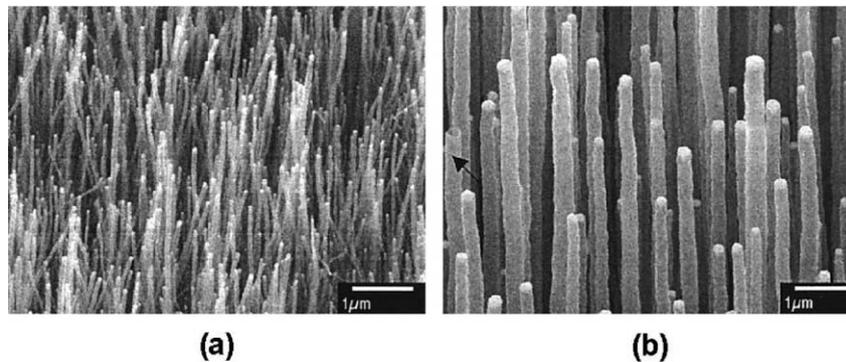

Fig. 8. Micrographs showing control over the nanotube diameter: (a) 40–50 nm and (b) 200–300 nm aligned carbon nanotubes [19].

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. The use of an alternating microwave frequency source to excite the plasma results in the growth of carbon nanotubes that occur directly normal to the surface of the substrate. Bower et al. [29] showed that in microwave plasma-enhanced CVD (MPECVD) alignment of the carbon nanotubes results from the self-bias that is imposed on the surface of the substrate from the microwave plasma. Fig. 9a shows the alignment of carbon nanotubes grown normal to the surface of an optical glass fiber. To gain further insight into the mechanism for tube alignment, the tubes were grown for two minutes under the microwave-induced plasma followed by 70 min with the plasma off. Fig. 9b shows the results of this experiment. The upper portion of the nanotubes are straight, indicating alignment in the plasma, and the base shows a random, curled structure associated with thermal CVD. In addition, the growth rate under the plasma enhancement was 40 times faster than the thermal CVD.

In addition to highly aligned arrays of carbon nanotubes, large quantities of carbon nanotubes can be processed by conventional CVD techniques. Unlike PECVD, which requires the use of specialized plasma equipment, tangled carbon nanotubes are grown in a tube furnace. Fig. 10 is a SEM micrograph of the furnace-grown carbon nanotubes showing the same random, curled structure associated with thermal CVD (shown in Fig. 9). 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.

4. Characterization of carbon nanotubes

Significant challenges exist in both the micromechanical characterization of nanotubes and the 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.

In order better to understand the mechanical properties of carbon nanotubes, a number of investigators have attempted to characterize carbon nanotubes directly. Treacy et al. [34] first investigated the elastic modulus of isolated multi-walled nanotubes by measuring, in the
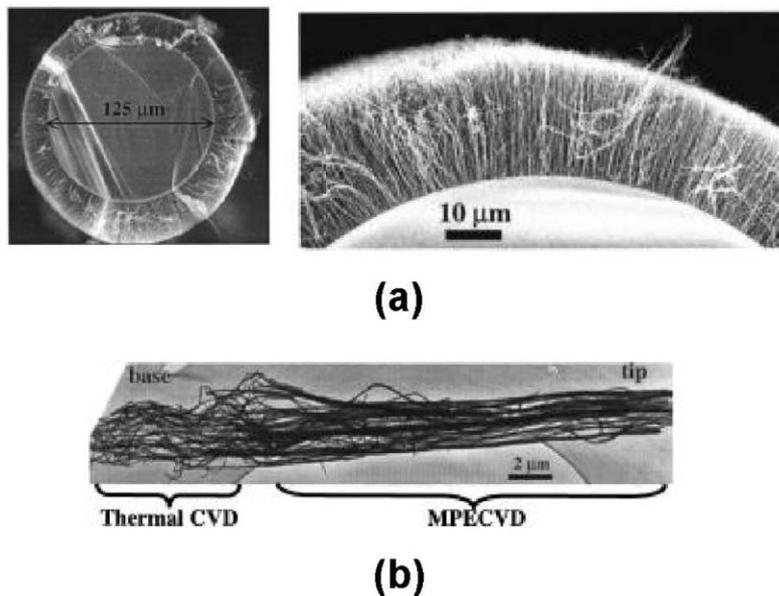
(a)

(b)

Fig. 9. Micrographs showing (a) nanotubes aligned normal to the surface of a glass fiber and (b) the influence of MPECVD on the structure of the nanotubes [29].
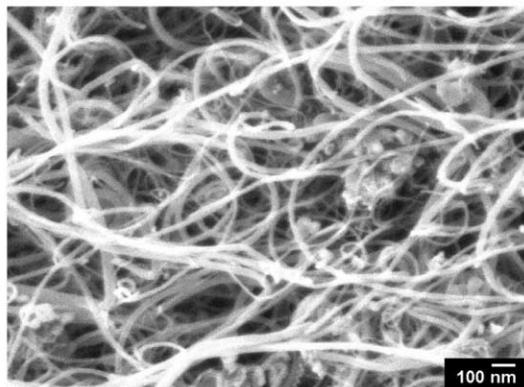

Fig. 10. Micrograph showing tangled, spaghetti-like carbon nanotubes grown with conventional CVD techniques.

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 with an atomic-force microscope (AFM). Wong and co-workers [35] were the first to perform direct measurement of the stiffness and strength of individual, structurally isolated multi-wall carbon nanotubes using atomic force microscopy. The nanotube was pinned at one end to molybdenum disulfide surfaces and load was applied to the tube by means of the AFM tip. The bending force was measured as a function of displacement 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±8 GPa.

Single-walled nanotubes tend to assemble in 'ropes' of nanotubes. Salvetat and co-workers [35] measured the properties of these nanotube bundles with the AFM. As the diameter of the tube bundles increases, the axial and shear moduli decrease significantly. This suggests slipping of the nanotubes within the bundle. Walters et al. [37] further investigated the elastic strain of nanotube bundles with the AFM. On the basis of their experimental strain measurements and an assumed elastic modulus of 1.25 TPa, they calculated a yield strength of 45±7 GPa for the nanotube ropes. Indeed, their calculated value for strength would be much lower if the elastic modulus of the nanotube bundle is decreased as a consequence of slipping within the bundle, suggested by Salvetat et al. [36].

Yu and co-workers [38,39] have investigated the tensile loading of multi-walled nanotubes and single-walled nanotube ropes. In their work, the nanotubes were attached between two opposing AFM tips and loaded under tension. Their experimental set-up is shown in Fig. 11. For multi-walled carbon nanotubes [38] the failure of the outermost tube occurred followed by pull-out of the inner nanotubes. This 'sword and sheath' telescoping failure mechanism of multi-walled carbon nanotubes in tension is also shown in Fig. 11. The experimentally calculated tensile strengths of the outermost layer ranged from 11 to 63 GPa and the elastic modulus ranged from 270 to 950 GPa. In their subsequent investigation of single-walled nanotube ropes [39], they assumed that only the outermost tubes assembled in the rope carried the load during the experiment, and they calculated tensile strengths of 13 to 52 GPa and average elastic moduli of 320 to 1470 GPa. Xie et
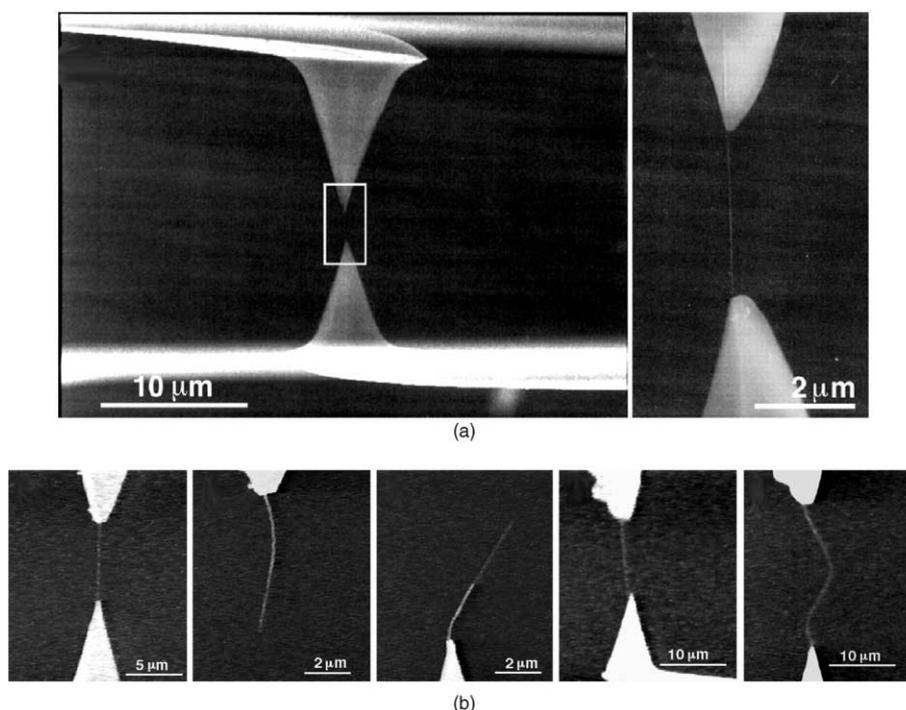
Fig. 11. Micrographs showing (a) the apparatus for tensile loading of MWCNTs and (b) the telescoping, "sword and sheath" fracture behavior of the MWCNT [38].

al. [40] also tested ropes of multi-walled nanotubes in tension. In their experiments, the obtained tensile strength and modulus were 3.6 and 450 GPa, respectively. It was suggested that the lower values for strength and stiffness may be a consequence of defects in the CVD-grown nanotubes.

5. Mechanics of carbon nanotubes

As discussed in the previous section, nanotube deformation has been examined experimentally. Recent investigations have shown that carbon nanotubes possess remarkable mechanical properties, such as exceptionally high elastic modulus [34,35], large elastic strain and fracture strain sustaining capability [41,42]. Similar conclusions have also been reached through some theoretical studies [43–46], although very few correlations between theoretical predictions and experimental studies have been made. In this section we examine the mechanics of both single walled and multi-walled nanotubes.

5.1. Single-walled carbon nanotubes

Theoretical studies concerning the mechanical properties of single-walled nanotubes have been pursued extensively. Overney et al. [43] studied the low-frequency vibrational modes and structural rigidity of long nanotubes consisting of 100, 200 and 400 atoms. The calculations were based on an empirical Keating Hamiltonian with parameters determined from first principles. A comparison of the bending stiffnesses of single-walled nanotubes and an iridium beam was presented. The bending stiffness of the iridium beam was deduced by 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.

Besides their experimental observations, Iijima et al. [47] examined response of nanotubes under compression using molecular dynamics simulations. They simulated the deformation properties of single- and multi-walled nanotubes bent to large angles. Their experimental and theoretical results show that nanotubes are remarkably flexible. The bending is completely reversible up to angles in excess of 110°, despite the formation of complex kink shapes. Fig. 12 shows their numerical and experimental results, demonstrating the exceptional resilience of carbon nanotubes at large strain.

Ru [48] noticed that actual bending stiffness of single-walled nanotubes is much lower than that given by the elastic-continuum shell model if the commonly defined representative thickness is used. Ru proposed the use of an effective nanotube bending stiffness as a material parameter not related to the representative thickness. With the aid of this concept, the elastic shell equations can be readily modified and then applied to single-walled nanotubes. The computational results based on this concept show a good agreement with the results from molecular dynamics simulations.
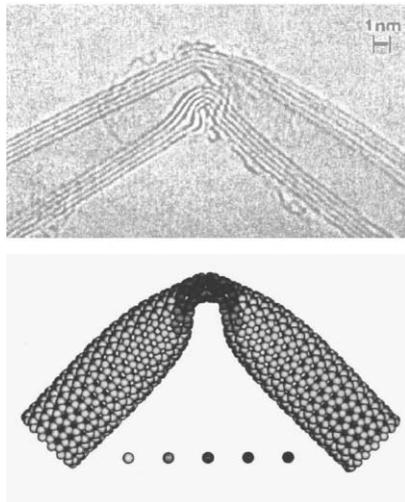
Fig. 12. TEM micrograph and computer simulation of nanotube buckling [47].

Vaccarini et al. [49] investigated the influence of nanotube structure and chirality on the elastic properties in tension, bending, and torsion. They found that the chirality played a small influence on the nanotube tensile modulus. However, the chiral tubes exhibit asymmetric torsional behavior with respect to left and right twist, whereas the armchair and ziz-zag tubes do not exhibit this asymmetric torsional behavior.

A relatively comprehensive study of the elastic properties of single-walled nanotubes was reported by Lu [44]. In this study, Lu adopted an empirical lattice-dynamics model [50], which has been successfully adopted in calculating the phonon spectrum and elastic properties of graphite. In this 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. Lu's work attempted to answer such basic questions as: (a) how do elastic properties of nanotubes depend on the structural details, such as size and chirality? and (b) how do elastic properties of nanotubes compare with those of graphite and diamond? Lu concluded that the elastic properties of nanotubes are insensitive to size and chirality. The predicted Young's modulus ($\sim$1 TPa), shear modulus ($\sim$0.45 TPa), and bulk modulus ($\sim$0.74 TPa) are comparable to those of diamond. Hernandez and co-workers [51] performed calculations similar to those of Lu and found slightly higher values ($\sim$1.24 TPa) for the Young's moduli of tubes. But unlike Lu, they found that elastic moduli are sensitive to both tube diameter and structure.

Besides their unique elastic properties, the inelastic behavior of nanotubes has also received considerable attention. Yakobson and co-workers [10,46] examined the instability behavior of carbon nanotubes beyond linear response by using a realistic many-body Tersoff-Brenner potential and molecular dynamics simulations. Their molecular-dynamics simulations show that carbon nanotubes, when subjected to large deformations, reversibly switch into different morphological patterns. Each shape change corresponds to an abrupt release of energy and a singularity in the stress/strain curve. These transformations are explained well by a continuum shell model. With properly chosen parameters, their model provided a very accurate 'roadmap' of nanotube behavior beyond the linear elastic regime. They also made molecular dynamics simulations to single- and double-walled nanotubes of different chirality and at different temperatures [45]. Their simulations show that nanotubes have an extremely large breaking strain (in the range 30–40%) and the breaking strain decreases with temperature. Yakobson [11] also applied dislocation theory to carbon nanotubes for describing their main routes of mechanical relaxation under tension. It was concluded that the yield strength of a nanotube depends on its symmetry and it was believed that there exists an intra-molecular plastic flow. Under high stress, this plastic flow corresponds to a motion of dislocations along helical paths within the nanotube wall and causes a stepwise necking, a well-defined new symmetry, as the domains of different chiral symmetry are formed. As a result, both the mechanical and electronic properties of carbon nanotubes are changed.

The single walled nanotubes produced by laser ablation and arc-discharge techniques have a greater tendency to form 'ropes' or aligned bundles [15,23]. Thus, theoretical studies have been made to investigate the mechanical properties of these nanotube bundles. Ru [52] presented a modified elastic-honeycomb model to study elastic buckling of nanotube ropes under high pressure. Ru gave a simple formula for the critical pressure as a function of nanotube Young's modulus and wall thickness-to-radius ratio. It was concluded that single-walled ropes are susceptible to elastic buckling under high pressure and elastic buckling is responsible for the pressure-induced abnormalities of vibration modes and electrical resistivity of single walled nanotubes.

Popov et al. [53] studied the elastic properties of triangular crystal lattices formed by single-walled nanotubes by using analytical expressions based on a force-constant lattice dynamics model [54]. They calculated various elastic constants of nanotube crystals for nanotube types, such as armchair and zigzag. It was shown that the elastic modulus, Poisson's ratio and bulk modulus clearly exhibit strong dependence on the tube radius. The bulk modulus was found to have a maximum value of 38 GPa for crystals composed of single-walled nanotubes with $\sim$0.6 nm radius.

5.2. Multi-walled carbon nanotubes

Multi-walled nanotubes are composed of a number of concentric single walled nanotubes held together with

relatively weak van der Waals forces. The multi-layered structure of these nanotubes further complicates the modeling of their properties.

Ruoff and Lorents [55] derived the tensile and bending stiffness constants of ideal multi-walled nanotubes in terms of the known elastic properties of graphite. It is suggested that unlike the strongly anisotropic thermal expansion in conventional carbon fibers and graphite, the thermal expansion of carbon nanotubes is essentially isotropic. However, the thermal conductivity of nanotubes is believed to be highly anisotropic and its magnitude along the axial direction is perhaps higher than that of any other material.

Lu [44] also calculated the elastic properties of many multi-walled nanotubes formed by single-layer tubes by means of the empirical-lattice dynamics model. It was found that elastic properties are insensitive to different combinations of parameters, such as chirality, tube radius and numbers of layers, and the elastic properties are the same for all nanotubes with a radius larger than one nm. Interlayer van der Waals interaction has a negligible contribution to both the tensile and shear stiffness.

Govindjee and Sackman [56] were the first to examine the use of continuum mechanics to estimate the properties of multi-walled nanotubes. They investigated the validity of the continuum approach by 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 was used.

Ru [57] used the elastic-shell model to study the effect of van der Waals forces on the axial buckling of a double-walled carbon nanotube. The analysis showed that the van der Waals forces do not increase the critical axial buckling strain of a double-walled nanotube. Ru [58,59] thereafter also proposed a multiple column model that considers the interlayer radial displacements coupled through the van der Waals forces. This model was used to study the effect of interlayer displacements on column buckling. It was concluded that the effect of interlayer displacements could not be neglected unless the van der Waals forces are extremely strong.

Kolmogorov and Crespi [60] investigated the interlayer interaction in two-walled nanotubes. A registry-dependent two-body graphite potential was developed. It was demonstrated that the tightly constrained geometry of a multi-walled nanotube could produce an extremely smooth solid-solid interface wherein the corrugation against sliding does not grow with system size. The energetic barrier to interlayer sliding in defect-free nanotubes containing thousands of atoms can be comparable to that for a single unit cell of crystalline graphite.

6. Nanotube-based composites

Although there is experimental variability in the direct characterization of carbon nanotubes, theoretical and experimental observations reveal their exceptional properties. As a consequence, there has been recent interest in the development of nanotube-based composites. Although most research has focused on the development of nanotube-based polymer composites, attempts have also been made to develop metal and ceramic-matrix composites with nanotubes as reinforcement. Here we review the recent work in this area and discuss the challenges that are associated with the development of these new composites.

6.1. Processing and characterization of nanotube-based polymer composites

The reported exceptional properties of nanotubes have motivated others to investigate experimentally the mechanics of nanotube-based composite films. Uniform dispersion within the polymer matrix and improved nanotube/matrix wetting and adhesion are critical issues in the processing of these nanocomposites.

The issue of nanotube dispersion is critical to efficient reinforcement. In the work of Salvetat et al. [36] discussed earlier, slipping of nanotubes when they are assembled in ropes significantly affects the elastic properties. In addition to slipping of tubes that are not bonded to the matrix in a composite, the aggregates of nanotube ropes effectively reduce the aspect ratio (length/diameter) of the reinforcement. It is, however, difficult to obtain a uniform dispersion of carbon nanotubes in the polymer matrix. Shaffer and Windle [61] were able to process carbon nanotube/polyvinyl-alcohol composite films for mechanical characterization. The tensile elastic modulus and damping properties of the composite films were assessed in a dynamic mechanical thermal analyzer (DMTA) as a function of nanotube loading and temperature. From the theory developed for short-fiber composites, a nanotube elastic modulus of 150 MPa was obtained from the experimental data. 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 imperfections in the graphite layers of catalytically grown nanotubes used for the investigation or whether it relates to a fundamental difficulty in stress transfer.

Qian et al. [62] characterized carbon-nanotube/polystyrene composites. With only the addition of 1% by weight (about 0.5% by volume) they achieved between 36–42% increase in the elastic stiffness and a 25% increase in the tensile strength. Fig. 13 is a TEM micrograph of their nanotube film showing the mechanisms of fracture. As for conventional fiber composites, we see nanotube pull-out, nanotube fracture, as well as crack
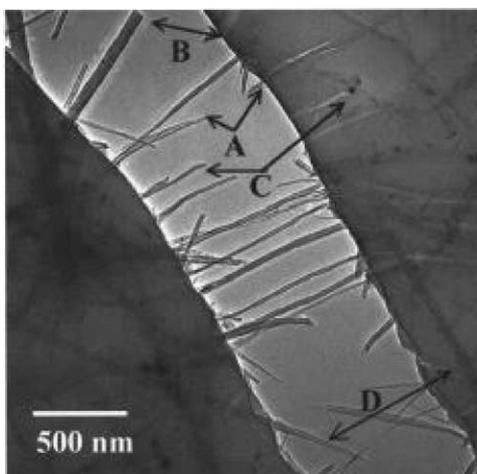
Fig. 13. Fracture mechanisms in nanotube-based composites [62].

bridging by the nanotubes. They also used short-fiber composite theory to demonstrate that 10% by weight of carbon fibers (about 5% by volume) in the research of Tibbetts and McHugh [63] would be required to achieve the same increase in elastic modulus with 1% (by weight) of carbon nanotubes.

Fig. 13 shows significant pull-out of the nanotubes from the matrix. Clearly there is reinforcement as evidenced by improvements in stiffness and strength of the composite, but to take full advantage of the exceptional stiffness, strength, and resilience of carbon nanotubes, strong interfacial bonding is critical. Jia et al. [64] showed that the nanotubes can be initiated by a free-radical initiator, AIBN (2,2′-azobisisobutyronitrile), to open their π bonds. In their study of carbon-nanotube/poly(methyl methacrylate) (PMMA) composites, the possibility exists to form a C–C bond between the nanotube and the matrix. Gong et al. [65] investigated surfactant-assisted processing of nanotube composites with a nonionic surfactant. Improved dispersion and interfacial bonding of the nanotubes in an epoxy matrix resulted in a 30% increase in elastic modulus with addition of 1 wt.% nanotubes.

Lordi and Yao [66] looked at the molecular mechanics of binding in nanotube-based composites. In their work, they used force-field-based molecular-mechanics calculations to determine the binding energies and sliding frictional stresses between pristine carbon nanotubes and different polymeric matrix materials. The binding energies and frictional forces were found to play only a minor role in determing the strength of the interface. The key factor in forming a strong bond at the interface is having a helical conformation of the polymer around the nanotube. They suggested that the strength of the interface may result from molecular-level entanglement of the two phases and forced long-range ordering of the polymer.

Because the interaction 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. [67] examined stress-induced fragmentation of multi-walled carbon nanotubes in polymer films. Their nanotube-containing film had a thickness of approximately 200 μm. 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. From 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 higher. 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. In further work, Lourie and Wagner [68–70] investigated tensile and compressive fracture in nanotube-based composites.

Stress transfer has also been investigated by Raman spectroscopy. Cooper and co-workers [71] 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 (2610 cm^{-1}) to a lower wavenumber. The shift in the G′ Raman band corresponds to strain in the graphite structure, 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/epoxy composites, Ajayan et al. [72] 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. Similar results were obtained by Schadler et al. [73]. Multi-walled nanotube/epoxy composites were tested in both tension and compression. The compressive modulus was found to be higher than the tensile modulus of the composites, and the Raman peak was found to shift only in compression, indicating poor interfacial load transfer in tension.

Even with improved dispersion and adhesion, micromechanical characterization of these composites is difficult because the distribution of the nanotubes is random. Thus, attempts have been made to align nanotubes in order better to elucidate the reinforcement mechanisms. Jin et al. [74] showed that aligned nanotube composites could be obtained by mechanical stretching of the composite. X-ray diffraction was used to determine the orientation and degree of alignment.

Bower et al. [42] further investigated the deformation of carbon nanotubes in these aligned films. Haggenmueller and co-workers [75] showed that melt spinning of single wall nanotubes in fiber form can also be used to create a well-aligned nanotube composite.

In addition to alignment of the carbon nanotubes, researchers have attempted to spin carbon fibers from carbon nanotubes [76–78]. Andrews et al. [77] dispersed 5 wt.% single-walled nanotubes in isotropic petroleum pitch. Compared to isotropic pitch fibers without nanotubes, the tensile strength was improved by ∼90%, the elastic modulus was improved by ∼150% and the electrical conductivity increased by 340%. Because the pitch matrix is isotropic, the elastic modulus is 10–20 times less than that of mesophase pitch fibers used in composite materials. Further developments in this area may potentially create a new form of carbon fiber that has exceptional flexibility as well as stiffness and strength. Fig. 14 shows the exceptional flexibility of the as-spun nanotube composite fiber produced by Vigolo and co-workers [78]. Their technique for spinning nanotube-based fibers involves dispersing the nanotubes in surfactant solutions followed by recondensing the nanotubes in the stream of a polymer solution to form macroscopic fibers and ribbons. Their work indicates that there is preferential orientation of the nanotubes along the axis of the ribbons. Although the elastic modulus of the nanotube fibers (9–15 GPa) is far below the values for individual nanotubes or conventional carbon fibers, the demonstrated resilience of the fibers gives hope for future improvements.

6.2. Ceramic- and metal-matrix composites

The focus of much of the research in nanotube-based composites has been on polymer-matrix materials, but

Fig. 14. Micrographs showing the exceptional flexibility of carbon nanotube-based fiber [78].

the unique properties of carbon nanotubes can also be exploited in ceramic- or metal-matrix composites.

Although ceramics have high stiffness and excellent thermal stability with relatively low density, their brittleness impedes the use as structural materials. Because of their exceptional resilience, carbon nanotubes might be particularly desirable as a reinforcement for ceramics. The combination of these nanotubes with a ceramic matrix could potentially create composites that have high-temperature stability as well as exceptional toughness and creep resistance.

Ma and co-workers [79] formed carbon-nanotube/silicon-carbide (SiC) composites via mixing nano-particles of SiC with 10 wt.% carbon nanotubes and hot pressing. They reported a 10% improvement in the strength and fracture toughness as compared to the monolithic ceramics. These modest improvements were attributed to nanotube/matrix debonding and crack deflection. Other researchers [80–84] have developed techniques to synthesize carbon nanotubes in situ to form carbon-nanotube/metal-oxide composite powders. These powders were then hot pressed to form macroscopic composites. The incorporation of the long nanotube bundles grown in situ, however, did not provide the expected improvement in mechanical properties.

Preliminary investigations by Chen et al. [85] focused on synthesis of carbon-nanotube/metal-matrix composites by electroless plating, and Xu et al. [86] showed slight improvements on the electrical conductivity of aluminum with increasing nanotube volume fraction.

7. Conclusions

The exceptional mechanical and physical properties demonstrated for carbon nanotubes, combined with their low density, make this new form of carbon an excellent candidate for composite reinforcement. Before these extraordinary properties observed at the nanoscale are realized in a macroscopic composite, considerable basic research is necessary. Full understanding of the thermo-mechanical behavior of nanotube-based composites, requires knowledge of the elastic and fracture properties of carbon nanotubes as well as of interactions at the nanotube/matrix interface. Although this requirement is no different from that in conventional fiber composites [3], the scale of the reinforcement phase diameter has changed from micrometer (e.g. glass and carbon fibers) to nano-meter. The change in reinforcement scale poses new challenges in the development of processing techniques for these composites as well as the development of characterization techniques and methodologies to measure the elastic and fracture behavior of carbon nanotubes and their composites. The nano-meter scale of the reinforcement presents additional

challenges in mechanics research since we now must account for interactions at the atomic-scale.

Preliminary research in nanotube-based composites has indicated that there is potential in carbon nanotubes for reinforcement, but, most importantly, it has illustrated the significant challenges that must be overcome before the potential is realized. Critical to the use of nanotubes as a structural material, there is a need for development of nanotube production techniques at the scale needed for producing macroscopic composites that are cost-effective. Fundamental work in processing, characterization, and analysis/modeling is crucial before the structural and functional properties of this new class of nanocomposites can be optimized.

Acknowledgements

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