



## Evaluation of Properties Carbon Nanotubes (CNTs) and CNT/Polymer Composites

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### Abstract

The mechanical properties of carbon nanotubes, such as high elastic modulus and tensile strength, make them the most ideal and promising reinforcements in substantially enhancing the mechanical properties of resulting polymer/carbon nanotube composites. It is acknowledged that the mechanical properties of the composites are significantly influenced by interfacial interactions between nanotubes and polymer matrices. The current challenge of the application of nanotubes in the composites is hence to determine the mechanical properties of the interfacial region, which is critical for improving and manufacturing the nanocomposites. In this work, a new method for evaluating the elastic properties of the interfacial region is developed by examining the fracture behavior of carbon nanotube reinforced poly (methyl methacrylate) (PMMA) matrix composites under tension using molecular dynamics simulations. The effects of the aspect ratio of carbon nanotube reinforcements on the elastic properties, i.e. Young's modulus and yield strength, of the interfacial region and the nanotube/polymer composites are investigated. The feasibility of a three-phase micromechanical model in predicting the elastic properties of the nanocomposites is also developed based on the understanding of the interfacial region.

**Key words:** Carbon Nanotubes, Mechanical Properties, Polymer, Composites, Elastic Properties

### 1. Introduction

Since the documented discovery of carbon nanotubes (CNTs) in 1991 by Iijima and the realization of their unique physical properties, including mechanical, thermal, and

electrical, many investigators have endeavored to fabricate advanced CNT composite materials that exhibit one or more of these properties. For example, as conductive filler in polymers, CNTs are quite effective compared to traditional carbon black microparticles, primarily due to their large aspect ratios. The electrical percolation threshold was recently reported at 0.0025 wt.% CNTs and conductivity at 2 S/m at 1.0wt.% CNTs in epoxy matrices. Similarly, CNTs possess one of the highest thermal conductivities known, which suggests their use in composites for thermal management. The main focus of this paper, however, will be on the use of CNTs as discontinuous reinforcement for polymer matrices. The CNT can be thought of as the ultimate carbon fiber with break strengths reported as high as 200 GPa, and elastic moduli in the 1 TPa range. This, coupled with approximately 500 times more surface area per gram (based on equivalent volume fraction of typical carbon fiber) and aspect ratios of around 103, has spurred a great deal of interest in using CNTs as a reinforcing phase for polymer matrices [1 & 2].

The outstanding electrical, mechanical, and thermal properties of carbon nanotubes (CNTs) have made them among the most promising materials in a wide range of applications such as nano-sensors and atomic transportation. In addition, the excellent mechanical properties of CNTs, such as ultra-high Young's modulus around 1 TPa and tensile strengths varying from 11–63 GPa, are promising ultra-high-strength reinforcements in high-performance polymer matrix composites.

## 2. Structure of Nanotubes

The primary symmetry classification of a CNT divides them into achiral or chiral [1]. An achiral nanotube is defined by a nanotube whose mirror image has an indistinguishable structure to the original one. And, as a consequence, it is superimposable to it. There are only two cases of achiral nanotubes: armchair and zig-zag nanotubes. The simplest way of specifying the structure of an individual tube is in terms of a vector, the chiral vector ( $C_h$ ) joining two equivalent points on the original graphene lattice. The cylinder is produced by rolling up the sheet such that the two end-points of the vector are superimposed (Figure 1). The chiral vector can be defined in terms of the lattice translational indices (n,m) and the basic vectors  $a_1$  and  $a_2$  of the hexagonal lattice and corresponds to a section of the nanotube perpendicular to the nanotube axis.

$$C_h = na_1 + ma_2 \quad (n, m \text{ are integers, } 0 \leq |m| \leq n) \quad (1)$$

The chiral angle,  $\theta$ , is defined as the angle between the vectors  $C_h$  and  $a_1, a_2$  with values of  $\theta$  in the range  $0^\circ \leq |\theta| \leq 30^\circ$ , due to the hexagonal symmetry of the honeycomb lattice.

$$\cos \theta = \frac{C_h \cdot a_1}{|C_h||a_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}} \quad (2)$$

The chiral angle  $\theta$  denotes the tilt angle of the hexagons with respect to the nanotube axis, and the angle  $\theta$  specifies the spiral symmetry. The two limiting cases, corresponding to the achiral nanotubes, exist where the chiral angle is at  $0^\circ$  (zig-zag) and  $30^\circ$  (armchair).

The diameter of the CNT ( $d_t$ ) is given by  $L/\pi$ , in which L is the circumferential length of the CNT:

$$d_t = L/\pi \quad (3)$$

$$L = |C_h| = \sqrt{C_h \cdot C_h} = a\sqrt{n^2 + m^2 + nm} \quad (4)$$

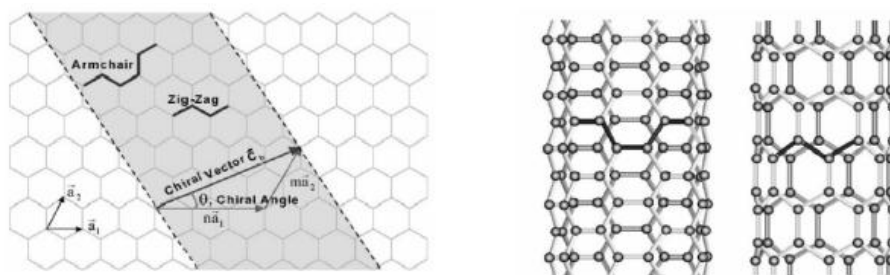


Figure 1. Schematic diagram showing how a hexagonal sheet of graphite is “rolled” to form a CNT [2]

Although the chirality has a relatively small influence on the elastic stiffness, the StoneWales transformation (Figure 2), 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.

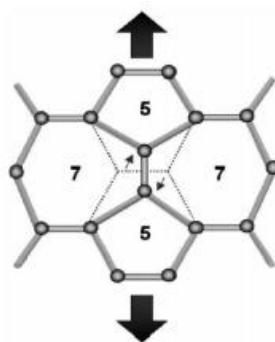


Figure 2. The Stone-Wales transformation occurring in an armchair nanotube under axial tension [2]

### 3. Synthesis of Nanotubes

The properties of CNTs are closely related to their method of production. In early work the arc discharge and laser vaporisations processes were the most common forms of nanotube production. However, in the interest of developing a process which could be easily scaled up for industrial production, more and more work has been devoted to chemical vapor deposition (CVD) techniques. In Table 1, a short summary of the above-mentioned techniques is given.

Table 1. Common methods for CNTs production

Method	Summary	Yield	Strength	Weakness
Arc discharge [8]	Graphite evaporated by a plasma via high current	30%	SWNT and MWNT with few structural defects	Tubes tend to be short and entangled
Chemical Vapor Deposition (CVD) [9]	Decomposition of carbon-based gas	20-100%	Easiest to scale up to industrial production	Typically MWNT with a high density of defects
Laser ablation [10]	Graphite blasted with intense laser pulses	Up to 70%	Diameter control via reaction temperature	More expensive than other methods
High Pressure CO conversion (HiPCO) [11]	Metal catalysts nucleate SWNT at high temperature and pressure	95%	Excellent structural integrity for CVD process	Production rates still relatively low

In the synthesis methods reported, CNTs are found along with other materials, such as amorphous carbon and carbon nanoparticles. The removal of these graphitic impurities has stimulated substantial levels of research, which have met significant success. However, considerable problems still remain for all present purification techniques. Most of these methods rely on the difference in resistance to oxidation, either thermal or chemical, between nanotubes and impurities. However, this difference is marginal, resulting in significant nanotube oxidation during purification. Alternatively, nondestructive methods such as microfiltration or size exclusion chromatography can be employed but tend to be prohibitively slow.

## 4. Properties of nanotubes

### 4.1. Electronic properties

The previously mentioned differences in chirality play an important role in the electronic properties of CNTs. Theoretical studies on the electronic properties of CNTs indicate that all armchair tubes have metallic band-structure, as well as zigzag nanotubes exhibiting values of  $m, n$  multiples of three [3,4]. In summary, the metallic transport condition for nanotubes can be expressed as:

$$\frac{(2m + n)}{3} = \text{integer} \quad (5)$$

It is noteworthy that SWNTs can be either metallic or semiconducting depending on the choice of  $(m, n)$ , although there is no difference in the chemical bonding between the carbon atoms within the nanotubes and no doping or impurities are present (Figure 3). The unique electronic properties of CNTs are caused by the quantum confinement of electrons normal to the nanotube axis. In the radial direction, electrons are confined by the monolayer thickness of the graphene sheet. Consequently, electrons can propagate only along the nanotube axis, and so to their wave vector points. The resulting number of one-dimensional conduction and valence bands effectively depend on the standing waves that are set up around the circumference of the carbon nanotube. The sharp intensities (spikes) shown in the density of states (DOS) of the tubes are known as van Hove singularities and are the result of this one-dimensional quantum conduction (Figure 3) that is not present in an infinite graphite crystal [5].

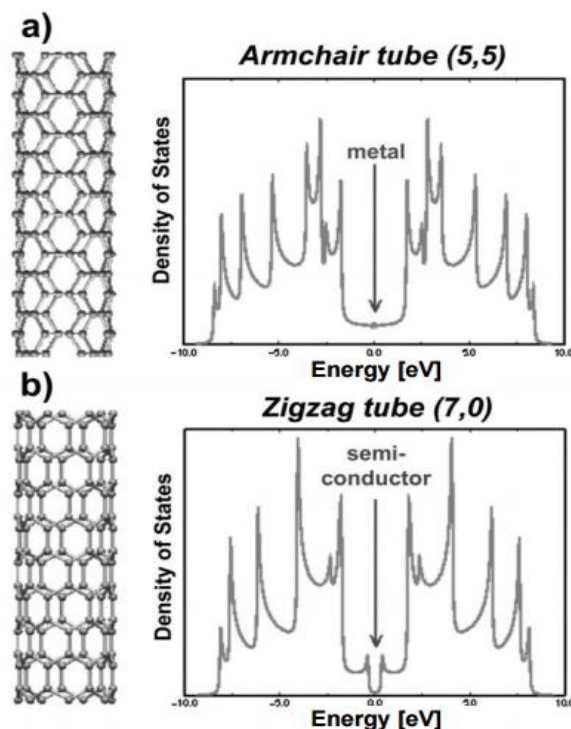


Figure 3. Density of states (DOS) exhibiting the valence-band (negative values) and conduction-band (positive values) and the Fermi energy ( $E_f$ ; centered at 0 eV) for (a) a metallic armchair (5,5) tube, which shows electronic states at the  $E_f$  (characteristic of a metal) (b) a zigzag tube revealing semiconducting behaviour caused by the energy gap located between the valence and conduction band (characteristic of semiconductors). The spikes shown in the DOS of the tubes are called van Hove singularities and are the result of the one-dimensional quantum confinement, which is not present in an infinite graphite crystal [6]

MWNTs are more complex objects than SWNTs since each one of their carbon shells can have different electronic character and chirality. However, in studies of MWNTs with a metallic outer shell that are side-bonded to metal electrodes, it was concluded that electrical transport at low energies is dominated by outer-shell conduction [6].

## 4.2. Transport properties

### 4.2.1. Theoretical conductivity

In a macroscopic conductor, the resistivity,  $\rho$ , and the conductivity,  $\sigma$ , are physical properties of a material. However, when the size of the conductor becomes small compared to the characteristic lengths for the motion of electrons, then  $\rho$  and  $\sigma$  will both depend on the dimension  $L$  through quantum effects. The quantized resistance of a CNT ( $R_0$ ) has been calculated [1] and is equal to:

$$R_0 = \frac{h}{2e^2} = 12.9064 * 10^3 \Omega \quad (6)$$

$$G_0 = \frac{1}{R_0} = \frac{2e^2}{h} = 77.4809 * 10^{-6} S \quad (7)$$

Ponchral et al. [7] measured the resistivity of nanotubes using a scanning probe microscope (SPM). They obtain a value of  $\rho < 100 \Omega/\mu m$ . Chemical doping of SWNTs with electron donors or acceptors has been used to enhance their electrical conductivity in analogy to the well-known graphite intercalation compounds.

### 4.3. Vibrational properties

#### 4.3.1. Phonon structure

Phonons denote the element of motion or quantized normal mode vibrations of a system. The graphene sheet has two atoms per unit cell, thus having six phonon branches (Figure 4 (a,b)). As for the electronic properties, the phonon dispersion relations and phonon density of states (DOS) for SWNTs can be deduced from those of the graphene sheet [6 & 8].

The phonon dispersion for a (10,10) SWNT obtained by a zone-folding procedure is illustrated in Figure 4(c), and the respective phonon DOS is shown in Figure 4(d). The large amount of sharp structure in the phonon density of states in Figure 4(d) for the (10,10) SWNT reflects the many phonon branches and the one dimensional nature of SWNTs relative to two dimensional graphite arising from the quantum confinement of the phonon states in van Hove singularities [1 & 8].

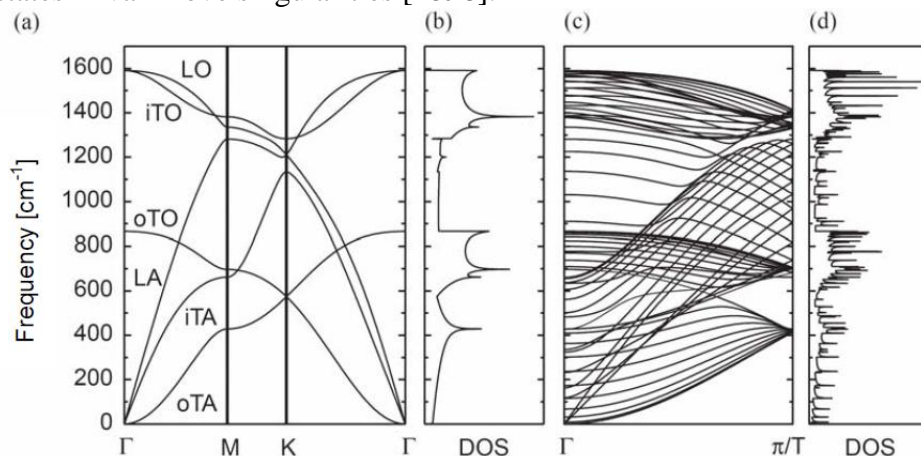


Figure 4. (a) Phonon dispersion of 2-D graphite using the force constants from Reference [9]. (b) The phonon density of states for a 2-D graphene sheet. (c) The calculated phonon dispersion relations of an armchair CNT with  $(n, m) = (10, 10)$ , for which there are 120 degrees of freedom and 66 distinct phonon branches [1], calculated from (a) by using the zone-folding procedure. (d) The corresponding phonon density of states for a (10,10) nanotube [8]

### 4.4. Mechanical properties

In this paragraph, a review of the most important results for the measurement of the mechanical properties of CNTs will be presented. Then, these results will be critically discussed and compared with commercial fibres. However, in order to have a more accurate idea of the real potential of CNTs as reinforcing fillers for composite materials, a clear definition of the cross-sectional area of the nanotube needs to be introduced. In fact, the majority of the studies presented in literature assumed that only the external layer of nanotubes carried the load. Hence they used only the area occupied by the external wall as cross-sectional area, ignoring the hollow part of the nanotube. However, this assumption leads to an overestimate of the nanotube's mechanical properties. When nanotubes are used as reinforcing fillers in nanocomposites, the whole volume they occupy needs to be considered in micromechanical models, hence their whole cross-sectional area including the hollow part should be considered. For this reason, the nanotubes effective properties must be calculated.

## 5. Conclusion

This Article presented an extensive overview of CNTs and CNT/polymer composites. The most relevant properties of CNTs have been listed together with their applications. The

current preparation methods of CNT/polymer composites have been described, with particular emphasis on the preparation of aligned nanocomposites materials. The factors affecting the macroscopic properties have been identified as (1) homogeneous dispersion of the CNTs throughout the polymer matrix, (2) adhesion between the nanotubes and the matrix and finally (3) uniaxial orientation, to exploit the intrinsic anisotropy of the nanotubes. Despite the fact that CNTs are considered the ultimate reinforcing fibres, the results reported in literature so far are rather disappointing, mainly because of the difficulty to create nanocomposites, which display these characteristics altogether. Only if this difficulty is overcome, the ultimate nanocomposite material can be created.

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