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Experimental and Theoretical Investigations on Carbon Nanotube-Based Materials for Sensors and Actuators

Erik T. Thostenson[1], Chunyu Li[1] and Tsu-Wei Chou[1]

Summary

With their well-known novel mechanical and electrical properties, carbon nanotubes are inherently multifunctional. Toward the development of multifunctional composite materials we have experimentally and theoretically investigated the use of carbon nanotubes as sensors and actuators. In this research work, we consider the nanotube within an external electric field with non-uniform charge distribution. Subsequently the charge induced deformations are investigated. We also demonstrate that conducting carbon nanotube networks formed in an epoxy polymer matrix can be utilized as highly-sensitive sensors for detecting the onset, nature and evolution of damage in advanced polymer-based composites. Using direct-current measurements the internal damage accumulation can be monitored *in situ*.

Introduction

Increasingly materials are being tailored to achieve multifunctional properties where they can combine active, sensory and adaptive capabilities. The development of "smart structures" requires the development of material systems which contain multifunctional elements for sensing and actuation. Owing to their distinctive mechanical and physical properties, nanotubes offer unique potential for reinforcing polymers. Considerable interest has focused on utilizing nanotubes as passive reinforcement to tailor their mechanical, electrical and thermal properties. Baughman and co-workers [1] first reported electro-mechanical actuation behavior of nanotubes. Because of this inherent multifunctionality and coupling between mechanical and physical properties makes nanotubes ideal candidates as both actuators and sensors.

Theoretical studies on electro-mechanical coupling of carbon nanotubes are important for the development of applications in nanoelectromechanical systems (NEMS). While there have been recent efforts to understand the electromechanical coupling in single walled carbon nanotubes, most studies on electromechanical coupling have used various models based on tight-binding or density functional theory (DFT) approaches [2-5]. These complicated models are time-consuming and their application is limited by computational resources. Computational results are not always consistent and are strongly dependent on specific assumptions. An efficient and accurate analysis of charge induced response is critical to the understanding of the electromechanical characteristics of nanotubes.

[1]University of Delaware Center for Composite Materials and Department of Mechanical Engineering Newark, DE 19716 USA

Long-term durability and performance of advanced fiber composites is governed by properties of the polymer matrix and fiber/matrix interface. In particular, fatigue life and damage tolerance are strongly affected by matrix cracks occurring between fibers as microcracks or between layers as ply delamination. Although in-plane fracture behavior of composites is dominated principally by breakage of load-carrying fibers, initiation of damage in the polymer matrix leads to premature fracture and reduced durability. Multi-walled nanotubes dispersed in the polymer matrix phase of an advanced fibrous composite can act as distributed sensors to evaluate the onset and evolution of damage. Here we show carbon nanotubes, which form a conductive percolating network throughout the polymer matrix, are remarkably sensitive to initial stages of matrix-dominated failure. Through experiments designed to promote different failure modes it is possible to identify the nature and progression of damage.

Atomistic Moment Method for Nanotube Charge Distribution

Recently, the authors developed a simple and accurate approach - Atomistic Moment Method [6], based on the moment method in classical electrostatics. The moment method has been extensively used to solve problems in electrostatics. The fundamental concept is to solve integral equations in electromagnetics by dividing the integral domain into subsections with equal areas and expanding the unknown function in a set of basis functions. The basis functions are known and can be integrated, and coefficients of the basis function can be obtained by solving algebra equations. Some modifications were made to the classical moment method for analyzing charge distribution of carbon nanotubes. The charge distributions can then be utilized to examine the electromechanical coupling behavior of nanotubes using the molecular structural mechanics method [7].

Assuming a nanotube in an infinite electric field, the induced charges are distributed on the nanotube outer surface. Because of the strong attraction of nucleus, the charge distributed in the vicinity of a carbon atom can be considered to be concentrated at the atom. For a freestanding nanotube in an infinite electric field the only boundary condition is that the entire outer nanotube surface is at the electric potential, V_0. If the nanotube has n atoms and the point charges on the nanotube are denoted as q_j, (j=1, 2, ... n), the potential at an arbitrary atomic position is given by:

$$V(\mathbf{r}_i) = \sum_{j=1}^{n} \frac{q_j}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{1}$$

where V is the electric potential, $\mathbf{r}_i$ denotes the position of atom of interest, $\mathbf{r}_j$ represents the location of the charged atom, and ε_0 is the permittivity of vacuum.

By assuming that the entire outer surface of the nanotube is at the same potential (V_0), n equations can be written in matrix form ($[A]\{q\}=\{V_0\}$where $\{q\}$ and

$\{V_0\}$ are the charge vector and the potential vector, respectively, and $[A]$ is the n x n order symmetric matrix). The voltage at atom i resulting from the charge on atom i needs to be carefully treated [6]. Figure 1 shows the charge distribution on an open-ended armchair (5, 5) SWCNT obtained by the atomistic method described above. It can be seen that there is a significant charge concentration at the nanotube open ends.

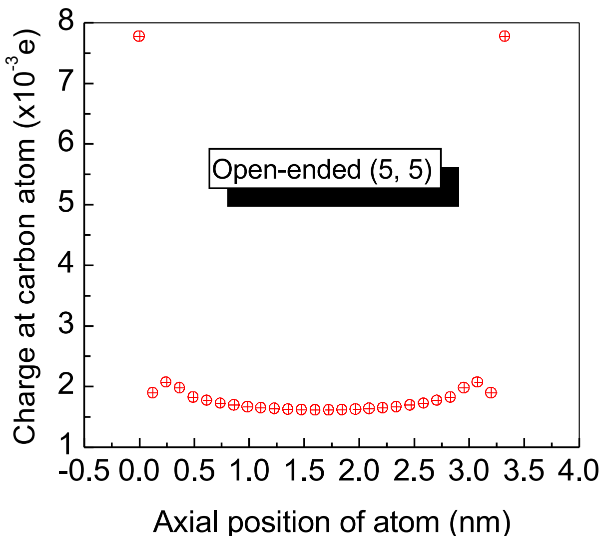

Figure 1: Charge distribution of a single walled nanotube in an infinite electric field.

Charge-Induced Deformation of Carbon Nanotubes

The electric charges distributed on the nanotube result in interatomic interactions due to the Coulombic effect. Carbon-carbon bond lengths are then changed by this interatomic interaction. To quantify the deformation of a nanotube resulting from the additional electric charge, we utilize the molecular structural mechanics method. This method, developed by Li and Chou over the past several years, has been successfully demonstrated for modeling the static, dynamic and thermal properties of carbon nanotubes [8-10].

Electrostatic interactions due to extra charges on two carbon atoms can be calculated by Coulomb's law. If the charges are represented in electronic unit and distance in Å, the electrostatic force (nN) between any pair of atoms can be expressed as:

$$F_{ij}^{q} = 23.04 q_i q_j / R_{ij}^2 \qquad (2)$$

where q_i and q_j are extra charges on carbon atoms, R_{ij} is the distance between the two interacting atoms, and ε is the permittivity.

Figure 2 shows the deformed shape of a charged open-ended nanotube. A trumpet form of open-ended nanotube can be seen, indicating that the radial strain is non-uniform because of charge concentrations at the nanotube ends. Numerical results also indicate that axial strain increases with increasing charge level.

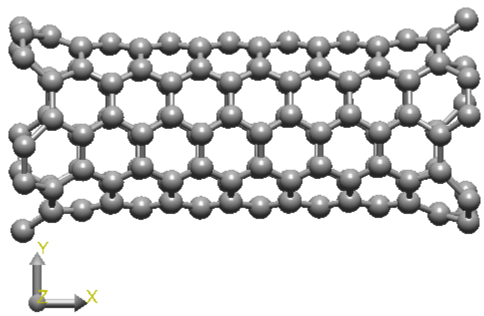

Figure 2: Electric-charge-deformed armchair (5, 5) carbon nanotube.

Multifunctional Nanotube Composites for In Situ Sensing

Owing to the difference in reinforcement scale between conventional micron-sized fiber reinforcement and carbon nanotubes with nanometer-level diameters, it is possible to have carbon nanotube reinforcement in the matrix rich areas between fibers in an individual bundle as well as between adjacent plies. By first dispersing the nanotubes in the polymer matrix and then infiltrating the dispersed mixture through layers and bundles of conventional fibers the nanotubes are able to penetrate throughout and form a conductive percolating network in the polymer matrix. This network formation in the polymer matrix offers significant potential to develop hierarchal sensing approaches for damage detection and health monitoring. Electrical percolation with multi-walled carbon nanotubes at extremely low volume fractions enables the creation of *in situ* sensors that are minimally invasive and not likely to substantially alter the in-plane mechanical properties of the fiber composite.

To fabricate the nanotube/epoxy/fiber composites the carbon nanotubes were first dispersed in the epoxy resin using a calendering approach [11]. The evolution of nanoscale composite structure during the process was evaluated using transmission electron microscopy to ensure a high degree of dispersion. The calendering technique maintains the relatively large aspect ratio of the nanotubes and results in percolation thresholds at or below 0.1 wt% carbon nanotubes. Vacuum-assisted resin transfer molding (VARTM) was then used to make the fiber/epoxy composites with embedded carbon nanotubes. As-processed nanotube/fiber composites were also electrically conductive indicating that nanotubes are able to penetrate throughout the glass preform and form a conductive percolating network in the polymer matrix [12].

Figure 3 shows the load/displacement and electrical resistance response of a unidirectional composite tested in tension. The resistance response is primarily linear relative to the applied deformation and offers potential for use in strain sensing applications. In order to initiate delamination as a failure mode during tensile loading, 5-ply unidirectional composites were fabricated with the center ply cut. The discontinuity at the center ply of the laminate results in the accumulation of shear stresses at the ends of the ply and these shear stresses initiate delamination of the center and adjacent plies. Figure 4 shows the results of the tensile test. The specimen resistance increases linearly with initial deformation and is consistent with our earlier observation of linear increase in resistance with deformation. A sharp increase in resistance occurs when the ply delamination is initiated. As the delamination grows with increasing load there is a large increase in resistance marked primarily by a progressive increase in the slope of the resistance curve with extension of the ply delamination.

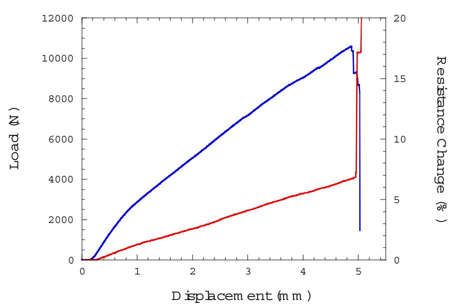

Figure 3: Load/displacement and resistance response of a unidirectional composite.

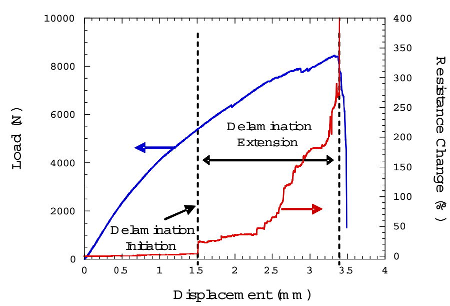

Figure 4: Load/displacement and resistance response of a 5-ply unidirectional composite with the center ply cut to initiate delamination.

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