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Tensile behaviors of graphene sheets and carbon nanotubes with multiple Stone–Wales defects

J.R. Xiao[a,*], J. Staniszewski[a], J.W. Gillespie Jr.[a,b,c]

[a] Center for Composite Materials, University of Delaware, Newark, DE 19716, USA
[b] Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA
[c] Department of Civil and Structural Engineering, University of Delaware, Newark, DE 19716, USA

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ABSTRACT

An atomistic based finite bond element model has been developed to study the effects of multiple Stone–Wales (5-7-7-5) defects on mechanical properties of graphene sheets and carbon nanotubes. The element formulation includes 8 degrees of freedom reducing computational cost compared to the 12 degrees of freedom used in other FE type models. The coefficients of the elements are determined based on the analytical molecular structural mechanics model developed by the authors. The model uses the modified Morse potential to predict the Young's modulus and stress–strain relationship of perfect and defective nanotubes and graphene sheets. The variation of ultimate stress, strain at failure, and Young's modulus values of carbon nanotubes and graphene sheets have been examined as a function of the distance between two defects aligned in the axial and hoop directions. The mechanical properties as a function of the number of defects in the hoop direction are also studied. It is found that the moduli are sensitive to the tube lengths when the total tube length is used to compute the strain. If one uses a local defective length to define the strain, a size independent modulus can be obtained for the defective region. The diameter of the affected region (2 nm) from a single defect is defined as the defective length and is used for all different tube lengths examined in the present study. The effects of defect density on mechanical properties of tubes of any lengths are also discussed.

1. Introduction

Carbon nanotubes (CNTs) [1] have shown several favorable physical attributes, such as small size, low density, high stiffness, and high strength as well as excellent electronic and thermal properties [2–7]. These exceptional mechanical and physical properties along with low weight of CNTs and recent improvements in their synthesis and purification techniques make CNTs excellent candidates for use in composite reinforcement [8–10].

There is evidence that defects can appear at the stage of CNT growth and purification [11,12] during device or composite processing (e.g. chemical functionalization) [13,14], or under mechanical strains [15]. Research has indicated that even a small number of defects in the atomic network will result in some degradation [16,17] of their mechanical properties. Such defects also act as scattering centers for phonons propagating along the tube axis, thus reducing intrinsic tube conductivity.

Molecular mechanics/dynamics and *ab initio* methods are suitable for studying defects but are limited in scale and are computationally expense. Recently, continuum mechanics based models for CNTs have been developed using the harmonic energy potential [18–20]. These models reduce computational cost significantly, but can only be used to investigate elastic properties, such as the Young's modulus or Poisson's ratio. To fully predict the stress–strain relationship and failure mechanism of CNTs, these methods are not sufficient. The Brenner potential function [21] is considered more accurate and versatile. It can handle changes in atom hybridization and bonds with atoms other than carbon. A continuum mechanics approach directly incorporating the Brenner potential function has been developed by Huang's group [22,23] to model elastic properties and stress–strain relationships of carbon nanotubes based on a modified Cauchy–Born rule. Based on the modified Morse potential function [23], which is simpler than the Brenner potential, the authors have developed models for perfect and defective CNTs [24,25]. The developments have the ability to predict the ultimate stress and other mechanical properties, including nanotube's nonlinear stress–strain relationship. The analytical model [24] has been extended to solve mechanical responses of defect-free single- and multi-walled CNTs under internal and external pressure loadings [26,27] as well as aligned nanotube

* Corresponding author. Currently at: Dow Advanced Materials, Newark, DE 19713, USA. Tel.: +1 3025886066; fax: +1 3025254046.
E-mail address: jrxiao@gmail.com (J.R. Xiao).

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composites [28]. The analytical model not only provides simple closed-form solutions but also presents a better insight of the role of the atomic networks.

Effects of defects on mechanical behaviors of graphene sheets and nanotubes have been investigated using computationally expensive methods [4,16,17,23,29–32]. While continuum mechanics based models have not been well developed for predicting the effects of defects on mechanical properties of CNTs and nanotube composites. Research involving the Stone–Wales defect preformed by Tserpes et al. [33,34] using the finite element (FE) based model does not include the deformation of the original nanotube structure around the nucleation site, which may not be true in general as atoms redistribute to minimize energy. The authors [25] proposed a simple way to simulate the formation of a Stone–Wales (5-7-7-5) defect using an interaction mechanics method to calculate the deformations caused by the formation of a Stone–Wales. In this study, the effect of multiple 5-7-7-5 defects on the Young's modulus, ultimate strength, and strain at failure of single-walled CNTs (SWCNTs) of various sizes will be further investigated.

2. An atomistic based finite bond element model

A single-walled carbon nanotube can be viewed as a hollow cylinder rolled from a graphene sheet, composed of carbon hexagons. The diameter of the nanotube can be calculated as $d = \left(\sqrt{3}a/\pi\right)\sqrt{(n_1^2 + n_2^2 + n_1 n_2)}$, where $a = 0.142$ nm is the carbon–carbon bond length, and the pair of integers (n_1, n_2) represent its chirality, such as armchair $(n_1 = n_2)$ and zigzag $(n_2 = 0)$ nanotubes.

The modified Morse potential function [23], which correlates to the Brenner potential function for strains below 10%, is used in the present study. The new term, $E_{torsion}$, has been added to include the bond energy in relation to bond twisting $\Delta\phi$. This term can be neglected for perfect nanotubes, but may be more significant in the case of defective tubes. This term was excluded in previous studies [20,24–27]. The energy potential function is given below:

$$E = E_{stretch} + E_{angle} + E_{torsion} \tag{1}$$

where $E_{stretch}$ is the bond energy due to bond stretch Δr, and E_{angle} is the bond energy due to bond angle variation $\Delta\theta$, and

$$E_{torsion} = \frac{1}{2}k_\phi(\Delta\phi)^2 \tag{2}$$

The parameters associated with the terms $E_{stretch}$ and E_{angle} are given in Refs. [24,25]. The force constant in Eq. (2) is taken as $k_\phi = 0.278$ nN nm/rad^2. [19,35,36].

It should be noted that the interaction between bond stretch, bond angle variation and bond twisting has been neglected in this nonlinear problem. The Brenner potential will be employed in our future work to evaluate the effect of such interaction. The effect of van der Waals interaction and the electrostatic interaction have also been neglected because they contribute much less than the covalent bond energies in the covalent systems as indicated in Ref. [20].

The stretch force, the angle-variation moment and the torsional moment can be obtained from differentiations of Eq. (1) as functions of bond stretch, bond angle variation and torsion angle variation, respectively:

$$F(\Delta r) = 2\beta D_e(1 - e^{-\beta\,\Delta r})e^{-\beta\,\Delta r} \tag{3}$$

$$M(\Delta\theta) = k_\theta\,\Delta\theta[1 + 3k_{sextic}(\Delta\theta)^4] \tag{4}$$

$$M_\phi(\Delta\phi) = k_\phi\ \Delta\phi \tag{5}$$

A constant bond torsional stiffness is implied by Eq. (5). The stretch stiffness and the angle-variation stiffness can be further obtained from differentiations of Eqs. ((3) and (4)) as functions of bond stretch and bond angle variation, respectively:

$$k_r(\Delta r) = 2\beta D_e^2(1 - 2e^{-\beta\,\Delta r})e^{-\beta\,\Delta r} \tag{6}$$

$$k(\Delta\theta) = k_\theta\left[1 + 15k_{sextic}(\Delta\theta)^4\right] \tag{7}$$

The effective "stick–spiral" model has been used to simulate the mechanics of defect-free SWCNTs based on a unit cell method [24]. The model uses Eq. (3) to simulate the stick, which is a force–strain relationship of a carbon–carbon (C–C) bond. It is assumed that the stick has finite torsional stiffness and infinite bending stiffness. To include the torsional stiffness term of the stick, Eq. (5) is used. Eq. (4) models the spiral spring behavior of the tube, which is angle bending moment that results from a change in bond angle.

A defective nanotube cannot be modeled with the unit cell approach because it lacks local symmetry. To effectively model the response of a defective nanotube, a molecular mechanics or finite element type model is needed. In this paper, a finite element model based on the "stick–spiral" method is developed.

In a typical finite element type model [19], beam elements have section stretch stiffness, flexural rigidity, and torsional stiffness, which amounts to 12 degrees of freedom (DOF). In the present model, we assume that bond element has an infinite bending stiffness with finite bending stiffness at the end joints, essentially the 'stick' and 'spiral'. The beam element will represent the C–C bond in this model with stretching, angle change, and bond torsion, and has a total of 8 DOF as shown in Fig. 1. This element can be stretched and twisted along its axis and bent by displacement without bond angle changes. The bond angle variation of the bond element can be associated with the relative transverse displacement (e) between the two ends as $d\theta = e/a$ (Fig. 1c). The present approach, designated the finite bond element model, is expected to give the same solution as the "stick–spiral" model [20,24] for defect-free CNTs. The models with infinite bending stiffness [20,24,25] represent the true physical deformation modes and are able to predict both in-plane stiffness (Young' modulus) and Poisson's ratio of CNTs accurately.

For the bond element defined in Fig. 1 in a three-dimensional space, the elemental equilibrium equation can be established for every bond element. The final system of equations with appropriate boundary conditions imposed can be solved by the displacement-control Newton–Raphson method. A MATLAB program has been written based on the finite bond element method for SWCNTs subjected to tensile loadings.

It has been verified [25] that the calculations based on our FE-based finite bond element model are giving the same results as those obtained from the analytical model [24] for defect-free CNTs.

3. Progressive failure analysis of defective graphene sheets and SWCNTs

3.1. Stone–Wales defect formation

Various types of defects exist in CNTs, such as vacancies and topological defects (e.g. 5-7-7-5). The Stone–Wales 5-7-7-5 defect involves the 90° rotation of a carbon bond with a new configuration as shown in Fig. 2. The effect of the SW defect on the configuration is believed to be local and limited to atoms in the neighborhood of the defect. Atoms far away from the defect undergo uniform deformation and their geometric configurations are the same as the defect-free tubes. It should be noted that the CNT's in the reference self-equilibrium configuration were assumed to have zero stress in our simulations as did in all referenced papers based on MM and/or MD [17–20,23,24,37]. For atoms near the defect, an interaction (similar to contact) mechanics concept is used to determine their initial equilibrium positions, which is possible by treating the defect formation as the result of interaction between