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Bending Properties of Carbon Nanotubes with Multiple Vacancy Defects using Atomistic Simulations

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Abstract: The effects of initial vacancy defects on the bending behavior of single walled carbon nanotubes are studied using molecular dynamics simulations. Vacancy defects are modeled by randomly removing atoms from the carbon nanotube structure. Carbon nanotubes with different vacancy defect densities are studied to find the effect of defect density on bending properties. A drop in bending modulus is found with the increase of defect density and there is no clear trend observed in critical bending angle.

Keywords: *Carbon Nanotubes, Bending, Defects, Molecular dynamics*

1. INTRODUCTION

The potential applications of carbon nanotubes (CNTs) as highly stiff and ultra strong constituents of nanotube based devices and materials have made them the focus of the research community. CNTs exhibit exceptional mechanical properties due to their seamless cylindrical graphitic structures. Topological defects such as Stone-Wales defects and vacancies are commonly present on the nanotube [1].The manufacturing process itself may introduce the defects; defects may also occur while manipulating with the tips of positioning instruments. These defects alter the electronic[2, 3] and thermal [4] properties and certainly decrease the mechanical properties [5-7] of CNTs. To realize the potential of carbon nanotubes for structural applications at nanoscale, a clear understanding of the effect of these defects on the mechanical behavior of CNTs is essential.

With the difficulty and expense of laboratory experiments at small scales, atomistic simulations provide an easier alternative to study the processes and behaviors of systems at nanoscale.

The effects of defects on tensile properties of SWCNTs were studied by Lu and Bhattacharya [5] who found that as the average number of defects increase, the stiffness, ultimate strength and ultimate strain decreases. They also found that for a given number of defects zigzag configuration has less strength. Hao et al. [6], studied the buckling properties of single as well as double walled carbon nanotubes (SWNTs and DWNTs) under compressive loading using MD and found that single vacancy defect greatly reduce the critical buckling load and buckling strain of CNTs and slightly reduce the elastic modulus of the nanotube. They also noticed that the buckling properties of smaller nanotubes are more sensitive to vacancy defect than those of comparatively larger tubes, this is because of, as the tube diameter decrease the density of missing interactions becomes larger. The effect of vacancy defects on the fracture of CNTs under axial tension was studied by Mielke et al.,[8] using molecular mechanics with Tersoff-Brenner potential, and using DFT, and semi empirical methods. They observed a reduction of failure stresses by 26% and a considerable drop in failure strains.

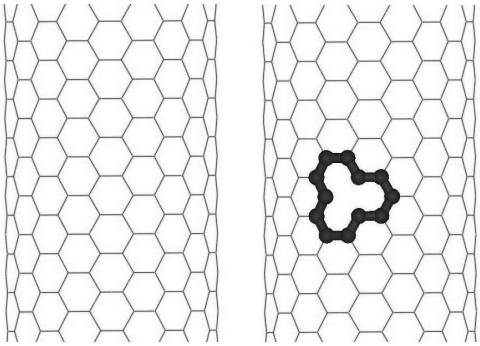

Fig.1. Illustrating the atomic configurations of a vacancy defect on (10,10) CNT.

Many other researchers attempted to study the effect of defects on mechanical properties of CNTs in either tensile or compressive loadings. In this work, MD simulations have been carried out to study the effect of vacancy defects on bending properties of single walled CNTs in simply supported configuration.

2. SIMULATION DETAILS

MD simulations were carried out in this work using the modified Morse potential, which has been extensively used to describe the short range interactions among carbon atoms, e.g., to simulate the CNT fracture under tensile loading[9], to evaluate mechanical properties[10], to find the stiffness and strength[11]. This specific potential has been also applied to study the effect of defects on mechanical properties of CNTs[5, 7].

For the modified Morse type force field, the potential energy for a system of atoms can be written as

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

$$E_{stretch} = D_e \left\{ 1 - \left[e^{-\beta(r-r_0)} \right]^2 - 1 \right\}, \tag{2}$$

$$E_{angle} = \tfrac{1}{2} k_\theta (\theta - \theta_0)^2 \left[1 + k_{sextic} (\theta - \theta_0)^4 \right], \tag{3}$$

where $E_{stretch}$ is the bond energy due to bond stretching, E_{angle} is the bond energy due to angle-bending, r ,theta are the bond length and bond angle respectively. The parameters used in the potential are[9]

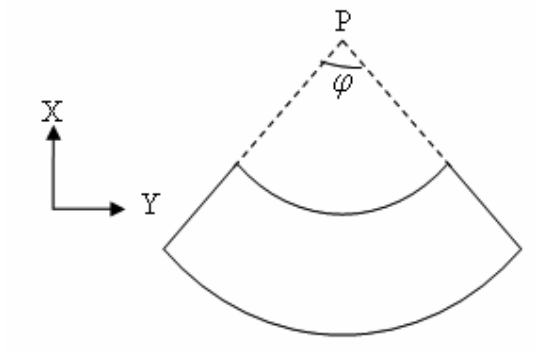

Fig.2. Sketch of bent carbon nanotube with bending angle φ.

$r_0 = 1.421 \times 10^{-10} m, \quad D_e = 6.03105 \times 10^{-19} N \quad m,$

$\beta = 2.625 \times 10^{10} m^{-1}, \quad \theta_0 = 2.094 \quad rad,$

$k_\theta = 0.9 \times 10^{-18} N \quad m/rad^2, \quad k_{sextic} = 0.754 \quad rad^{-4}.$

Velocity Verlet integration scheme is used to solve Newton's equations of motion and a time step of 1 fs is used in all the simulations. To avoid the effect of thermal fluctuations, the system was maintained at a low temperature of 0.01 K using Berendsen thermostat scheme[12].

The (10,10) SWNT of 9.7 nm in length is adopted for this study. Fig.1 represents the atomic configuration of a vacancy defect on a (10,10) SWNT. Removing an atom from the CNT's hexagonal bonding network resembles a vacancy defect. Locations are chosen randomly on the surface of CNT to create vacancy defects. Effect of multiple vacancy defects with various densities on the (10,10) tube is also studied. To model the multiple vacancies, vacancy defects were modeled on the CNT by randomly removing some carbon atoms. A range of interdefect distances i.e., 2.9-75.5 nm were reported experimentally[13] for the study of tuning of conductance of CNTs by ion irradiation, and observed that irradiation time is the key parameter which defines the average interdefect distance. Here we have maintained 7 angstroms as the minimum radial distance between any two randomly created vacancies. Starting from 0.5%, up to 2 % of total atoms were removed in steps of 0.5 % to create the vacancy defects.

Bending deformation has been carried out by displacing the atoms of the both end rings with a steady increment of bending angle, by applying a

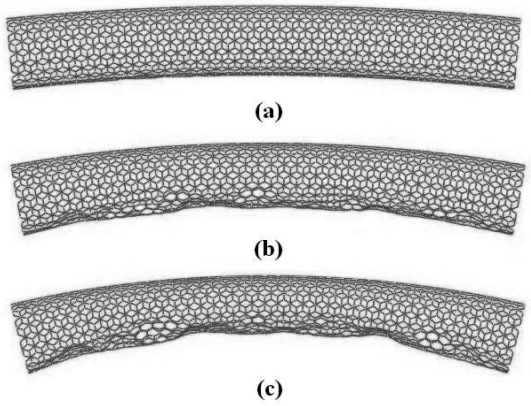

Fig.3. Snap shots of the (10,10) perfect CNT in bending at the bending angles of (a) 0.210, (b) 0.407 and (c) 0.582 rad.

global curvature of 10^{-5} nm^{-1} until an end curvature of 0.05 nm^{-1} is reached. Figure 2 describes about the bending angle. After each increment of bending angle the whole system is relaxed for 1000 steps by constraining the end ring atoms. Initially the whole system was equilibrated for 50 ps.

3. RESULTS AND DISCUSSIONS

Bending of the prefect (10,10) CNT along with the 4 cases with different densities of vacancy defects is simulated to elucidate the effect of defect density on the bending properties of CNT.

Fig.3. show the snapshots of the (10,10) perfect CNT while loading process. Fig.3.(a)-(c) shows the configurations of perfect CNT at the critical bending angle 0.210 rad, at an angle of 0.407 rad which is higher than the critical bending angle and at an angle 0.582 rad which is at the end of bending respectively. Configurations of initial and bent CNTs (with a bend angle of 0.582 rad) of 0.5%, 1.0%, 1.5%, and 2.0% defect densities are presented respectively in Fig.4 (a)-(d).

Figure 5 shows the plot of strain energy (SE) per atom versus the bend angle. SE is the difference between total energy of strained and unstrained carbon nanotube, and the bend angle is defined as the included angle between the tangents at the two ends of the bending tube drawn normal to the neutral axis. The bent CNT with a bending angle of φ is shown in Fig.2. The quadratic dependence of SE on the bending angle until the initial local buckle

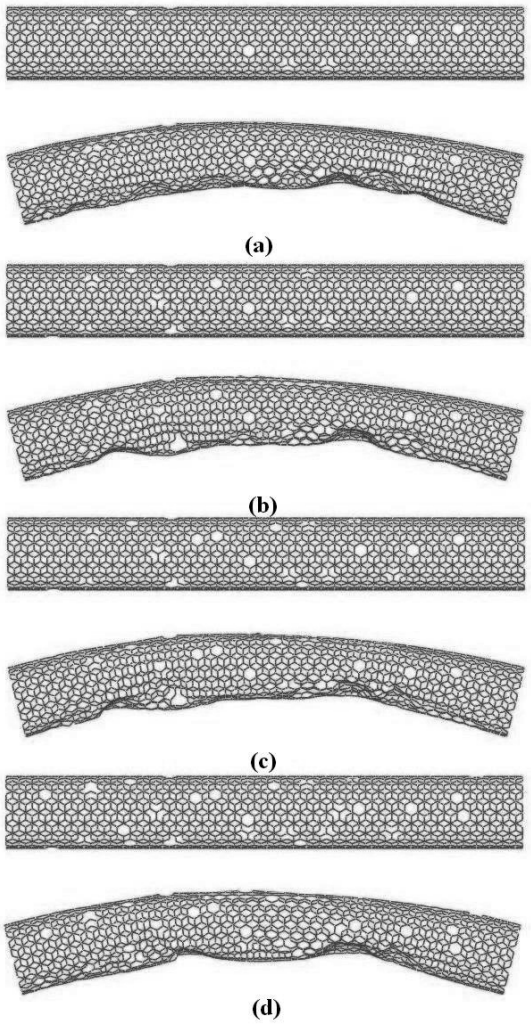

Fig.4. Initial and bent configurations of (10,10) CNTs with random vacancy defects of different densities. (a) 0.5% (b) 1.0% (c) 1.5% (d) 2.0%.

of CNT (identified by a sudden change of slope) is clear from Fig.5. This trend is qualitatively similar to that of Iijima, et al.,[14] and Yakobson, et al [15]. From Fig.5 it can be seen that the critical buckling angle for perfect CNT is about 0.2 rad and the strain energy trends for all the studied cases with different vacancy densities are also presented.

Buckling location for the perfect CNT is almost at the middle of the tube. For the defective tube, the initial defects control the buckling locations which occur in the vicinity of a vacancy defect.

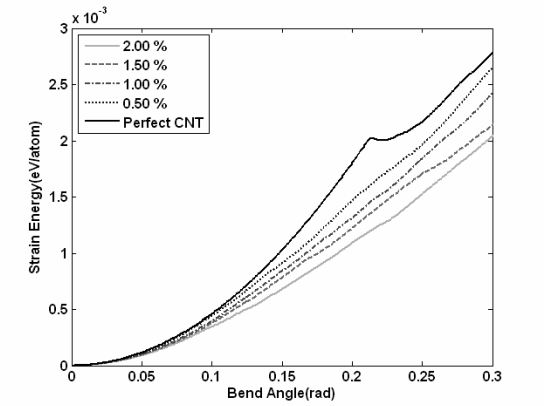

Fig.5. Strain energy versus bending angle for (10,10) CNT at various vacancy densities. Perfect (10,10) CNT is also presented for comparison.

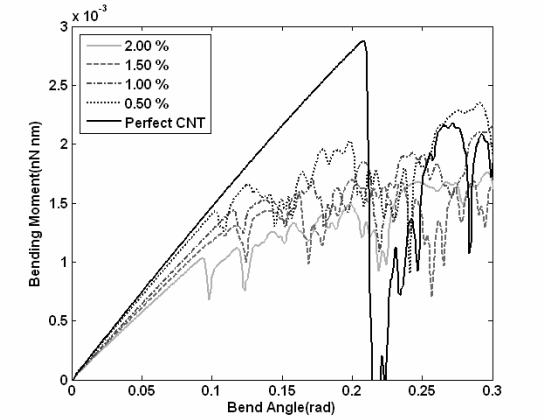

Fig.6. Bending moment versus bending angle for (10,10) CNT at various vacancy densities. Perfect (10,10) CNT is also presented for comparison.

The bending moment can be computed from the SE, U, using the following relations:

$$M = \frac{\partial U}{\partial k}\frac{1}{L} = \frac{\partial U}{\partial \varphi} \quad (4)$$

$$k = \frac{\varphi}{L} \quad (5)$$

where M is bending moment, and φ is the bending angle. k is the principal curvature which is constant through out the length, L, of the tube as the bending is applied by opposing couples on two ends of the simply supported tube.

Bending moment versus bend angle is plotted in Fig.6 for all the cases to observe the initial buckle with clarity. Critical buckling angle for all the cases of defects is smaller than the perfect CNT which indicates multiple vacancy defects weaken the CNT considerably, but there is no clear trend of critical buckling angle with the increase of density of defects. It indicates the need of statistical study to evaluate the trend of critical buckling angle for a CNT under bending having with a randomly initiated multiple defects. It can be seen that from the Fig.6 as the defect density increases the bending modulus (initial slope of M – φ curve) decreases because the tube gets weaker.

4. CONCLUSIONS

In summary, we have investigated the bending behavior of CNTs with initial vacancy defects using molecular dynamics simulations. Multiple vacancies are randomly located on CNT surface at different densities to study the effect of defect density on the bending properties. With the increase of defect density, a linear decrease in bending modulus is observed but the critical bending angle does not show a clear trend.

We found that the multiple vacancy defects affect the CNT bending behavior. The results of this study emphasizes that there is a need of further studies of effect of different kinds of defects on bending properties of CNTs.

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