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Effect of Multiple Stone-Wales and Vacancy Defects on the Mechanical Behavior of Carbon Nanotubes Using Molecular Dynamics

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Abstract

Carbon nanotubes (CNT) without any defects possess high mechanical properties. However, CNTs suffer from defects which may occur because of production inabilities, purification or be deliberately introduced by irradiation with energetic particles or by chemical treatment. In this study, mechanical properties of defective single-walled carbon nanotubes (SWCNTs) are studied. Two types of defects i.e. Stone-Wales (S-W) and Vacancy with different defect densities are considered in the present investigation. Molecular dynamics (MD) simulations are implemented to study the mechanical properties like Young's modulus, stress, and strain of armchair SWCNTs with an increasing number of S-W and vacancy defects, by varying their relative position and orientation. In the present work, calculations of fundamental mechanical properties of SWCNTs are performed using the MD simulation software Material Studio Presence of one and four vacancy defects; reduces on an average the tensile strength of CNT by 22.61% and 24.42% respectively, and tensile failure strain by 34.17% and 16.74%, respectively for different diameters. However, in case of Stone-Wales defect this reduction in strength (and strain) is only 11.33% (28.88%) and 13.16% (26.70%) for one and four defects, respectively. It can be concluded that for the same defect densities, vacancy defect deteriorates the tensile strength of nanotubes much more since such type of defect creates hole or void in the nanotubes at which the failure of the nanotubes can easily start.

Keywords: Carbon nanotubes; Mechanical properties; Molecular dynamics; Stone-Wales defect; Vacancy defects.

1. Introduction

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Carbon nanotubes (CNTs) have attracted deep research interest due to their unique properties such as high stiffness against bending and high tensile strength [1]. Using CNTs as a reinforcement material to enhance the mechanical properties of composite materials has been pursued extensively in both experimental and theoretical studies. Defective CNTs play vital role in decreasing the mechanical strength of the composites and S-W as well as Vacancy defects have received considerable attention. Using CNTs as reinforcing agents to design and fabricate strong composites with desirable mechanical properties needs thorough understanding of the mechanical behaviour of such nanotubes. In recent years, mechanical, thermal and electrical properties have spurred considerable interest among researchers [2, 3] Computer simulations are increasingly used to guide experimentalists in interpreting the results and even to reduce some of the laboratory tests. However, as with any other man-made products, CNTs were also found to be susceptible to defects. Belytschko *et al.* [4] used molecular mechanics approach on Morse and Brenner potentials to study the fracture of a CNT. They observed that even a single missing atom can reduce its strength by about 25%. Zhang *et al.* [5] investigated the effects of one and two atomic vacancy defects, slits and holes on the fracture of SWCNTs, double-walled CNTs (DWCNTs) and triple-walled CNTs (TWCNTs) using atomistic simulation and multi-scale methods.

Several studies have been conducted to explore the effect of S-W defects on the tensile properties and fracture of CNTs. Tserpes and Papanikos [6] studied the S-W effect on tensile behavior of SWCNTs and predicted a significant reduction in failure stress and failure strain; ranging from 18 to 25% and 30 to 41 % respectively. Chandra *et al.* [7] adapted three different stress measures at atomic scales and introduced strain measures as energetically conjugate quantities to study the local properties of S-W defects in SWCNTs under axial tension. The study involved the consideration of one S-W defect in various SWCNTs with different diameters. It was found that stiffness of defects reduces by about 30-50% and is dependent on a number of factors such as chirality, diameter of nanotubes and the loading conditions. The defects considered by Troya *et al.* [8] were: one S-W defect, an aggregation of two S-W defects and an aggregation of five S-W defects. The reduction has been observed in failure strain, which ranges from 6.3 to 53.5% according to the method of calculations. Several groups have theoretically predicted that the mechanical properties of a CNT, such as its Young's modulus, were insensitive to helicity under small strains [9].

In this paper, atomistic computer simulation is used to understand the role of defects and defect density on mechanical properties (i.e., Young's modulus, failure strength and failure strain) of single-walled nanotubes (SWCNTs) subjected to tensile and compressive loads. Two types of defects-S-W and vacancy with different defect densities are considered in this study. From our simulation results, stress-strain curve of defective SWCNTs is compared with that of pristine SWCNTs. Failure stress and failure strain of defective SWCNTs under tensile and compressive loads are also compared with those of pristine SWCNTs for different diameters.

2. Defect Formation

Defects in CNTs introduced either during the synthesis process or are stress induced ones, may be divided into the following three categories:

- incomplete bonding and other defects, such as impurity attachments, substitutions and vacancies,
- topological defects, such as the SW transformation, and
- rehybridization defects, which refer to the change from sp^2 to sp^3 of a C-C bond due to highly localized deformation.

To create an S-W defect, four neighbouring hexagons are converted into two pentagons and two heptagons with a 90° rotation of the horizontal bond of the hexagonal structure as shown in fig. 1**.** In case of single S-W defect, the defect is placed at the middle of the CNT structure whereas in case of four S-W

defects are placed at equal distance from the middle defect. The orientation of all four S-W defects is along the same vertical line.

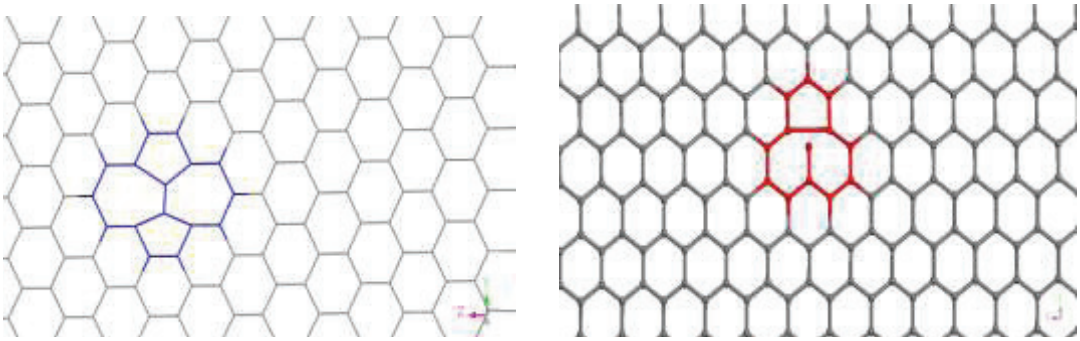

Fig.1. Computer constructed modelling of 1 S-W and 1 vacancy defect

To create a vacancy defect, carbon atoms are removed from the perfect hexagonal structure of the CNTs creating a vacancy at the place of missing atom as shown in fig. 1. Like S-W defect, in case of 1 vacancy defect the defect is placed at the middle of the CNT structure whereas in case of 4 vacancy defects the other two defects are placed at equal distance from the defect at the middle. The orientation of all four vacancy defects are also along the same vertical line.

3. MD Simulations

Constant temperature (NVT ensemble) and constant number of particles, constant pressure, and constant temperature (NPT ensemble) both were used to apply the dynamics on to the CNTs. The COMPASS (Condensed-phase optimized molecular potentials for atomistic simulations studies) force field was used for these calculations. The simulation in each case was performed with an interval of 1 femto second (fs) with total time of 50 pico seconds. In each case and the dynamic atom configurations were saved as trajectories every 10 frames.

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4. Tensile and Compressive Test Procedure

The structure of CNT is identified by using the nomenclature (n, m) [10]. The accuracy of MD simulation models has been increased by applying periodic boundary conditions. Periodic and super cells for different SWCNTs (Pristine along with 1 and 4 Vacancy and S-W defects) are built by using the Material Studio software 5.0 [11]. By applying the periodic boundary conditions, the effect of bulk environment can be created within this unit configuration, which improves the accuracy of MD simulation. A super cell is built with 10 repeated units in the Z-direction to achieve a length of SWCNT equal to 42.59Å and diameter equal to 3.92Å (i.e. aspect ratio of 10.87). The major reason of making the super cell in the Z- direction is to identify the elastic modulus in the axial direction of the nanotube from elastic constant matrix.

The lattice parameters have been assigned with all the angles as 90 deg. to achieve a periodic box around the CNT. The lattice size has been assigned in terms of a=23.628, b=23.628 and c=24.595 in x, y and z directions respectively. Once the lattice parameters have been set, the potential as well as the non-bond energy is minimized to get a stabilized structure. Discover program along with Steepest Descent algorithm have been used to achieve the energy minimization of CNTs. 5,000 numbers of iterations along

with convergence rate of 0.1 kcal/mol/Å have been used to perform this minimization. During the equilibration period, end atoms are kept fixed in a plane as shown in fig. 2. The stress is calculated by

$$\sigma = \frac{F}{S} \quad (1)$$

Here, the axial force $F=F_1–F_0$, where F_0 is the total inter-atomic force of the atoms of two extreme rings of one end at zero strain, and F_1 is the total inter atomic force of these atoms at the corresponding strain. Cross-sectional area $S= \pi dh$, where d is the diameter and h is the thickness of the CNT. Here, h= 0.34 nm is used.

$$\varepsilon = \frac{X_1 - X_2}{X_1} \quad (2)$$

Where ε is the axial strain, X_2 is the initial length and X_1 is the current length of the CNT.

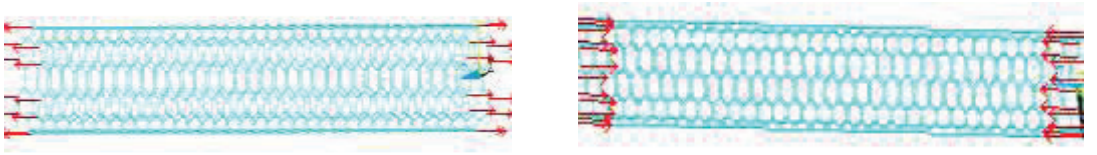

Fig.2. Atomistic model for tensile and compressive tests

5. Results and Discussions

To examine the effect of defects on the mechanical properties of nanotubes, tensile and compressive tests on (6, 6), (8, 8), (10, 10) and (12, 12) nanotubes are conducted using MD simulation. Simultaneous existence of vacancy and S-W defects in the nanotubes should affect each other. However, to investigate the effect of vacancy and S-W defects along with their densities only one type of defect is considered at a time.

The obtained Young's modulus of pristine (6, 6), (8, 8), (9, 9) and (10, 10) SWCNTs are 0.98 TPa, 0.91 TPa, 0.87 TPa, and 0.76 TPa, respectively. These values are approximately 1 TPa and are close to each other, which agree with the results obtained by MD simulation [12], by molecular structure mechanics model [13], from ab-initio computation [14], and from experiments using TEM [15], and AFM [16]. It can be concluded from these moduli values that SWCNTs with larger radii have slightly higher values of Young's modulus in comparison with SWCNTs of the same chirality but of smaller radii. These trends are similar to those described by Gianno *et al*. [17].

5.1 Tensile Test of SWCNTs

The stress-strain curves of pristine SWCNT along with defective SWCNT are shown in Figs. 3 and 4 for vacancy and S-W defects, respectively. It is seen from these figures that the defective structure behaves in a similar manner as pristine structure. From the stress-strain curves it seems that Young's modulus does not significantly change for defective SWCNTs. But failure strength and failure strain change due to the presence of defects in the nanotubes. For a particular type of defect, failure strength is almost same for one and four defects but failure strain increases with an increase of defect density (i.e. number of defects). Failure stress does not decrease with the increase of defect density because whatever the number of defects, stress concentration occurs at a specific single defect site from where fracture of the nanotube starts. The increase of vacancy or S-W defects slope of the stress-strain curve at higher strain decreases behaving like softer materials which indicates lower stiffness or strain hardening at relatively larger deformation. The trend of variation of the tensile failure strength and strain are the same for different diameters nanotubes (Figs. 3 and 4). With the presence of one and four vacancy defects, tensile strength of the nanotube reduces by 22.61% and 24.42% on an average, respectively, and tensile

failure strain reduces by 34.17% and 16.74% on an average, respectively for different diameters. However, in case of S-W defect this reduction in strength (strain) is only 11.33% (28.28%) and 13.16% (26.70%) for one and three defects, respectively. The results are in good agreement with L. Chen *et al.* and R.Khare *et al.* (Table 1). It is seen that for the same defect density, vacancy defect deteriorates the tensile strength of nanotubes much more since such type of defect creates a hole or void in the nanotubes at which failure of the tubes can easily start.

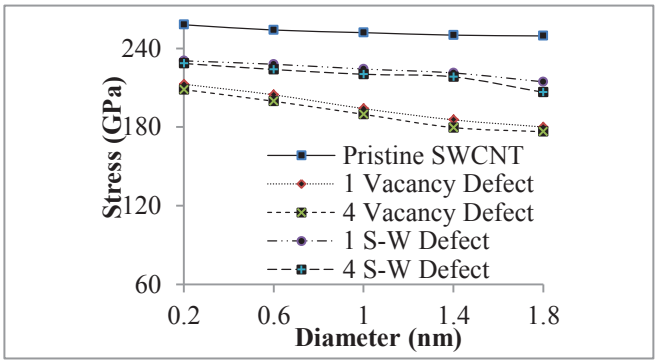

Fig.3. Tensile strength of different pristine and defective SWCNTs

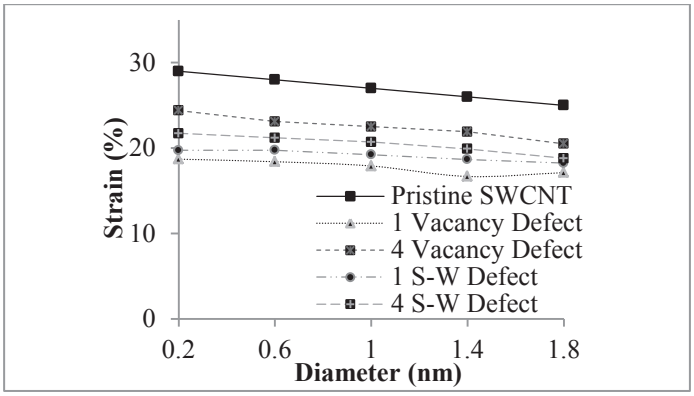

Fig.4. Tensile strain of different pristine and defective SWCNTs

Table 1. A comparison between our results and other results

CNT Type	Young' Modulus (TPa)			
	Ref. 18	This work	Ref.19	Ref. 20 (Y.M *and C.M*)
Pristine	1.033	0.928	1.02	1.04
Tube with one vacancy (Ref.18)	1.002	0.901	0.829	------
Tube with two vacancy	0.983	------	-------	-------
Four vacancy defects	------	0.783	-------	------
One S-W defect	------	0.896	0.785	0.792 and 1.198

* Y.M and C.M are Young's modulus and Compressive modulus respectively.

5.2 Compressive Test of SWCNTs

The stress-strain behaviour of pristine and defective nanotubes in compressive load is the same as that obtained in tensile load. Fig. 5 shows the comparison of compressive strength of pristine and defective nanotubes with vacancy and Stone-Wales defects for different diameters. The presence of vacancy defects reduces the compressive strength of the nanotube by 31.51% and 34.49% on an average for one and four defects, respectively while the presence of Stone-Wales defects by 28.19% and 26.25% on an average for one and three defects, respectively. The variations of compressive failure strains of pristine and defective nanotubes are depicted in fig. 6. It is seen that failure strain also increases with the increase of defect density in compressive load.

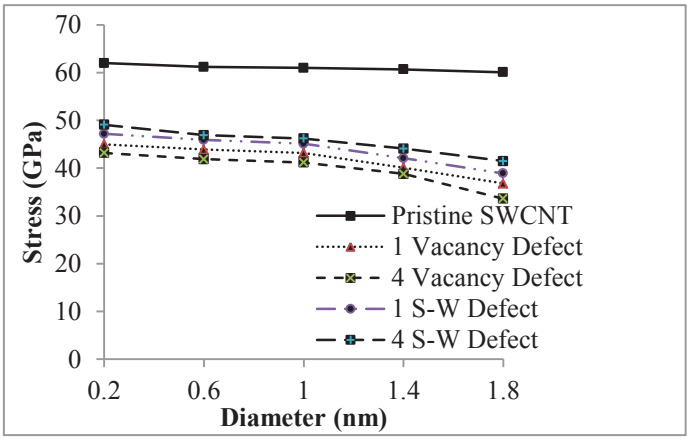

Fig.5. Compressive strengths of different pristine and defected SWCNTs

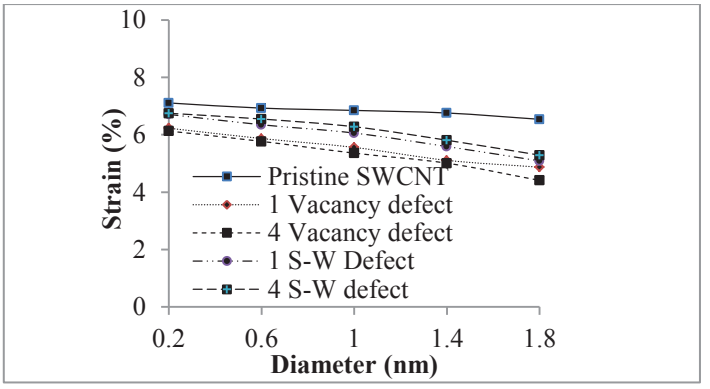

Fig.6 Compressive strains of different pristine and defected SWCNTs

6. Conclusions

In this paper, we carried out MD simulation of pristine and defective SWCNTs under axial tensile and compressive loads. Two types of defects, vacancy and Stone-Wales are considered here. From simulations, the stress- strain relationship to describe the elastic and plastic behaviours of SWCNTs with defects are obtained and compared with that of pristine SWCNTs. From the simulation results, the following conclusions are drawn:

- A gradual degradation of strength is observed with increasing diameter and the number of defects of armchair CNTs, as the defects creates a hole or void in the nanotubes at which failure of the tubes can easily start.
- Failure strain increases with the increase of defect density.
- For the same defect density, vacancy defect deteriorates nanotubes strength much more compared to Stone-Wales defect.

The above nanoscopic phenomena will also be true in microscopic and macroscopic structures though in these cases the defects will be in respective sizes. Vacancy defects in nanotube will resemble the voids or cavities in the microscopic and macroscopic structures whereas Stone-Wales defects will resemble the local geometric imperfection

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