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CARBON NANOTUBES WITH VACANCY DEFECTS AND THEIR MECHANICAL PROPERTIES

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ABSTRACT

Carbon nanotubes (CNTs) offer very high mechanical properties with huge scatter in amount. The scatter in properties is believed to occur mainly due to the defects originated inherently during production. The tensile behavior of SWNTs having two vacancy defects positioned next to each other were simulated in this study to investigate the influence of spatial arrangement of defects on the mechanical properties. The simulations were performed using classical molecular dynamics (MD) in atomic scale. Two neighboring vacancy defects reduced the failure strength as much as 45% and the failure strain as much as 80% in comparison with those of pristine SWNT. SWNTs having two defects in the loading (axial) direction showed higher failure strength than SWNTs with defects perpendicular to the loading direction. In general, the closer the defects, the weaker the SWNTs. The defect arrangement in the SWNT structure is one of the key factors in determining its mechanical properties as well as the population of defects.

Keywords: Carbon Nanotubes, Neighboring Defects, Vacancy Defects, Mechanical Properties.

1. INTRODUCTION

Carbon nanotubes (CNTs) consisting of a single carbon layer or multiple coaxial carbon layers seemingly are ideal perfect structures [1] with ultra high strength, high electrical and thermal conductivity etc. [2, 3]. However there are many defects when the nanotubes are prepared in the practical process [4-7]. The defects including vacancy of atoms, holes, Stone-Wales defects, even line defects etc. [8-10] create heterogeneous structures which harm the symmetry of the carbon layer, hence reduce its mechanical and electrical properties, and in consequence, seriously influence their potential application such as nanoelectronics, nanoelectro-mechanical systems (NEMS) and nanocomposites [11-13].

Theoretically it is known that carbon nanotubes (CNTs) have high tensile modulus around 1 TPa and tensile strength around 300 GPa [14, 15]. On the other hand, using molecular dynamic simulations based on empirical interatomic potential for carbon Yakobson et al. [16] suggested that the breaking strain of CNTs could be as large as 55%. In this context, some experimental results are worth noting [17-20]. In all the cases, carbon nanotubes were considered as cylindrical tube having wall thickness of 3.4 Å, and the wall cross section was taken as the area to calculate properties. Two sets of measurements [17, 18] have been reported for the fracture of ropes of single-walled CNTs (SWCNTs), and the observed maximum failure strains were less than 6%,

tensile strengths were between 13 and 52 GPa and Young's modulus ranged from 0.32 to 1.47 TPa. Demczyk et al. [19] reported results for the fracture of single multi-walled CNT (MWCNTs) that contained 1-5% boron, which indicated a modulus of 0.91 TPa, a failure strain of 4-7% and a failure stress of 150±45 GPa. The most extensive set of CNTs fracture measurements was reported by Yu et al. [20] and consisted of data for 19 MWCNTs placed under tensile load. The observed failure strains ranged from 2 to 13%, the Young's modulus ranged from 0.27 to 0.95 TPa, and the failure stress ranged from 11 to 63 GPa with an average value of 28 GPa. Another study reported that MWCNTs with outer diameter in the range of 12 to 30 nm possessed Young's modulus in the range of 0.1 to 1.6 TPa [21]. Such observations conflicted with the theoretical and numerical analysis outcomes of [14-16].

However this conflict between the theoretical and experimental results can be explained by existence of defects in CNTs structures. Defects in CNTs can arise from various causes. Topological defects can be defined as the presence of rings other than regular hexagons and mainly as Stone-Wales (pentagon-heptagon) defects [22, 23]. Incomplete bonding defects like vacancies, very often in the structure, are caused due to the exposure of high temperature for long time during manufacture, the impact with high energy electrons in the transmission electron microscopy environment and the damage resulted from harsh oxidative purification process [24].

Effect of Stone-Wales defects on the mechanical properties and their nucleation under loading as well as degradation of load carrying capacity in the defected zone has been reported in [23]. Recently the effect of random distribution of Stone-Wales defects on the mechanical properties has been reported in [25, 26] where mean value of the stiffness, strength and ultimate strain are found to decrease as the average number of defect increases. On the other hand, one or two-atom vacancy defects, which are naturally expected to occur during most synthetic schemes and other processes, are observed [27, 28] to reduce failure stresses of CNTs by as much as 26% and to reduce the expected failure strains by as much as factor of two. These reductions are much larger than those caused by Stone-Wales defects reported in [23, 25 and 26].

Though degradation in properties of CNTs was observed due to the presence of one or more vacancy defects in the structure, the reason for the scatter in properties found in the measurement is still unanswered. In exploration of this answer we focus on the spatial arrangement of neighboring two vacancy defects. Particularly, the understanding of interference between two defects will be the first step toward the characterization of the strength of defected CNT structure in case that the global failure is determined by a local bond breakage between two defects. Through the technique of MD simulation in atomic scale, we investigate the effect of spatial arrangements of two defects in CNT such as relative distance between defects and their local orientations on mechanical properties such as failure strength, failure strain and Young's modulus.

2. MODELING OF VACANCY DEFECT

In this paper, we employed a (10, 10) armchair SWNT of length 36.65 Å in all the simulations. A one-atom vacancy defect was modeled by taking out an atom and then reconstructing bonds as shown in Fig. 1. If a single atom is removed from an armchair tube, a 12-membered ring exists (Fig. 1(b)). Such a ring can be reconstructed to a pentagon and an enneagon as shown in Fig. 1(c). The reconstructed configuration can be symmetric or asymmetric according to perpendicular to the loading (axial) direction.

3. MD SIMULATION

MD simulation provides the possibility of determining the basic mechanical properties and failure of small-scale structure such as carbon nanotubes that are difficult and laborious to access in the laboratory. Stress-strain relationship, elastic modulus, thermal expansion coefficient, glass transition temperature and density can be obtained from MD simulation. However, MD simulations are limited by the multiplicative combination of the number of atoms to be modeled and the amount of running time for the simulation.

In this study the Material Studio 4.0 was used to model the SWNT structure with defects and MD simulation was performed by LAMMPS [29]. LAMMPS was chosen
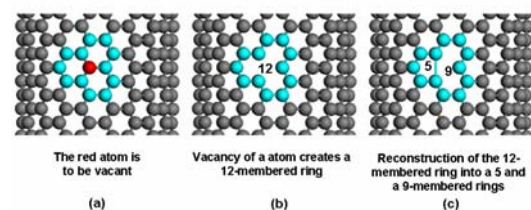

Fig 1: Modeling of vacancy defect.

because it is open source code and has the ability to work with large sets of atoms.

A single walled (10, 10) armchair nanotube of length 36.65 Å was considered. A (10, 10) armchair has a diameter of 13.65 Å and the model of nanotube had 600 atoms in total (when defect free). The distance between the neighboring carbon atoms in the CNT structure is 1.42 Å which is the C-C sp^2 bond length in equilibrium. The SWNT model was in a simulation cell box. Periodic boundary condition (PBC) was imposed to all the direction of the simulation box and CVFF (Consistent-Valence Forcefield) force field was used [29, 30]. The potential between pairs of atoms that are within a cutoff distance were defined by cut-off Lennard-Jones potential. The bond interactions between pairs of directly bonded atoms were defined by Morse potential. The parameters for Morse potential needed in the simulation were taken from [27]. A distance based criteria between the atoms was adopted to determine the failure such that the bonds between atoms are regarded as broken if the separation between atoms exceeds a critical distance and the very first bond breaking is taken as an indicator of global failure of the entire structure. The critical distance is considered as equivalent to the cutoff distance of potential energy functions. Based on the previous studies [24, 25, 31 and 32] we used 1.77 Å as a critical distance. To prove the adequacy of our potentials, we simulated a pristine as well as a single Stone-Wales defected (6, 6) armchair SWNT of length 49.2Å under 300K at 10^{10} s^{-1} loading rate, and compared the results with [25]. Considering the same definition of cross sectional area to
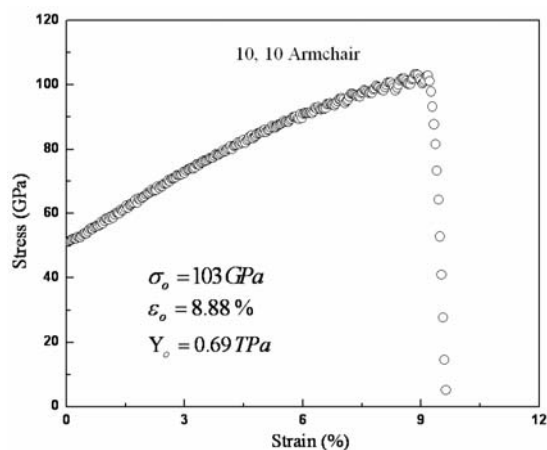

Fig 2: Stress-strain behavior of a pristine (10, 10) armchair SWNT.
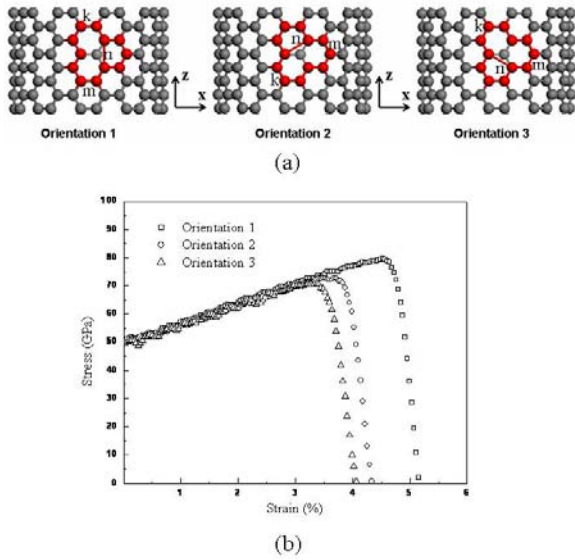
(a)

(b)

Fig 3: Stress-strain behavior of (10, 10) armchair SWNT with single one-atom vacancy defect (defect is in different possible orientation in each case as shown intact).

[25], we obtained the failure strength and failure strain as 101.14 GPa and 10.1% respectively which are close to 105.5 GPa and 12% respectively as found in [25]. Moreover in case of failure strength and failure strain of the SWNT with a single Stone-Wales defect, we found 85.1 GPa and 7.3% respectively which are close to the failure strength and failure strain of 89.7 GPa (with 13.8% variation from the mean value for random spatial distribution of defects in CNT) and 8.69% (33.91% variation from the mean) respectively. It is noted here that we always consider the defect in the middle of the nanotube in our simulation. In chapter 4, results of reduction in failure strength and failure strain of SWNT due to the vacancy defects are compared with [33] which also confirm the accuracy of the simulations of this study.

Prior to loading the initial configuration was relaxed to ensure that the system was in relative equilibrium. The constant temperature-constant pressure (NPT) ensemble was used to maintain a constant temperature, 300 K, and to allow the system volume to change so that the relaxed density is achieved at an external pressure of 1 atm. The relaxation was run for 50 ps with integration time step of 1.0 fs. Uniaxial tension behavior of CNTs was simulated to acquire the stress-strain relationship. For uniaxial tensile loading, the surface set of load direction of the simulation cell box was displaced at a specified strain rate of 10^{10} s^{-1} and the remaining sets of surfaces perpendicular to the load direction were set at constant ambient pressure of 1 atm for the duration of loading. Strain was derived from displacement of moving surface of the simulation cell box. Instead of averaging virial stress of all atoms, stress was calculated from the force component of the simulation cell box in loading direction.

4. DISCUSSION

Three mechanical properties were calculated from the simulated force and displacement time histories:
(1) The failure strength was calculated at the maximum point of the force-displacement curve, $\sigma_c = F_{max}/A$, where F_{max} is the maximum axial force and A is the wall cross section area, assuming the thickness of the tube wall is 0.34 nm;
(2) The failure strain, which corresponds to the failure strength, is calculated as $\varepsilon_c = \Delta L_u/L$, where ΔL_u is the maximum displacement of the moving surface of the simulation cell box and L is the original SWNT length;
(3) The Young's modulus was calculated as the initial slope of the stress-strain curve.

We started with simulating the tensile properties of a pristine (10, 10) armchair SWNT of length 36.65 Å and obtained the failure strength (σ_o), failure strain (ε_o) and Young's modulus (Y_o) as 103 GPa, 8.8% and 0.69 TPa respectively as shown in Fig. 2. It was done to present the results of the simulations of defected SWNTs of this study as normalized properties.

For the armchair SWNT considered in this study, the reconstructions of a one-atom vacancy defect can be of three types i.e. three orientations according to x axis (perpendicular to loading direction) as shown in Fig. 3. The reconstructions result in one symmetric configuration and two asymmetric configurations (Fig. 3(a)). We assume that the defect is present in the middle of the nanotube. Tensile stress-strain behaviors of SWNTs having single vacancy defect with different orientations in each are shown in Fig. 3(a). Presence of a single vacancy defect reduces the failure strength and failure strain of a SWNT as much as 32% and 72% respectively (orientation 3 in Fig. 3(b)). The SWNT with symmetric defect (Fig. 3(a)) is found to be stronger than the SWNT with asymmetric defects. When the SWNT with asymmetric defects are under tensile load, bonds k and m of the enneagon (orientation 2 and 3 indicated in Fig. 3(a)) become unstable and broken first. Then the crack propagates perpendicular to the loading direction of the SWNT until the SWNT is fractured. While in case of symmetric configuration (orientation 1 in Fig. 3(a)), bonds k and m are perpendicular to the loading direction (z axis) and the defect is also supported by the stronger dangling bond n which makes the SWNT stronger against the fracture than asymmetric configuration. It is instructive to relate our findings to the results of Yang M et al. [35] where the authors showed the reduction in failure strength caused by single one-atom vacancy defect in SWNT. For a single vacancy defect, the reduction in failure strength from our simulation is 23% (orientation 1 in Fig. 3(b)) while that in [33] is 25%. Though there are different orientations, during the reconstructions for a one-atom vacancy defect, we preferred the weakest (orientation 3 in Fig. 3) one for the rest of the calculations where appropriate to get the lower bound of mechanical properties.

A vacancy defect reduces the failure stresses of pristine SWNT (without defect) by as much as 26% and to reduce the expected failure strains by as much as a factor of two [26, 27]. We may expect that the presence of an additional adjacent vacancy defect in CNT structure will reduce the mechanical properties more
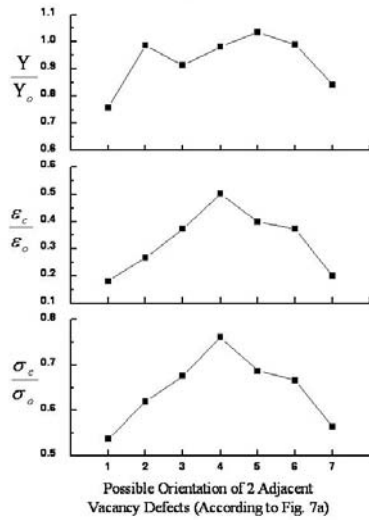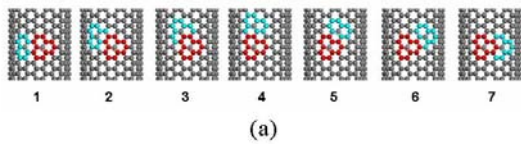
Fig 4: (a) Possible arrangements of two adjacent vacancy defects and (b) normalized mechanical properties for the SWNTs having defect arrangements shown in figure 4(a).

significantly. Seven possible arrangements of two adjacent defects are studied considering all the symmetric and asymmetric conditions with respect to axes as shown in Fig. 4(a). All the defects are reconstructed following the weakest configuration (orientation 3 in Fig. 3(a)) providing that the defect arrangements are in the middle of the SWNTs. Simulated mechanical properties of SWNTs having these defect arrangements normalized by those of pristine SWNT such as normalized failure strength (σ_c/σ_o), normalized failure strain ($\varepsilon_c/\varepsilon_o$) and normalized Young's modulus (Y/Y_o) are shown in Fig. 4(b). It can be revealed that presence of an additional vacancy defect reduces the failure strength and failure strain of a SWNT as much as 47% and 80% respectively with a least reduction in the loading type Weibull statistics allowing for a broad spectrum of strength of CNT by [26] and [33] may be analyzed through the worst local configuration of neighboring defects. SWNT having defects arranged in the loading direction is the strongest while the CNT with defects arranged perpendicular to the loading direction is the weakest (Fig. 4(b)). CNTs with defects arranged non-axially (arrangements 2, 3, 5 and 6 of Fig. 4(a)) possess the intermediate failure strength and failure strength.

Effect of two neighboring defects gradually separated in loading, perpendicular to the loading and non-axial directions on the mechanical properties were also studied in this study. Starting from the configurations 1, 4 and 5 shown in Fig. 4(a), two adjacent defects were moved away in their respective directions. Figs. 5(a) and (b) are showing the structures and the obtained mechanical
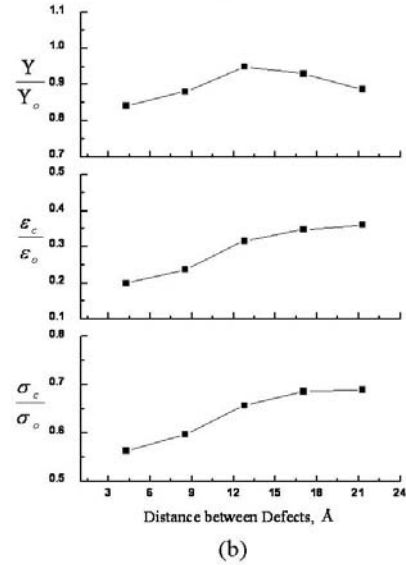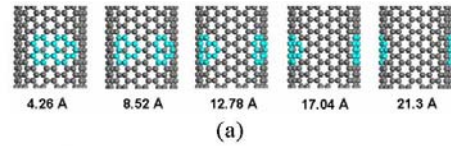

Fig 5: (a) Arrangements of vacancy defects perpendicular to the loading direction with various distances between them and (b) normalized mechanical properties for the SWNTs having defect arrangements shown in figure 5(a).
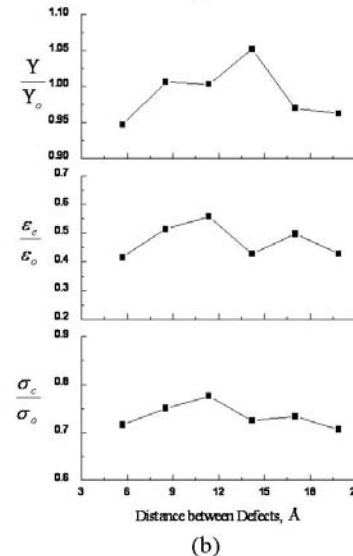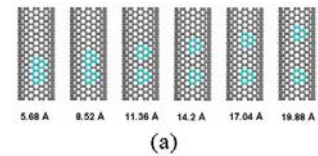

Fig 6: (a) Arrangements of vacancy defects in the loading direction with various distances between them and (b) normalized mechanical properties for the SWNTs having defect arrangements shown in figure 6(a).

properties of SWNTs having two one-atom vacancy defects in the middle of the SWNTs gradually separated
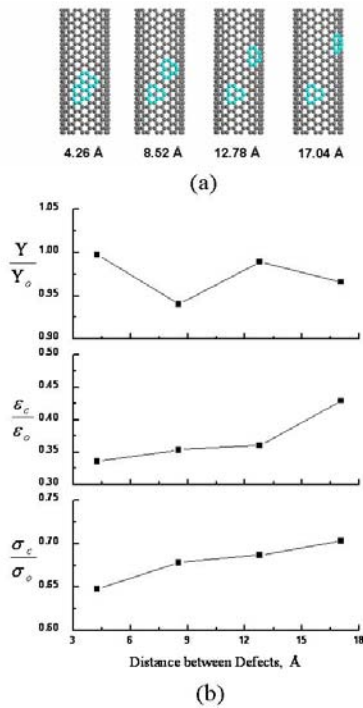
Fig 7: (a) Arrangements of vacancy defects in the non-axial direction with various distances between them and (b) mechanical properties for the SWNTs having defect arrangements shown in figure 7(a).

Fig 8: Variation in failure strengths of SWNTs with different defect arrangements of vacancy defects in various directions.

5. CONCLUSION

The role of the relative positions of vacancy defects and their local orientations in the mechanical properties of SWNTs was explored in this study. It was demonstrated that the local orientations of neighboring two defects with respect to the axis and their relative distance have significant influence on mechanical properties of CNTs. The worst mutual arrangement and relative separation of defects on mechanical properties were clarified with a least number of defects. As result, two neighboring vacancy defects reduced the strength and the failure strain as much as 45% and 80% in comparison with those of pristine SWNT. Thus the interference between two neighboring defects turned out to be an important mechanism in determining the strength of defected CNT structure.

6. REFERENCES

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perpendicular to the loading direction. It is evident that the closer the two defects in that direction, the weaker the SWNT. Both the failure strength and failure strain increased by 15% as the distance between the defects increased. This fact also indicates that the closer the position of two defects, the less strain energy for separation and the shorter duration to release strain. On the other hand, SWNTs with defects in the loading direction (Fig. 6(a)) show no particular trend in properties (Fig. 6(b)) for distances between defects. Mechanical properties seemed to increase up to a distance between the defects of 11.36Å and after that decrease. Similarly to the behavior of SWNTs having vacancy defects perpendicular to the loading direction (Fig. 5(b)), SWNTs with defects in non-axial direction (Fig. 7(a)) show the lowest strength for adjacent configuration of two defects while it is improved (about 7% for a distance between defects of 17.04Å) as the distance between defects is increased.

It can be revealed that SWNTs with two defects in loading direction (Fig. 8) are stronger than those with two defects in the other two directions. Moreover, slopes of the strength versus distance between defects curves (Fig. 8) i.e. the rate of increase in failure strength with respect to distance between defects is the highest along perpendicular to the loading direction and the lowest in the loading direction while in non-axial direction the rate of improvement in strength is between them. As the defect arrangement deviates from loading direction, the mechanical properties degrade gradually. However as the defect arrangement deviates from the loading direction the rate of improvement in failure strength with the distance between the defects increases.
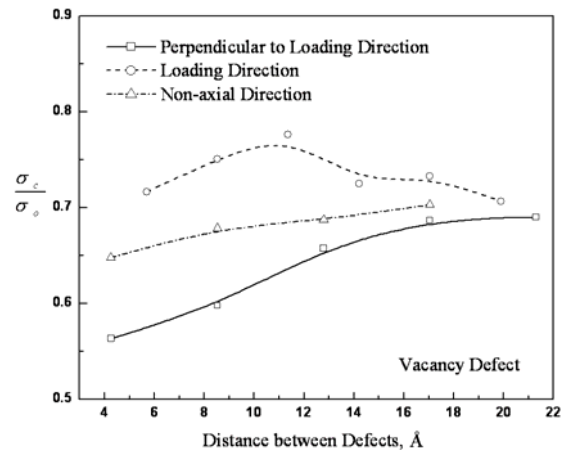
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7. NOMENCLATURE

Symbol	Meaning	Unit
σ	Failure Strength	(MPa)
ε	Failure Strain	(%)
Y	Young's Modulus	(TPa)