Molecular Dynamics Simulation Of Capped Single Walled Carbon Nanotubes

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Abstract

Molecular dynamics simulation has been used to study the effect of capping the carbon nanotube (CNT) with hemispherical caps on mechanical properties of CNTs. Simulation has also been performed for studying the effect of volume fraction (V_f) on mechanical properties of CNT reinforced poly methyl metha acrylate (PMMA) composites. Materials Studio 6.1 has been used as a tool for finding the longitudinal (E_{11}), transverse (E_{22}) and shear moduli of composites. CNT composition in PMMA was varied by volume from 0 to 16%. Results show that capped CNTs have lower moduli in comparison to the uncapped CNTs. Adding CNTs into PMMA increases E_{11} till V_f of 12%. Thereafter, though the value of E_{11} increases but the rate of increase is very less. The results of this study have been compared with Gao and Li [14] and also with Elliott and Han [17].

***Keywords*:** Carbon nanotube; Mechanical properties; Elasticity; Molecular dynamics; Polymer.

1. INTRODUCTION

The fullerenes, named after Buckminster Fuller were brought to light in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien and Harold Kroto [1], the researchers at the Rice University. C60, the allotrope of carbon was the first discovered fullerene. The carbon atoms in C60 are sp^2 hybridized and their arrangement is in such a manner that it takes a shape similar to that of a soccer ball. The discovery of C60 was also an accident like many other scientific breakthroughs. Smalley and Curl found a way to examine the atom clusters formed by laser vaporization with mass spectroscopy. It caught the attention of Kroto [1] subsequently as he was researching on interstellar dust, the long chain polyenes formed by red giant stars. When they vaporized graphite using laser, they could create and evaluate extended chain polyenes. Two major peaks were observed in mass 720 and a little lower at mass 840 corresponding to 60 and 70 carbon atoms, respectively. The band structure of graphite was first discovered by Wallace [2] in 1947 but multi -walled nanotubes (MWCNTs) were not discovered up to that time. In this article, we have concentrated on single walled carbon nanotubes (SWCNTs).

In 1990, Richard Smalley [3] proposed the presence of a tube-shaped fullerene and a bucky tube that could be finished by extending a C60 molecule. In

1991, Dresselhaus [4] recommended for CNT capped at both end by fullerene hemispheres at a fullerene workshop in Philadelphia. But only after Iijma [5] imaged MWCNTs using transmission electron microscope (TEM), the presence of CNTs was experimentally recognized. After two years of his surveillance on MWCNTs, Iijima [5] along with his coworkers and Bethune with his coworkers simultaneously and self-sufficiently spotted SWCNTs.

Cho and Sun [19] examined Young's modulus of polymeric nanocomposite with MD simulation. Spherical nano particles were added to create a model. With the help of numerical performed tensile test it was observed that elastic modulus of nanocomposites were affected by the size of nano-particles and also by the interaction strength between nano-particles and polymer chains. It was observed that elastic modulus of the nanocomposite was inversely proportional to the size of the nanoparticles. As long as the strength was more or equal to the polymer-polymer interaction the elastic modulus increase with a decrease in the size of nano particles. Gan and Zhao [20] performed Hartree-Fockland density functional analysis on capped SWCNT with the number of atoms up to 400. The hypothetical analysis of capped SWCNT was done. The average bond length determined for SWCNTs with smaller diameter was large as compared to the SWCNTs with larger diameter. It was also observed that the average bond length decrease with the number of atoms. Ganji et al. [21] studied the effect of curvature, elastic modulus of armchair SWCNTs and the average energy of atoms under axial strains using self-consistent charge density function. It was concluded that by increasing the amount of curvature the average density and elastic modulus of (7-7) SWCNTs was decreased and equilibrium carbon-carbon distance was increased. It was also discovered that (5-5) SWCNTs did not show any variation in average energy of atoms and Young's modulus with increase in curvature. The Young's modulus and the average energy of atoms of SWCNTs armchair was less for small diameter as compared to large diameters. The elastic modulus of straight (7,7) CNT was 1.22 TPa , for 1-curve was 1.20 TPa, for 2-curve was 1.12 TPa and for 3-curve was 0.98 TPa.

Fereidoon et al. [22] studied SWCNTs in both periodic and non-periodic system. Elastic properties of (6,6) SWCNTs were investigated with the help of density functional theory. Axial and torsional strains were applied on both periodic and C-capped CNTs. It was observed that elastic modulus of the CNT was directly proportional to the length of nanotubes. As the length of nanotube increases the modulus of periodic CNT also increases and after a certain value it become constant. It was concluded that C-capped CNT display opposite behavior to a periodic CNT under compression. The elastic modulus for capped CNTs was always high than other types of CNTs. Gao et al. [23] compared the electrical resistance of capped CNT/Cu interface and open end CNT/Cu interface. It was concluded that capped CNT/Cu interface has lack of dangling bonds of

carbon atoms at the capped end of CNTs which leads to a decrease in the interfacial bonding. The electrical resistance of capped CNT/Cu interface was much higher. Haghighatpanah and Bolton [24] investigated a (6,6) CNT/PE system for minimum energy structure as well as binding energy between CNT/PE with molecular mechanics and with first principle method. It was concluded that force fields were in qualitative promise with the first principles results and PE chains may wrap everywhere on SWCNTs. It was calculated using the COMPASS force field for (5, 5) SWCNTs relating to a PE chain. This force field was utilized to calculate the mechanical properties of (5, 5) SWCNT/PE nano composites. It was discovered that interfacial shear stress of SWCNT/PE was 141.09 MPa and interfacial bonding energy of SWCNT/PE was 0.14 N/m. The simulations indicated that mechanical properties were not affected when small size SWCNTs were used in CNT/PE whereas using large SWCNTs enlarged the Young's modulus of CNT/PE axial direction.

2. STIFFNESS OF SWCNTs

The stiffness of capped and uncapped SWCNTs has been simulated using Materials Studio 6.1 software. Simple steps for predicting the stiffness of capped and uncapped SWCNTs have been discussed below.

2.1 Modeling of SWCNTs

The primary step was to model the SWCNTs using "Build" tool in Materials Studio. We can build SWCNTs with dissimilar chirality (n, m). In this study, we have built capped and uncapped armchair (n, n) SWCNTs. Here, the integer 'n' controls the total size of the CNT. The minimum value for 'n' is 1. Models of capped and uncapped SWCNTs have been shown in Figures 5-6.

2.2 Geometry optimization

The second step in MD simulation was the optimization or minimization of the model that we're going to investigate. It is necessary to improve the structure after it has been sketched because sketching generates the molecules in higher energy configuration and beginning our simulation without optimizing our structure may lead to wrong results. There are different kinds of optimization methods present in Material studio viz., steepest descent method, conjugate gradient and Newton-Raphson method. In the steepest descent method, the line search direction was well-defined along the direction of the local downhill gradient. These entire line search forms a new direction which was always perpendicular to the earlier gradient. This ineffective performance was characteristic of steepest descents, particularly on energy surfaces ensuring constricted valleys. Convergence was slow near the minimum as the gradient approaches zero, but the process was tremendously healthy even for structures that are far from being equilibrated. This method was generally used for generating low energy structure. It does not depend on what the function was or where the process has begun. So this method of optimization was used

when the configurations were far from the minimum and gradients are very large. In this study, smart algorithm has been used which is a cascade of all the overhead stated approaches. The parameters that were used in the optimization of models have been listed in Table 1.

2.3 Dynamics

After geometry optimization or when an optimized structure has been achieved, the next step was dynamics simulation. Classical equation of motion was modified in this step to agree with the result of temperature and pressure of the model. The constructed model was put into an ensemble with constant number of atoms, volume and temperature (NVT) simulation at a temperature of 298°K for 5ps with a time step of simulation 1fs. In the NVT approach the structure was thermally stabilized. After that Anderson thermostat was provided in the simulation and a temperature was maintained at 298°K. The main purpose of the dynamics run was a trajectory file that has data for the atomic configuration, velocities and other information that were recorded in a period of time steps. The different parameters that were used in these steps have been listed in Table 2.

2.4 Mechanical properties

After the dynamics run the next step was to calculate the mechanical properties. For the calculation of mechanical properties of capped and uncapped SWCNTs, the "Forcite" module has been used. With the help of Forcite module, elastic modulus of single structure or series of structures can be calculated. External stresses balanced the internal forces if the structure was in equilibrium. For the calculation of mechanical properties of the capped and uncapped SWCNTs the parameters that were used have been listed in Table 3.

3. RESULTS AND DISCUSSION

In this section the results obtained for the mechanical properties of capped and uncapped SWCNTs have been discussed in detail. Several models of capped and uncapped (5,5) armchair SWCNT of different length but having the same diameter were constructed. Two capped armchair (5,5) SWCNTs having lengths of 12 and 34 Å have been shown in Figures 7 and 8 respectively. The variation in temperature with time for capped armchair (5,5) SWCNT has been shown in Figure 9. The dynamics run was performed for 50 ps using Forcite module of Material Studio 6.1. The structures of uncapped armchair (5,5) SWCNTs with lengths of 12 and 34 Å have been shown in Figure 10 and 11.

Variation in Young's modulus (E_{11}) for capped and uncapped armchair (5,5) for different lengths has been shown in Figure 12. Gao and Li [14] have explored the dependence of Young's modulus of capped and uncapped SWCNT for different length using MD simulation and observed that Young's Modulus for capped and uncapped SWCNT increases quickly when length was less than 20 Å and after that becomes almost constant. It has been observed that Young's modulus for

capped and uncapped armchair (5,5) SWCNT increases with an increase in the length of CNT.

The average Young's modulus, E_{11} for capped (5,5) armchair SWCNT was 843.23 GPa whereas for the uncapped (5,5) armchair SWCNT, E_{11} was 988.94 GPa. Figure 12 shows the variation in the Young's modulus of capped and uncapped armchair (5,5) SWCNT for the different lengths. The results of the present study differ slightly from those given by Gao and Li [14] because of the length and simulation technique. Gao and Li [14] used molecular structural mechanics for calculation of Young's modulus of capped SWCNT and the present study was based on MD simulation. The present study concludes that Young's modulus of capped and uncapped armchair (5,5) SWCNT increase with the increase in length.

Table 4 display the values of Young's modulus (E_{11}) for capped and uncapped SWCNT for different length. Table 4.5 shows the values of Bulk modulus (K) and Shear modulus (G) for capped and uncapped SWCNT for different lengths. Figure 4.9 shows the variation in the Young's modulus of capped and uncapped armchair (5,5) SWCNT for the different lengths and present study was also compared with studies of Gao and Li [14]. The present study concludes that Young's modulus of capped and uncapped armchair (5,5) SWCNT increase with increase in length. Table 4.4 displays values of Young's modulus for capped and uncapped SWCNT for different length and Table 4.5 display values of Bulk (K) and Shear modulus (G) for capped and uncapped SWCNT for different lengths.

Variation of Bulk modulus (K) for capped and uncapped armchair (5,5) for different lengths has been displayed in Figure 13. The average Bulk modulus (K) of uncapped armchair (5,5) SWCNT was 110.14 GPa and average Bulk modulus (K) of capped armchair (5,5) SWCNT was 49.36 GPa. Similarly, Figure 14 displayed a variation in shear modulus (Voigt) of capped and uncapped SWCNT for different lengths. Average shear modulus of uncapped armchair (5,5) SWCNT is 59.204 GPa and average shear modulus for capped armchair (5,5) SWCNT was 10.11 GPa. It was concluded that the Bulk modulus for capped and uncapped SWCNT increased gradually with an increase in length. Shear modulus (G) for uncapped SWCNT remains same with increase in the length of CNT whereas for capped SWCNT, the value of shear modulus was very less as compared to the uncapped CNT.

4. CONCLUSION

With the help of MD simulation, Young's modulus of capped and uncapped armchair (5,5) SWCNT has been investigated. It was observed that Young's modulus of uncapped armchair (5,5) SWCNT was 988.94 GPa and Young's modulus of capped armchair (5,5) SWCNT was 834.23 GPa.

Main findings of the present study have been highlighted below:

(i) Young's modulus of capped and uncapped SWCNT increases with increase in length of CNT. The shear modulus and bulk modulus also increase with increase in length of CNTs.

(ii) Uncapped SWCNTs have higher Young's modulus as compared to capped SWCNTs for the same length of CNTs.

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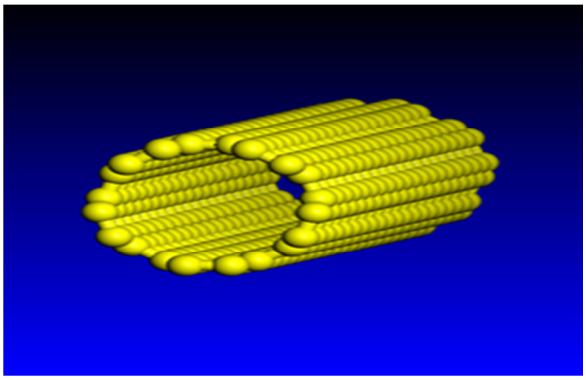
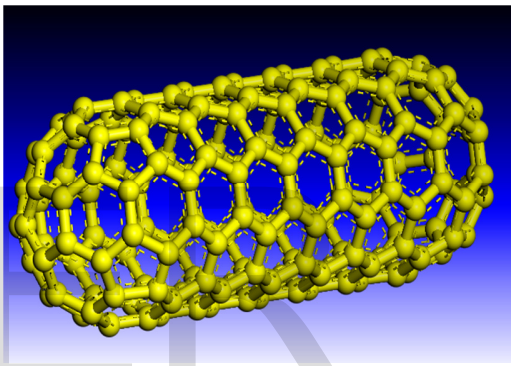


Figure uncapped SWCNT (5,5)



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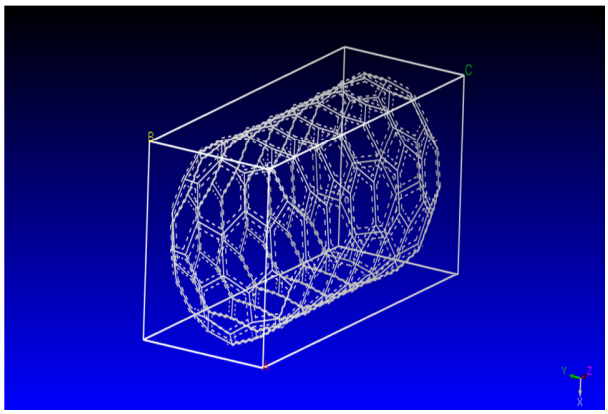

Figure Model of armchair (5,5) capped SWCNT

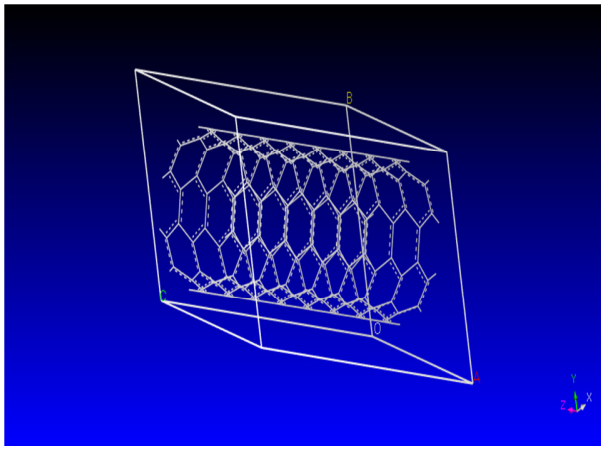

Figure Model of armchair (5,5) uncapped SWCNT

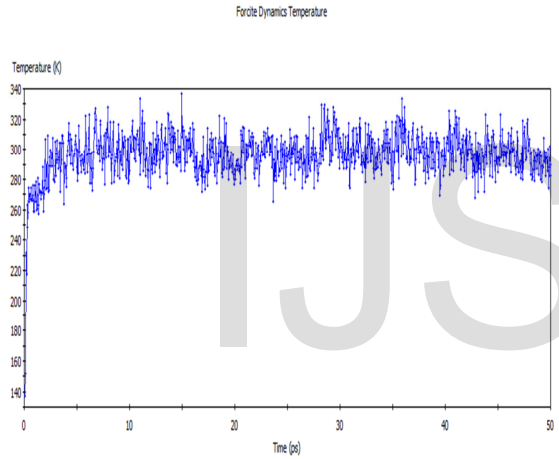

Figure Dynamics run showing the variation of temperature with time for capped (5,5) SWCNT

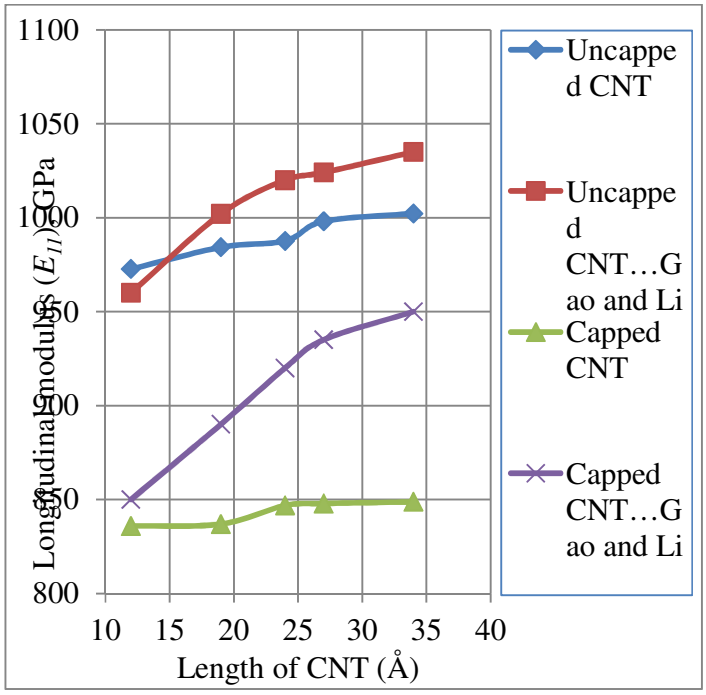

Figure 12 Variation of Young's modulus for capped and uncapped SWCNT for different length

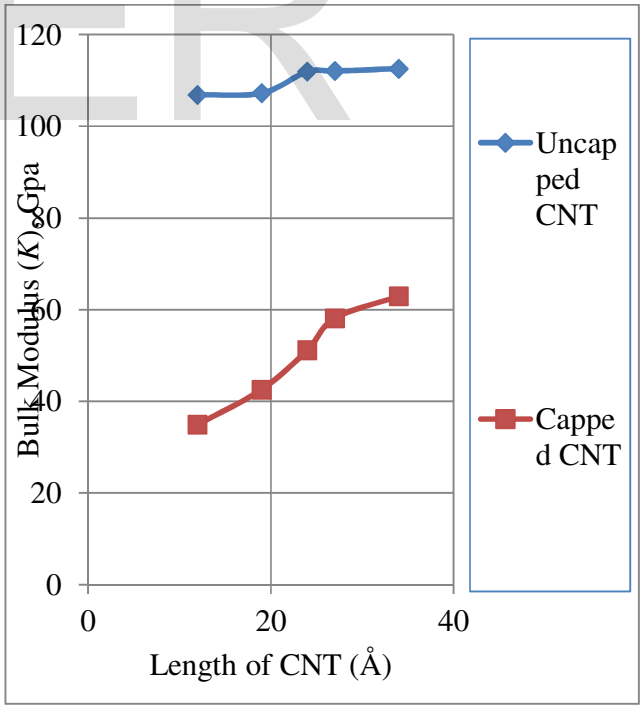

Figure 13 Variation in Bulk modulus of capped and uncapped SWCNT for different length.

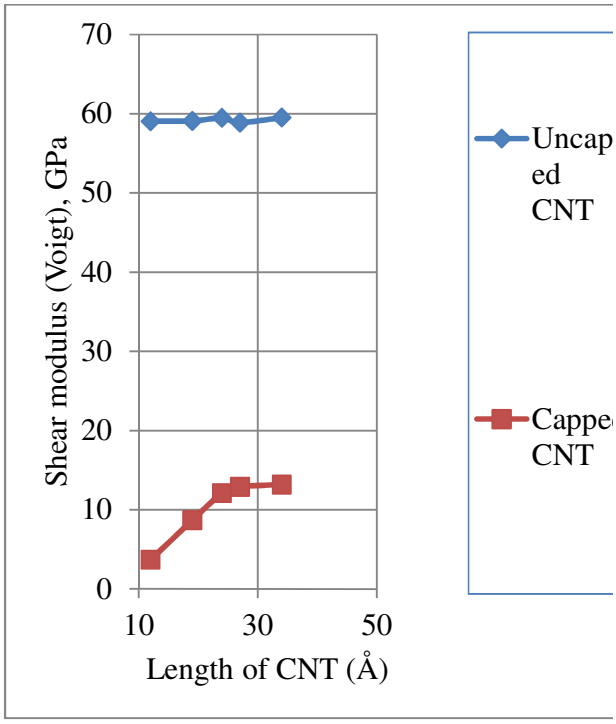

Figure 14 Variation in Shear modulus of capped and uncapped SWCNT for different lengths.