MULTISCALE MODELING OF CARBON NANOTUBE BUNDLE REINFORCED POLYMER COMPOSITES

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1 Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], they have been extensively studied due to their remarkable mechanical, electrical and thermal properties. Due to the exceptional properties, CNTs are now being used in the fields of electronics, field emission devices, nano-electro-mechanical devices, sensors, medical appliances, data storage devices, nano robotics and in light weight structural composites [2-9]. The use of CNTs in polymer materials is now being increasingly studied to produce advanced nano-composites for aerospace, automotive, and military applications [8-9]. Nanostructured composite materials especially polymer composites are incorporating CNT reinforcement by dispersing individual CNTs, nano-filamentary bundles/ropes of CNTs to yield unprecedented mechanical properties. The elastic properties and load carrying capacities of CNTs in nano-composites have been demonstrated in several research works [10-16]. Some of these investigations show that the load-carrying capacity of CNTs in a matrix as well as the improvement of the elastic properties of the composites is significant and the CNT-based composites have the potential to provide extremely strong and ultralight new materials.

In the production processes, it is quite difficult to get isolated CNTs. CNTs have a propensity to aggregate to bundle or wrap together due to high surface energy and surface area. It is very difficult to disperse the CNTs evenly in the matrix. Generally CNTs form clusters and are found in bundles in the composites. Compared to the researches done on isolated CNT reinforced composites, there are not much works on CNT bundle reinforced composites. Lourie et al. [17] have studied CNT bundle-polymer systems using Transmission Electron Microscopy (TEM). They have reported that load is transferred from the surrounding matrix to the nanotubes through the nanotube-polymer interface, which is quite strong. Ajayan et al. [18] have experimentally investigated the mechanical properties of CNT bundle based composite and they have reported that slipping of the tubes in the nanotube bundle limits load transfer from the polymer to the nanotubes. Ashrafi et al. [19] have studied the elastic properties of CNT array based polymer composites. They have determined the elastic properties of twisted single walled nanotubes (SWNTs) array using finite element method (FEM) and then using those properties they have calculated the elastic properties of the polymer nano-composites by traditional micromechanics. Using TEM studies, Singh et al. [20] have reported that nickel/CNT interface is well bonded in CNT bundle reinforced nickel nano-composites. Nah et al. [21] have examined the adhesion of multi-walled CNT bundles to a natural rubber (NR) and have reported that interfacial interactions between CNTs and NR are quite weak.

Evaluating the effective material properties of such CNT bundle based polymer nano-composite is very important at present. In this work, a suitable finite element model is developed to investigate the effects of CNT bundle morphology on the elastic moduli of CNT bundle reinforced nano-composites where the properties of interface element have been derived from nonlinear cohesive law [22] which deals with the atomistic level interaction. CNT bundle consisted of four SWNTs is considered here. Regarding the CNT bundle morphology, bundle diameter, bundle length and cross-link between the

CNT-CNT within the bundle [23] have been considered. Bundle diameter is varied by varying the constituent CNTs diameter. Regarding the length of the CNT bundle, both short and long bundles are considered. Cross-links effect is incorporated in this research by introducing interface with different stiffness between the CNT-CNT within the bundle. Present investigation demonstrates that the elastic moduli of the CNT bundle reinforced polymer nano-composite are significantly affected by the morphology of the CNT bundle.

2 Interface Stiffness

Nano-composites posses a large amount of interfaces due to the small size of reinforcements. The interface behavior can significantly affect the mechanical properties of nano-composites, since load from the matrix to the fibers is transferred through this interface. Jiang et al. [22] have established a nonlinear cohesive law for the CNT-polymer matrix interfaces directly from the Lennard-Jones (LJ) potential for the non-bonded van der Waals (vdW) interactions given by:

$$\sigma^{\text{int}} = 3.07\sigma_{\max}\left[\left(1+0.682\frac{\sigma_{\max}}{\phi_{total}}[u]\right)^{-4} - \left(1+0.682\frac{\sigma_{\max}}{\phi_{total}}[u]\right)^{-10}\right] \quad (1)$$

Here

$$\sigma_{\max} = \frac{6\pi}{5}\rho_1\rho_2\varepsilon\sigma^2 \quad (2)$$

and

$$\phi_{total} = \frac{4\pi}{9}\sqrt{\frac{5}{2}}\rho_1\rho_2\varepsilon\sigma^3 \quad (3)$$

Where ρ_1 is the CNT area density, ρ_2 is the volume density, ε is the bond energy, σ is the equilibrium distance, u is the interface opening distance, σ_{max} is the maximum stress, and Φ_{total} is the total energy. All cohesive law properties (e.g. cohesive strength, cohesive energy) are obtained analytically in terms of the parameters in the LJ potential. The values used for the parameters of CNT-CNT and CNT-matrix (polystyrene) interfaces are tabulated in Table 1. The cohesive law gives analytically the normal cohesive stress at the interface, σ^{int}, in terms of the interface opening displacement, u. Variations of cohesive stress with the interface opening for CNT-CNT and CNT-polymer matrix interface with only vdW interaction are shown in Fig. 1. Initial slope of the tangent of stress-strain curve derived from this stress-displacement curve indicates the modulus (i.e., stiffness) of the interface. Modulus obtained for CNT-CNT and CNT-polymer interface with non-bonded vdW interaction are 5.35 MPa and 2.70 MPa, respectively.

3 Finite Element Modeling

The concept of unit cell or representative volume element (RVE) which has been applied successfully in the studies of conventional fiber-reinforced composites at the micro scale, can be extended to study the CNT-based composites at the nano scale. In the present study 3D nano scale square RVE as shown in Fig. 2 is employed to determine the elastic modulus of nano-composites. Due to symmetry, quarter portion of this RVE is considered in finite element (FE) modeling. The RVE with FE meshing is shown in Fig. 3. Solid 187 element which is a tetrahedral three-dimensional element consisting of 10 nodes is used to discretize the CNT, matrix and interfaces. General purpose finite element analysis code ANSYS is used to carry out the analysis where the meshing of the RVE is done automatically.

3.1 CNT Volume Fraction

In case of long CNT bundle based composite, the CNT is throughout the RVE. For the square RVE with long CNT bundle, the volume fraction of the CNT is defined by the following equation.

$$V^t = \frac{\pi\left(r_o^{\,2} - r_i^{\,2}\right)}{a^2 - \pi r_i^{\,2}} \quad (4)$$

In case of short CNT bundle based composite, the CNT is embedded inside the RVE. For the square RVE with short CNT bundle, the volume fraction of the CNT is defined by the following equation.

$$V^t = \frac{\pi(r_o^2 - r_i^2)L_b}{a^2 L - \pi r_i^2 L_b} \quad (5)$$

Here V^t is the CNT volume fraction, r_o is the CNT outer radius, r_i is the CNT inner radius, a is the lateral dimension of the RVE, L is the RVE length, and L_b is the CNT embedded length for short CNT bundle.

3.2 Elastic Modulus

Longitudinal and transverse displacements (loads) are applied to the RVE to compute the corresponding Young's modulus. The Young's modulus can be found from the following equation.

$$\mathrm{E} = \frac{\sigma}{\varepsilon} = \frac{L}{\Delta L}\sigma \qquad (6)$$

Where ΔL is the applied longitudinal/transverse displacement and σ is the developed corresponding average normal stress. In FE simulation, average normal stress is calculated at a particular section of the RVE. Therefore, once applied displacement ΔL and the corresponding developed stress σ are known, Eq. (6) can be used to calculate the corresponding Young's modulus of the RVE.

4 Results and Discussion

As mentioned earlier, FE analysis has been carried out with both long and short CNT bundles of different diameters. CNT bundle consisted of four SWNTs each of 0.34 nm wall thickness is considered here. Diameter of the CNT bundle is varied by varying the diameter of the constituent SWNTs of the bundle. Length of the RVE is considered as 100 nm and its cross section area is determined according to the requirement to maintain certain CNT volume fraction. CNT-matrix interface thickness is considered as 0.2 nm. Moduli of CNT and matrix are considered as 1000 GPa and 3.8 GPa, respectively and those for CNT-CNT interface and CNT-matrix interface with non-bonded vdW interaction are considered as 5.35 MPa and 2.70 MPa, respectively. Poisson's ratio of all materials is considered the same, which is 0.4.

Here at first the FE model has been validated and then using this model effects of CNT bundle morphology on the elastic moduli of CNT bundle reinforced nano-composites have been investigated. To validate the present FE model for CNT bundle based composite, present FE simulation results are compared with those of Ashrafi et al. [19]. For that purpose CNT bundle with aspect ratio of 12 and CNT modulus of 580 GPa are considered. CNT bundle aspect ratio is calculated based on average bundle diameter which is calculated using the following equation.

$$D_{bundle} = 2\left(\sqrt{2}+1\right)r_o \qquad (7)$$

For 5% CNT volume fraction, the simulated longitudinal Young's modulus of the CNT bundle composite with interfaces of non-bonded vdW interactions is found to be 9.5 GPa, which is quite close to that (9.3 GPa) found by Ashrafi et al.

4.1 Effect of Bundle Diameter

To check the bundle diameter effect on composite elastic moduli, long and short bundles of three different diameters with CNT of indices (50, 50), (80, 80), and (110, 110) are considered. For short bundle, bundle length of 50 nm is considered and for all cases CNT volume fraction is considered as 5%. Table 2 shows the effect of the change of CNT bundle diameter on the longitudinal and transverse Young's moduli. Here longitudinal modulus (E_z) and transverse modulus (E_x) are expressed in dimensionless form by dividing these with matrix modulus (E_m). With the increase of CNT bundle diameter, both longitudinal and transverse Young's moduli are found to decrease.

4.2 Effect of Bundle Length

To check the bundle length effect on composite elastic moduli, long and short bundles with CNT of index (80, 80) are considered. For short bundle, bundle length of 25 nm, 50 nm, and 75 nm are considered and for all cases CNT volume fraction of 5% is considered. Figure 4 shows the effect of the change of CNT bundle length on the longitudinal and transverse Young's moduli. With the increase in CNT bundle length, longitudinal modulus is found to increase, however, transverse modulus is found to decrease. As the interface stiffness of CNT-CNT and CNT-matrix are considered with only vdW interaction, these stiffness are quite low in

comparison to CNT and matrix stiffness. With the increase of CNT bundle length the interface region increases, which results in the reduction of composite modulus in transverse direction.

4.3 Effect of Bundle Cross-link

Presence of cross-links between CNT-CNT within the bundle increases the interface stiffness and strength significantly [23]. To check the bundle cross-link effect on composite elastic moduli, bundle interface stiffness of 5.35 MPa (only vdW interaction), 500 MPa, and 500 GPa are considered. Long and short bundles with SWNT of index (80, 80) are used for all cases with a CNT volume fraction of 5%. For short bundle, bundle length is considered as 50 nm. Table 3 summarizes the results of cross-link effects on the composite moduli. It is found that with the increase of bundle interface stiffness (i.e., with the increase of the amount of cross-link in the interfacial region of the bundle), both longitudinal and transverse Young's moduli of the composite increase significantly.

5 Conclusions

In this paper the effect of the morphology of the CNT bundle on the elastic moduli of CNT bundle based composite is investigated. For that purpose, a 3-D finite element model is developed where the properties of interface element have been derived from nonlinear cohesive law which deals with the atomistic level interaction. Regarding the CNT bundle morphology, bundle diameter, bundle length and cross-link between the CNT-CNT within the bundle have been considered. Base on the present FE analyses, the following conclusions are made:

- Change of CNT bundle diameter affects the composite Young's modulus. With the increase of CNT bundle diameter both longitudinal and transverse Young's moduli of the composite decrease.
- Change of CNT bundle length has significant effects on the composite modulus. The modulus of CNT bundle based composite increases in longitudinal direction with the increase of CNT bundle length. However, in the transverse direction, composite modulus decreases with the increase of CNT bundle length.
- With the increase of cross-link between CNT-CNT within the bundle, both the longitudinal and transverse Young's moduli increase quite significantly.

Table 1. Parameters for interfaces.

Parameters	CNT-CNT	CNT-Polymer
ρ_1 (/m^2)	3.82×10^{19}	
ρ_2 (/m^3)	1.1×10^{29}	3.1×10^{28}
ε (J)	4.58×10^{-22}	7.46×10^{-22}
σ (nm)	0.3468	0.3825
σ_{max} (MPa)	892	487
Φ_{total} (J/m^2)	0.181092	0.109139

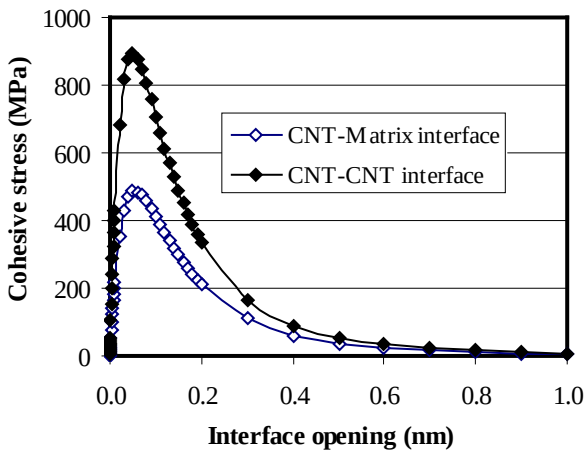


Fig.1. Cohesive stress versus interface opening displacement curves for vdW interaction.

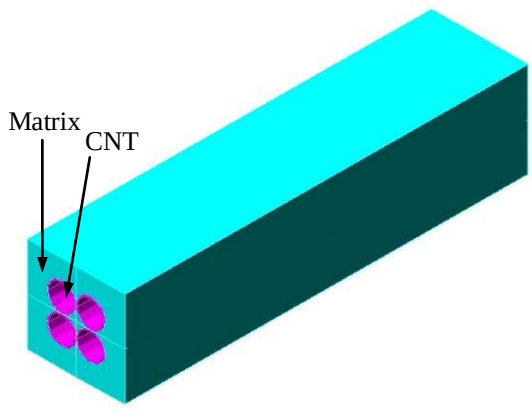
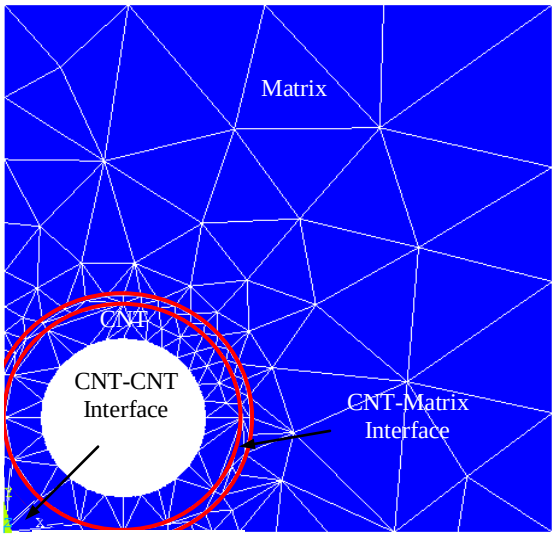
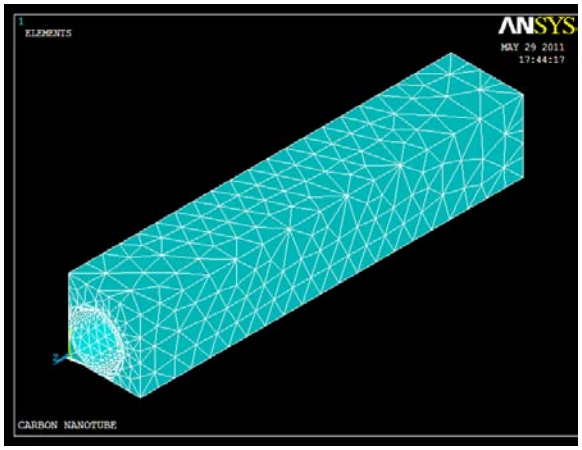


Fig.2. RVE of CNT bundle composite.



(a)



(b)

Fig. 3. Wire frame view of the RVE. (a) End view, (b) 3D view.

Table 2. Effect of bundle diameter.

CNT Index	E_z/E_m		E_x/E_m	
	Short	Long	Short	Long
(50, 50)	1.828	10.927	0.508	0.037
(80, 80)	1.742	10.916	0.505	0.027
(110, 110)	1.612	10.906	0.502	0.022

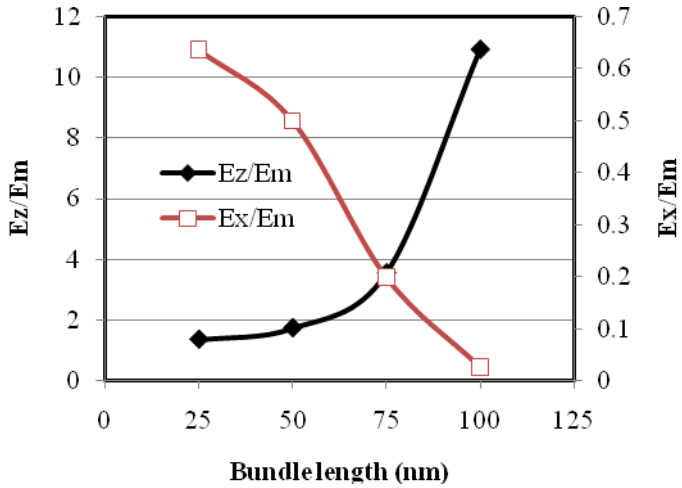


Fig. 4. Variation of composite moduli as a function of bundle length.

Table 3. Effect of bundle interface.

Interface stiffness	E_z/E_m		E_x/E_m	
	Short	Long	Short	Long
5.35 MPa	1.742	10.916	0.505	0.027
500 MPa	2.441	15.311	0.550	0.320
500 GPa	3.111	20.211	0.881	0.523

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