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MODELING OF THE LONGITUDINAL ELASTIC MODULUS OF CARBON NANOTUBE REINFORCED NANOCOMPOSITES

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ABSTRACT

Carbon nanotubes (CNTs) possessing extremely high stiffness, strength, and resilience may be the ultimate reinforcing materials for the development of nanocomposites. Unlike conventional fiber reinforced composites, there are wide variations in the diameter and length of the CNTs in the CNTs reinforced composites. In this work a numerical model has been developed to calculate the longitudinal elastic modulus of short CNTs reinforced composites considering the variation of diameter and length of the CNTs. According to this model, the whole composite is divided into several composite segments which contain CNTs of almost same diameter and same length. Longitudinal elastic modulus of the composite is then calculated by weighted summation of the longitudinal modulus of each composite segment. Existing micromechanical approach for modeling of short fiber composites is modified to account for the structure of the CNTs to calculate the elastic modulus of each segmented CNTs reinforced composites. Statistical variations of the diameter and length of the CNTs are modeled by the normal distribution. Results obtained from this numerical model are compared with the available experimental results and the comparison concludes that the developed model can be used to predict the elastic modulus of CNTs reinforced composites.

Keywords: Modeling, Elastic modulus, Nanocomposites.

1. INTRODUCTION

The discovery of carbon nanotubes (CNTs) in the early 1990`s by Iijima [1] has sparked a revolution in research activities in science and engineering devoted to nanostructures and their application. A single-walled nanotubes (SWNTs) is a hollow strucuture formed by covalently bonded carbon atoms [2-3]. It can be visualized a graphene sheet rolled into a cylindrical tube. For multi-walled nanotubes (MWNTs), a number of graphene layers are co-axially rolled together to form a cylindrical tube. The spacing between graphene layers is about 0.34 nm. CNTs have exceptional mechanical, electrical and thermal properties [4-5]. For example, the stiffness and strength of CNTs are in the range of TPa and GPa, whereas the nearest competing materials exhibit these properties in the range of GPa and MPa respectively. CNTs are now being used in the fields of electronics, field emission devices, nano-electro-mechanical (NEMS) devices, sensors, medical appliances, nano robotics and of course in light weight structural composites [6-7]. The use of CNTs in polymer materials is now being increasingly studied to produce advanced nanocomposites for aerospace, automotive, and military applications [7-9].

However, super strong CNTs alone do not ensure super strong composites because the mechanical properties of CNTs reinforced composites are strongly influenced by the amount of load transfer from the matrix to the CNTs within the composites. Load transfer within the CNTs reinforced composites is influenced by the physical structure (i.e. diameter and length) of the CNTs and the interfacial conditions (i.e., with or without cross-link) between the CNTs and matrix. It should be mentioned that although CNTs can now be readily produced, it is quite difficult to produce CNTs with completely perfect structure with specific diameter and length. Depending on the production process, CNTs are of different diameters and lengths with different imperfections (i.e., missing atoms in the wall of CNT, curved CNTs etc.) [3, 10].

In the literature on CNTs based composites (especially polymer composites), there is wide variation in the reported elastic properties [11-14]. Reported improvements in the elastic modulus are lower than the expected if the CNTs are assumed to act as reinforcing elements with an elastic modulus of 1 TPa. Discrepancies in the reported elastic moduli as well as reported lower elastic moduli in the literature may be due to the insufficient load transfer through the interface between CNT and polymer matrix of the composites. Since load transfer through the interface is affected by several factors like CNTs diameter, CNTs length and interface condition, it is necessary to investigate their effects on the elastic properties of CNTs based polymer composites. Thostenson et al. [15] have developed a model to predict the elastic modulus of CNTs based composites considering the variation of nanotube diameter. However, numerical model to predict the elastic properties of CNTs based composites considering the variation of nanotube diameters and lengths simultaneously is necessary in designing CNTs based composites.

Here a numerical model has been developed to calculate the longitudinal elastic modulus of CNTs based composites considering the variation of diameter and length of the CNTs. According to this model, the whole composite is divided into several composite segments which contain CNTs of almost same diameter and same length. Elastic modulus of the composite is then calculated by weighted summation of the modulus of each composite segment. Existing micromechanical approach for modeling of short fiber composites [16] is modified to account for the structure of the CNTs to calculate the elastic properties of each segmented CNTs reinforced composites. In the conventional micromechanical approach, where the model deal with the geometric heterogeneity is at the microscopic level (i.e., microstructure), the reinforcing fibers have solid structure. However, CNTs have hollow structure. Therefore, here the hollow structured CNTs are converted into equivalent solid fibers and elastic properties of the equivalent solid fibers are determined as well. The variations of the diameter and length of the CNTs are modeled by the normal distribution. Results obtained from this numerical model are compared with the available experimental results of CNTs reinforced composites.

2. MODULUS OF EQUIVALENT SOLID FIBER

To model the properties of the nanotube based composite, it is important to consider the nanoscale structure of SWNTs and MWNTs and how the nanotube interacts with the polymer matrix. For fibre-like materials, load is transferred to the reinforcement through shear stresses at the fibre/matrix interface. As mentioned earlier, CNTs can be visualized as a graphene sheet, where carbon forms a planar hexagonal structure, rolled into a seamless cylinder. In SWNT there is only one graphene layer whereas MWNT is simply formed of concentric SWNTs with an interlayer spacing equal to about 0.34 nm. In each concentric layer the bonding is covalent, but there is no bonding between the walls of the MWNT. As a consequence of this weak layer-to-layer nonbonded interaction in the MWNT, the outer layer of the multi-walled tube will carry almost the entire load transferred at the nanotube/matrix interface [17].

To determine the elastic modulus of the equivalent solid fiber, the load carrying capability of the outer layer of the nanotube must be applied to the entire solid cross-section of the equivalent fiber. The elastic modulus of the nanotube is modelled by considering that the outer wall of the nanotube acts as an effective solid fiber with the same deformation behavior and same diameter and length as shown in Fig. 1. An applied external force on the nanotube and the equivalent solid fiber will result in an iso-strain condition. Therefore,

$$\varepsilon_{NT} = \varepsilon_{eqv}, \tag{1}$$

where the subscripts NT and eqv refer to the nanotube and equivalent solid fiber, respectively. Using equation (1) we can relate the elastic properties of the nanotube to that of an equivalent solid fiber as

$$E_{eqv} = \frac{\sigma_{eqv}}{\sigma_{NT}} E_{NT}. \tag{2}$$

Because the applied external force is the same, the moduli of the equivalent solid fiber can be expressed in terms of the ratio of their cross-sectional areas given as

$$E_{eqv} = \frac{A_{NT}}{A_{eqv}} E_{NT}. \tag{3}$$

After substituting, the modulus of the equivalent solid fiber can be expressed in terms of the elastic modulus of the nanotube, the nanotube outer layer thickness (=0.34 nm) and the nanotube diameter given as

$$E_{eqv} = \frac{4t}{d} E_{NT}. \tag{4}$$

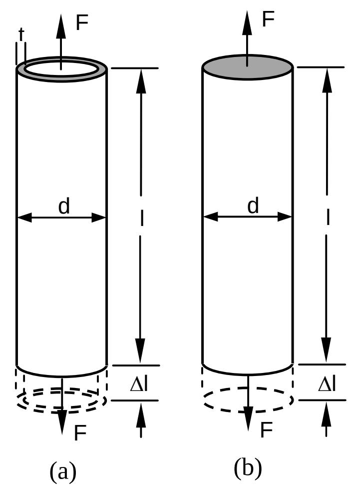

Fig 1. Schematic of (a) nanotube and (b) equivalent solid fiber.

3. NANOTUBE DENSITY

For the conversion of weight fraction, measured when processing the nanocomposite, to volume fraction, needed for predicting the elastic properties, we must know the density of the nanotubes and the matrix. For fibrous composites, the fiber volume fraction can be calculated based on the density of the constitutents using the following equation [16].

$$V_f = \frac{W_f}{W_f + (\rho_f / \rho_m) - (\rho_f / \rho_m) W_f}. \tag{5}$$

Where subscripts f, m and c refer to the fiber, matrix and composite, respectively.

From the measurements of outside diameter and inside diameter the nanotube density can be calculated to be

$$\rho_{NT} = \frac{\rho_g (d^2 - d_i^2)}{d^2}. \qquad (6)$$

Here d and d_i refer to nanotube outer and inner diameter respectively and subscript g refers to fully dense graphite. Obviously, the density of a MWNT will increase with the number of walls. The variation of density of equivalent solid nanotubes with outer diameters is shown in Fig. 2.

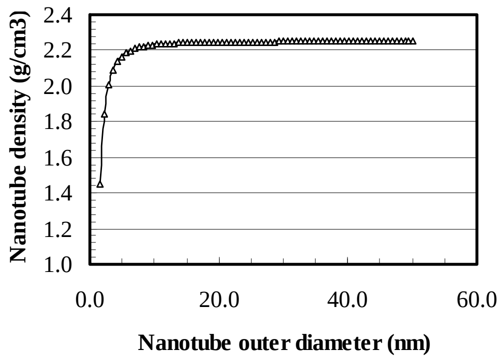

Fig 2. Variation of density with outer diameter for equivalent solid nanotubes.

4. NANOTUBE DIAMETER AND LENGTH DISTRIBUTION

Although CNTs can now be readily produced, it is quite difficult to produce CNTs with completely perfect structure with specific diameter and length. Depending on the production process, CNTs are of different diameters and lengths. The distribution of nanotube diameter and length for a specific nanotube sample can be determined by measuring the outside diameter and length of a statistically large sample of nanotubes and then using the experimental data to determine the probability distribution of nanotubes for diameter and length $\xi(d,l)$. With a view to model the composite elastic properties, we study the volume fraction of carbon nanotubes within the composite. From the diameter and length distribution we can define the volume distribution of nanotubes $\psi(d,l)$ as follows

$$\psi(d,l) = \frac{d^2 l \xi(d,l)}{\int_0^\infty \int_0^\infty d^2 l \xi(d,l) d(d) d(l)}. \qquad (7)$$

The above volume distribution will need to be considered when calculating the overall nanocomposite properties.

5. CALCULATION OF NANOCOMPOSITE ELASTIC MODULUS

A wide variety of models have been developed to predict the elastic properties of fiber composites in terms of the properties of the constituent materials [16]. Here we have used the most popular Halpin and Tsai [18] model according to which the longitudinal Young's modulus of composites can be determined from the following equations

$$E_{11} = E_m \left(\frac{1 + \zeta \eta_l V_f}{1 - \eta_l V_f} \right), \qquad (8)$$

$$\eta_l = \frac{(E_f / E_m) - 1}{(E_f / E_m) - \zeta}. \qquad (9)$$

Here the value of $E_f (= E_{eqv})$ can be obtained from equation (4). In equations (8) and (9), the parameter ζ is dependent on the geometry and boundary conditions of the reinforcement phase. For an aligned short fiber composite with low fiber volume fraction, this parameter can be expressed as [16]

$$\zeta = 2\frac{l}{d}. \qquad (10)$$

By substituting equations (4), (9) and (10) into (8) we can express the nanocomposite longitudinal Young's modulus in terms of the properties of the polymer matrix and the nanotube reinforcement given as

$$E_{11} = E_m (1 + 2(\frac{l}{d}) \left(\frac{(E_{NT}/E_m) - (d/4t)}{(E_{NT}/E_m) + (l/2t)} \right) V_{NT})$$
$$\times \left(1 - (\frac{(E_{NT}/E_m) - (d/4t)}{(E_{NT}/E_m) + (l/2t)} \right) V_{NT})^{-1} \qquad (11)$$

Equation (11) expresses the diameter and length dependence of the carbon nanotube reinforcement on the nanocomposite elastic modulus. However, with distribution of nanotube diameters and lengths we can not use equation (11) directly to calculate the nanocomposite elastic modulus. To accurately model the elastic properties of the composite, we must take into account the contribution to the overall elastic moduus for each nanotube diameter and length and the volume fraction that tubes of a specific diameter and length occupy within the composite. If the nanotubes are uniformly dispersed and aligned throughout the matrix phase, the contribution of each diameter and length can be considered to act in parallel. Therefore, the elastic modulus of the composite can be calculated as a summation of parallel composites over the range of nanotube diameters and length.

The concept of parallel composites is illustrated in Fig. 3. Within the entire volume of the composite we can divide the volume into N individual composites containing nanotube with specific diameter and length. Each of the N individual composites will have a specific elastic modulus that depends on the local volume fraction of nanotubes at a given diameter and length. With the assumption of iso-strain, we can express the modulus of the whole composite as a summation of the moduli scaled by the partial volume of each nth composite given as

$$E_c = \sum_{n=1}^{N} v_n E_n (d_n, l_n). \qquad (12)$$

Where $E_n(d_n, l_n)$ is the elastic modulus of the nth composite segment calculated from equation (11) at the specific nanotube diameter and length and v_n is the partial volume of the nth composite segment given as

$$v_n = \frac{VC_n}{VC}, \tag{13}$$

$$\sum_{n=1}^{\infty} v_n = 1. \tag{14}$$

To calculate the modulus at a given nanotube diameter and length, E_n in equation (12), the local volume fraction at a given nanotube diameter and length can be calculated from the volume distribution of nanotubes (equation (7)) given as

$$V_{NT}(d_n, l_n) = \frac{\int_{d_n}^{d_n+\Delta d_n} \int_{l_n}^{l_n+\Delta l_n} (V_{NT}\psi(d,l))d(d)d(l)}{v_n} \tag{15}$$

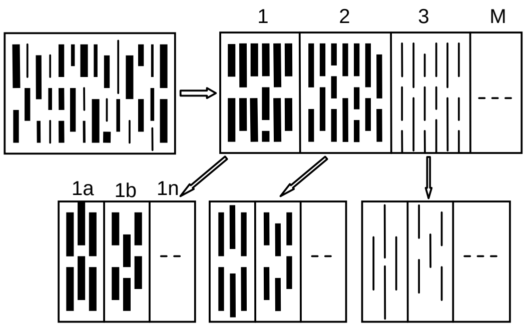

Fig 3. Composite segments. (Composite segment numbering with 1, 2, 3 etc. have CNTs of same diameter and different length whereas segments numbering with 1a, 1b etc. have CNTs of same diameter and same length.)

6. RESULTS AND DISCUSSION

To determine the longitudinal elastic modulus of the CNTs reinforced composites, the variation of the nanotube diameters and lengths are modeled with normal distribution. To calculate the composite elastic modulus, the whole composite is divided into 1000 composite segments with specific nanotube diameter and length. Young's modulus of the CNT and matrix are considered to be 1000 GPa and 1.2 GPa, respectively. To validate the present simulation model, we have compared our simulation result with that of Qian et al. [11] for the same type of nanotubes and polymer matrix. Figure 4 shows the comparison of present simulation results with that of Qian et al. Qian et al. have reported that adding 1% wt. of nanotubes (with average dia 34 nm and average length 15 μm) to polystyrene matrix increases the overall tensile modulus of composite by 35%. Using our model we have observed such increase in the composite modulus for 2.5 % wt. of nanotube, which is comparable. Figure 5 shows the effects of variation of nanotube diameter on the elastic modulus of composite. It is seen that with the increase of nanotube diameter elastic modulus of the composite decreases for a particular nanotube weight fraction. Figure 6 shows the effects of variation of nanotube length on the elastic modulus of composite. It is seen that with the increase of nanotube length elastic modulus of the composite increases for a particular nanotube weight fraction.

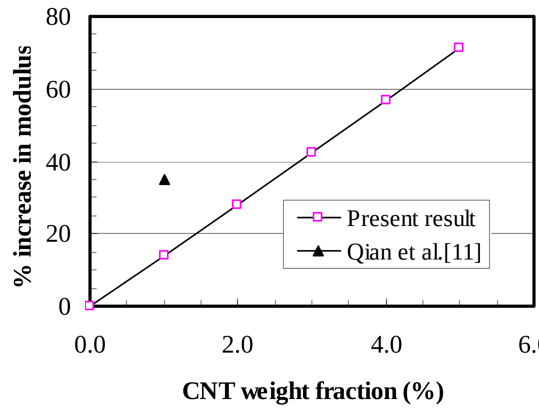

Fig 4. Variation of composite modulus with nanotube weight fraction.

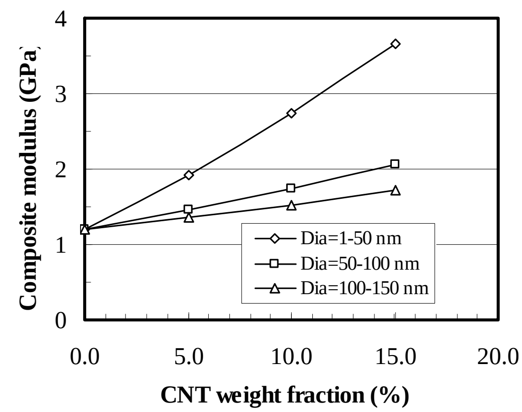

Fig 5. Variation of composite modulus with nanotube diameter (tube length = 800-1200 nm).

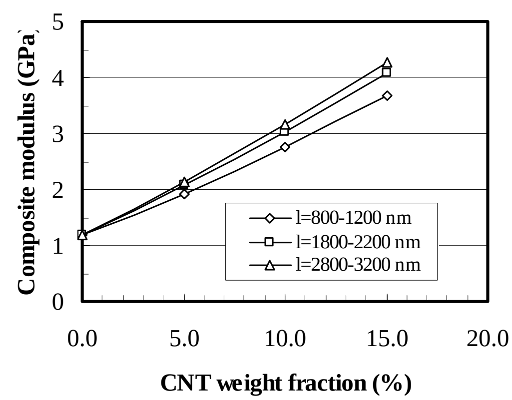

Fig 6. Variation of composite modulus with nanotube length (tube dia = 1-50 nm).

7. CONCLUSIONS

A numerical model has been developed to calculate the longitudinal elastic modulus of short CNTs reinforced composites considering the variation of diameter and length of the CNTs. According to this model, the whole composite is divided into several composite segments which contain nanotubes of almost same diameter and same length. Longitudinal elastic modulus of the composite is then calculated by weighted summation of the longitudinal modulus of each composite segment. Existing micromechanical approach for modeling of short fiber composites is modified to account for the structure of the CNTs to calculate the elastic modulus of each segmented CNTs reinforced composites. Statistical variations of the diameter and length of the CNTs are modeled by the normal distribution. Results obtained from this numerical model are compared with the available experimental results and the comparison concludes that the developed model can be used to predict the elastic modulus of CNTs reinforced composites. It has also been observed that composite modulus increases with the increase of nanotube length and decrease of nanotube diameter.

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9. NOMENCLATURE

Symbol	Meaning	Unit
d	CNT diameter	(nm)
l	CNT length	(nm)
ε	Strain	(nm/nm)
σ	Stress	(Pa)
E	Young's Modulsu	(Pa)
A	CNT cross section area	m^2
t	CNT layer thickness	(nm)
F	Force	(N)
Δl	Length increment	(nm)
V	CNT volume fraction	--
W	CNT weight fraction	--
ρ	Density	(kg/m^3)
v	Volume fraction of composite segment	--
Ψ, ξ	Distribution function	--
VC	Whole Composite volume	m^3
VCn	Composite segment volume	m^3

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