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A Finite Element Model for estimating Young's Modulus of Carbon Nanotube Reinforced Composites Incorporating Elastic Cross-Links

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***Abstract*—**The presence of chemical bonding between functionalized carbon nanotubes and matrix in carbon nanotube reinforced composites is modeled by elastic beam elements representing covalent bonding characteristics. Neglecting other reinforcing mechanisms in the composite such as relatively weak interatomic Van der Waals forces, this model shows close results to the Rule of Mixtures model's prediction for effective Young's modulus of a Representative Volume Element of composite for small volume fractions (~1%) and high aspect ratios (L/D>200) of CNTs.

***Keywords*—**Beam Element, Carbon Nanotube Reinforced Composite, Cross-link, Young's modulus.

I. Introduction

CARBON Nanotubes (CNTs) have attracted researchers' great attention due to their outstanding mechanical, electrical, thermal, chemical, and even biological properties. Young's modulus, strength, strain before failure, and aspect ratio in CNTs are significantly high which bring about application of CNTs as composites reinforcement, and thus providing versatile characteristics for composites.

The small size of nanostructure of such composites brings sever limitations in conducting experimental studies, thus encouraging scientists to develop theoretical models in order to explore their mechanical behavior. CNT reinforced composites have been investigated by multiscale modeling bridging the length scales from nano- through the mesoscale [1-3].

Description of the interaction between the CNT (reinforcement) and the matrix is of great importance in analysis of CNT reinforced composites, as several models have been developed in this regard. Molecular dynamics and continuum mechanics models have considered different binding conditions between CNT and matrix such as the presence of Van der Waals force fields or perfect bonding assuming conventional Rule of Mixtures for evaluating effective elastic response of the composites under loading [4-8].

On the other hand, chemically functionalized CNTs are recently being frequently used in fabrication of CNT reinforced composites regarding the activity of functional groups inducing links between the CNT and the matrix. There are evidences demonstrating that functional sites on the CNT surface can provide chemical bonding between CNT and matrix [1,9-11].

In this paper, a model is developed for determining effective Young's modulus of a Representative Volume Element (RVE) of the composite assuming covalent bonding between CNT and matrix introduced as elastic cross-links.

II. Methods

A. Building the RVE

In this model, the RVE of composite is composed of a CNT surrounded by matrix, having elastic cross-links in the interfacial space between them. (Fig. 1)

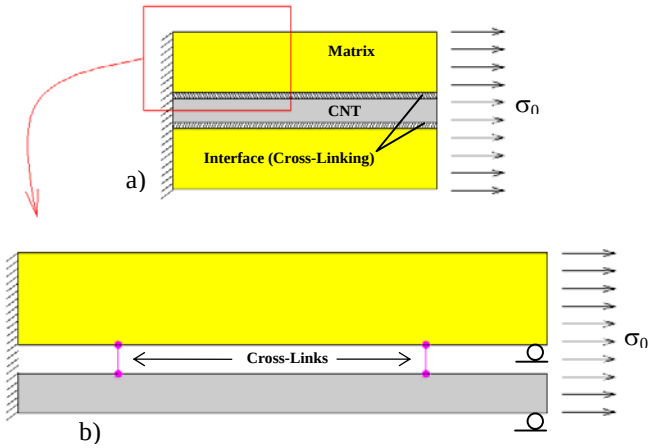

Fig. 1 a) RVE of CNT reinforced composite under uniform loading, b) illustration of cross-links between CNT and matrix

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According to [12] which takes the CNT as a solid fiber in a composite, a (8,8) armchair single walled carbon nanotube (SWCNT) having a diameter, *D*, of 1.08 nm is assumed as an elastic cylindrical beam on the central axis of RVE. The matrix is also taken to be a linear elastic material surrounding cylindrically all around the CNT in the RVE.

The assumption of embedding functionalized CNTs into the matrix brings the idea of taking into account the chemical bonding between CNT and the matrix on the functional group site. For instance, a carboxylated CNT may present a C-C covalent bond between a carbon atom on CNT and the carbon atom in carboxyl (-COOH) group, and thus linking to the matrix through the functional groups. (Fig. 2)

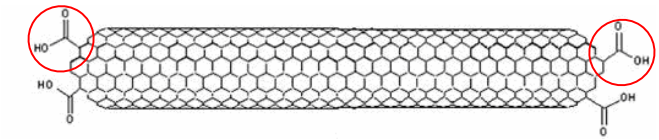

Fig. 2 Carboxylated (functionalized) SWCNT, showing C-C bonds on functional sites [13]

Therefore, regarding that each carbon atom on the CNT presents three sp^2 bonds with three adjacent carbon atoms on the CNT and the fourth bonding of carbon with functional group makes a sp^3 hybridization, the interfacial spacing between the CNT and matrix is taken to be equal to the cross-link length of sp^3 covalent carbon-carbon bond. It should be noted that chemical functionalization is feasible on both tip and side wall of CNTs [9,13].

B. Finite Element Modeling

The CNT and matrix are modeled in form of Voigt's model of parallel springs using 3D elastic beam elements (ANSYS BEAM4 elements) with solid circular cross-sectional area in the RVE. The elastic properties of the (8,8) SWCNT and matrix are shown in Table I.

TABLE I
ELASTIC CONSTANTS FOR CNT AND MATRIX IN FINITE ELEMENT MODEL

	Young's Modulus (GPa)	Poisson's Ratio
(8,8) SWCNT	1010 [14]	0.3 [3]
Matrix	130*	0.3*

* assumed by the authors

The atomic structure of the cross-links in the interface showing the chemical bonding is also modeled as structural beam element; i.e. the C-C bond is represented by 3D elastic elements (ANSYS BEAM4) with solid circular cross-sectional area. For evaluating the characteristics of cross-link beam elements, the linkage approach between molecular and continuum mechanics used in [14,15] for simulating SWCNT as a space frame containing structural elements as bonding is used. In this approach, the total atomic bonding energy is set equal to total strain energy of a uniform beam of length, *l*, and cross-sectional area of *A*.

The molecular mechanics parameters k_r, k_υ and k_τ for sp^3 carbon-carbon bond according to [15-17] are 632 kcal/mole.Å^2 = 4.39×10^{-7} N/nm, 126 kcal/mole.rad^2 = 8.76×10^{-10} N.nm/rad^2, and 40 kcal/mole.rad^2 = 2.78×10^{-10} N.nm/rad^2, respectively. The C-C bond length *l* is assumed to be 1.522 Å for the cross-link [16]. Elastic characteristics of the cross-link beam element can be obtained using the following equations [14,15]:

$$\frac{EA}{l}=k_r,\qquad \frac{EI}{l}=k_\theta,\qquad \frac{GJ}{l}=k_\tau \tag{1}$$

where *E* and *G* are Young's and shear modulus of elasticity for the beam element and $A=\pi d^2/4$, $I=\pi d^4/64$, and $J=\pi d^4/32$ for the circular beam cross-section with a diameter of *d*. So, the values for *d*, *E*, and *G* are obtained as 0.179 nm, 2.67 TPa, and 0.42 TPa, respectively.

III. RESULTS

Elastic response of the RVE to uniform loading is investigated. Effective Young's modulus of the RVE obtained by cross-link modeling and Rule of Mixtures are compared. Considering that the Rule of Mixtures offers perfect bonding between CNT and matrix, its formulation for Voigt's arrangement of two elastic phases of composite can be written as follows:

$$E_{RoM}=v_{CNT}E_{CNT}+v_{matrix}E_{matrix} \tag{2}$$

where, *v* and *E*, go respectively for volume fraction and Young's modulus of CNT and matrix, and $v_{CNT}+v_{matrix}=1$.

Obviously, volume fraction of CNT in the composite plays a determining role in affecting the reinforcing mechanism. Fig. 3 shows the Young's modulus with respect to CNT volume fraction for both Rule of Mixtures and cross-linking models for a RVE having two cross-links in its 5 nm length. Different volume fractions are obtained by changing the matrix cross-sectional area in the RVE.

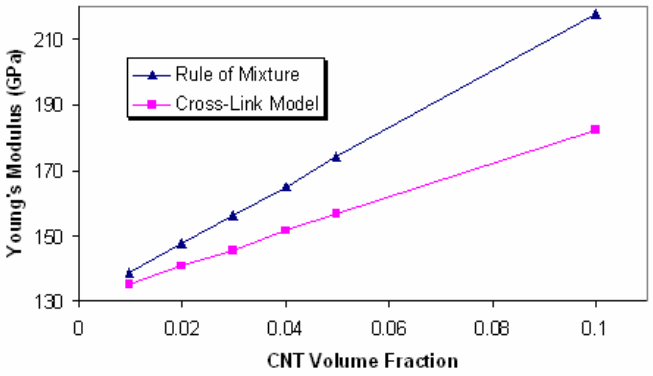

Fig. 3 Young's modulus vs CNT volume fraction

The more the CNT volume fraction, the more deviation is shown by the present model from Rule of Mixtures.

Although Rule of Mixtures does not take into account the effect of RVE length, our model shows significant change of Young's modulus with altering the RVE length (CNT and

matrix are assumed to have the same length in the RVE). On the other hand, increasing the number of cross-links distributed between the CNT and matrix in the RVE length enhances the reinforcing which makes a very good physical sense. As a result, in this study, RVEs of different lengths with evenly distributed cross-links have been considered by allocating one cross-link per each 4 nm of the RVE length. The two last cross-links close to two RVE ends are assumed to hold a distance of 0.5 nm from the ends in order to avoid possible stress concentration on cross-link sites in the Finite Element model. In this case, the RVE length, L, and the number of cross-links distributed in it, N, are related in the following form:

$$L = 4N - 3 \quad (3)$$

Fig. 4 shows the effective Young's modulus of the RVE with respect to the number of cross-links in the RVE length.

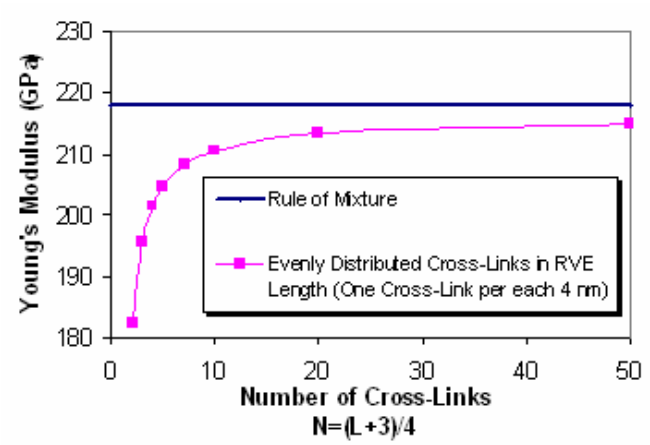

Fig. 4 Young's modulus vs number of evenly distributed cross-links in different RVE lengths (CNT volume fraction = 10%)

Fig. 5 shows the Young's modulus of RVEs of 5 and 9 nm lengths, having 2, 4, 6, 8, and 10 cross-links along their length.

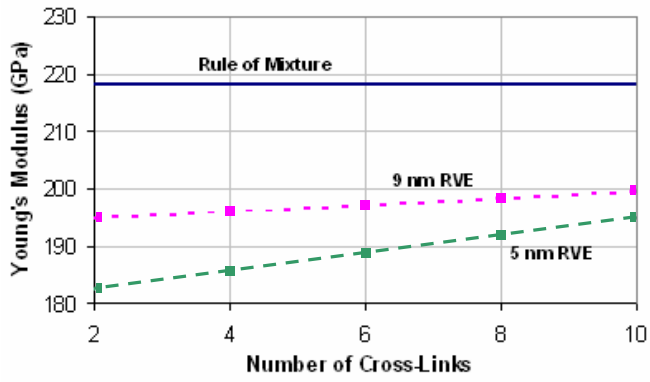

Fig. 5 Young's modulus vs number of cross-links for 5 and 9 nm RVE length (CNT volume fraction = 10%)

Increasing cross-links from 2 to 10 in constant RVE lengths increases Young's modulus of the RVE in a nearly linear fashion according to Fig. 5.

Fig. 6 brings Young's moduli of two types of RVEs: one, having only two end cross-links, and the other, the corresponding RVEs having one cross-link per each 4 nm of their length.

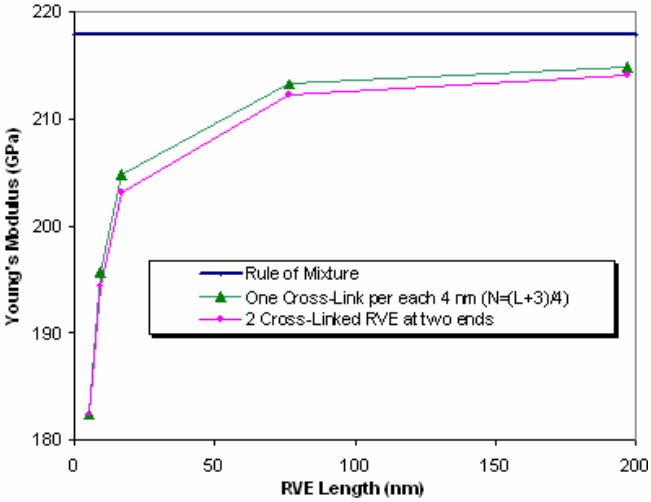

Fig. 6 Young's modulus vs RVE length (CNT volume fraction = 10%)

It is clear from Fig. 6 that by increasing RVE length, which in general is equivalent to an increase in CNT aspect ratio (L/D), effective Young's modulus of cross-linking model increases for both two ends cross-linked and one cross-link per 4 nm RVEs.

IV. Conclusion

The results of this study show that the effective Young's modulus obtained from cross-linking model is less than that predicted by Rule of Mixtures. Our model also predicts that by increasing the volume fraction of CNT in composite, the difference between Young's modulus of cross-linking model and that of the Rule of Mixtures' modulus will increase. The reason of overestimation of Young's modulus by Rule of Mixtures comparing to cross-linking model is the assumption of perfect bonding in Rule of Mixtures. In other words, cross-linking model does not assume perfect bonding between CNT and matrix which seems more realistic in functionalized CNT reinforced composites.

Moreover, it is shown here that by increasing the RVE length, and thus the CNT aspect ratio, also the number of cross-links in the interface between CNT and matrix, our cross-linking model approaches the assumption of perfect bonding and closely predicts the Young's moduli introduced by Rule of Mixtures.

Another interesting result is that the effect of RVE length on Young's modulus is more evident than that of number of cross-links for the same RVE length (see Figs. 5 and 6). Finally, comparison between two ends cross-linked and one per each 4 nm cross-linked RVEs shows a slight difference in the Young's modulus.

Alteration of Poisson's ratio of the cross-link beam element does not affect this model results. The Poisson's ratio for the cross-link beam element is calculated using *E* and *G*. Shear modulus, *G*, is obtained from molecular mechanics force field parameter k_τ, using Eq. (1). In [14,15], likely, weak influence of force field constant k_τ on the computation has been reported.

Current model is valid for elastic linear assumption for cross-links and thus, is applicable to the atomic bond force linearly related to atoms separation distance but not for large bond strains in which the atomic forces show nonlinear behavior with respect to atoms separation distance [3,18].

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