Multi-scale Modeling of Nonlinear Tensile Behavior in Single-walled Carbon Nanotube Reinforced Nanocomposites

S.M.R. Khalili and A. Haghbin

Abstract-Multi-scale material modeling was used to investigate the role of nanotubes specifications on the nonlinear tensile behavior of nanocomposites. Particularly, the effect of diameter, chirality and volume fraction of nonlinearly modeled SWCNTs is studied on their composites. Multi-scale modeling is applied to assemble various RVEs composed of different SWCNTs embedded in polymer. Nanotubes are modeled in continuum mechanics based on their atomic structures in the case of space frame structures. Elements in this structure are defined in such a way to resemble carbon bonds characteristics in molecular mechanics. Polymer portion of RVE is modeled as a linear elastic continuum material, regarding the modeling convenience. Attained stress-strain curves of modeled nanocomposites revealed that using Armchair SWCNTs in RVEs rather than Zigzags makes nanocomposites tougher in tensile loading. Also diameter of CNT has an inverse effect on the stress-strain curves level. Using CNTs with lower diameter in RVEs, regardless of the chirality and CNTs type, make nanocomposites more strengthen in tension. Furthermore, the effect of diameter is more obvious in higher volume fraction of CNTs.

Index Terms—Carbon nanotubes, Multi-scale modeling, Nanocomposites, Tensile behavior.

I. INTRODUCTION

Following the discovery of carbon nanotubes (CNTs) [1], many efforts are being dedicated to utilize their extraordinary specifications in routine applications. Investigations in mechanical engineering in order to compose advanced materials prepared nanocomposites emersion in recent years. CNTs that recognized as low density, high stiffness and high strength materials are extremely attracted the attention of scientist as proper reinforcing agents in nanocomposites [2].

Qian [3], Andrews [4], Kearns [5] and their coworkers are the primaries in performing experiments to study the effect of inserting CNTs in polymers. The considerable point is that in nanocomposites there are many different design factors that influence its final mechanical behaviors. General behavior of polymer, volume fraction (VF) of CNT, chirality and diameter of CNT, dispersion and orientation of CNTs in nanocomposites are the main parameters. Thus, there is a useful need to clarify the effect of CNTs addition in polymers

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by the aid of modeling and simulations.

Frankland et al. [6] applied molecular dynamics to study the tensile behavior of nanotube reinforced polymers. They presented longitudinal and transverse stress-strain relation of just one representative volume element (RVE) of these nanocomposites.

Multi-scale modeling is identified a versatile tool in simulation of materials that consist of different size scale components. This technique is more powerful in nanomechanics in which the mechanical behavior of material is extremely dominated by nanoscale phases.

Odegard et al. [7] introduced a multi-scale model which is based on the equivalent continuum modeling technique for nano-structured materials. In their work the elastic parameters of model was obtained through same loading conditions in both continuum model in finite element and discrete model in molecular mechanics.

Li and Chou [8] applied a multi-scale method to analyze the stress distributions in nanotube/polymer composites under tension. They combined the molecular structural mechanics approach i.e. their previous technique in single-walled carbon nanotubes (SWCNTs) modeling [9] with the continuum finite element method (FEM) to form a RVE of nanocomposites.

Tserpes et al. [10] proposed a multi-scale RVE to model the tensile behavior of CNT reinforced composites. CNTs behavior in RVE was taken from a frame structure that was assembled with nonlinear beam elements.

The significant point that has never paid attention chiefly, was the effect of CNTs variables on the tensile behavior of nanocomposites in modeling investigations. These variables are the amount and the kind (chirality and diameter) of SWCNTs that have been inserted into the RVEs.

In present study, the effect of volume fraction, diameter and chirality of SWCNTs on the tensile behavior of their nanocomposites is investigated via multi-scale modeling. To reach this scope, several RVEs including diverse range and amount of SWCNTs are prepared.

SWCNTs are modeled considering their atomic structure in space frame structures. Beam elements are defined in the structure based on carbon bond characteristics in molecular mechanics. Then, the structure is inserted to a cubic continuum medium as polymer to form a RVE. All modeling procedure and analysis are done in ABAQUS finite element software [11].

II. SINGLE-WALLED CARBON NANOTUBES (SWCNT) STRUCTURE

A SWCNT can be viewed as a rolled graphene sheet to

form a seamless cylinder with a constant radius and is closed off at each end by hemispherical caps. Graphene sheet is a lattice of hexagonal bonds between carbon atoms in which every atom is bonded to three nearest neighbors via very strong covalence bonds of length 1.421Å. Many of SWCNT's mechanical and electrical properties particularly depend on the direction and the length of rolling vector that describes the atomic arrange of bonds in its side walls.

This vector namely chiral vector C_h is generated from the two a_1 and a_2 primitive vectors of unit cell in graphene sheet. The vector is specified by two numbers that are chirality index of SWCNT. Principally chiral vector is produced through resulting *n* units of a_1 and *m* units of a_2 , i.e. (Fig. 1) [12]:

$$C_h = na_1 + ma_2, n \ge m \tag{1}$$

Chirality index that is specified like (m,n) is expressing the length and direction of chiral vector on graphene sheet and accordingly diameter and twist of bonds with respect to axis of nanotube. Since, the chiral vector with the length of **L** is roll up and form the nanotube circumference, nanotube diameter can be obtained by the following equation [12]:

$$D = \frac{L}{\pi} = \frac{a(3(n^2 + m^2 + nm))^{\frac{1}{2}}}{\pi}$$
(2)

where *a* is the carbon-carbon bond length and *m*,*n* are chiral indices.

Regarding the chiral index, three types of SWCNTs are defined. The Armchair nanotubes are defined by (m,m) and the Zigzag nanotubes by (m,0). Other ones with different chirality indices are Chiral nanotubes.

In present work Armchair and Zigzag nanotubes in two diameters are modeled to embed in RVEs in following steps.



Fig1. Schematic of graphene sheet including definition of primitive vectors of SWCNT formation.

III. CARBON NANOTUBE (CNT) MODELING

Molecular mechanics based on finite element modeling approach is used to model the SWCNTs. In this approach atomic structure of CNTs are modeled in finite element as a space frame structures by transforming dimensions in a scale factor. The joints of this structure that are nodes in FEM model are inserted in software in the place of carbon atoms in its atomic arrangement. Load carrying members in the structure are beam elements that are situated between carbon atoms to connect pertinent nodes regarding the chirality of CNT (Fig. 2). Beam elements are supposed to resemble the carbon bonds in atomic structure of CNT. In order to identify the beam elements characterizations, modified Morse potential energy function (PEF) in molecular mechanics is employed. This PEF initially introduced by Belytschko et al. [13] to simulate the fracture of CNTs in molecular mechanics. After that, this PEF successfully applied to some studies to model the nonlinear tensile behavior of CNTs [8,14]. In the following part, a brief description of modified Morse PEF is cited.



Fig. 2. Simulation of a SWCNT as a space-frame structure.

A. Interatomic potential energy and force field function

In computational nanoscience, the energy of a system including several hundred to billions atoms is evaluated using interatomic potentials. The total potential energy function of an N-body nanostructure, always understood to refer to the configurational potential energy that can be expressed in terms of coordinates of its constituent atoms. The simplest way is to express this energy as a cluster expansion involving two- and three-body, etc., potential energy functions as follows [12]:

$$H_{I} = \frac{1}{2!} \sum_{i} \sum_{j \neq i} V_{2}(r_{i}, r_{j}) + \frac{1}{3!} \sum_{i} \sum_{j \neq i} \sum_{k \neq i, j} V_{3}(r_{i}, r_{j}, r_{k}) + \dots$$
(3)

where V_n are n-body interatomic potential functions. The potentials are functions of atomic coordinates, but in practice they are expressed in terms of interatomic distances. Thus potential energy is depends on interatomic separation and also the angles between the bonds connecting individual atoms.

The total interaction in a molecular system can be modeled with a force-field function. This force-field function is a combination of a set of individual potential energy functions; each one models a particular aspect of the total interaction. The actual functional forms of these potential energy functions and their corresponding parameters can differ widely depending on system bonds conditions. The priorities of the force-fields terms and constants are also in associated with the bonds state, loading conditions and material situation.

In molecular mechanics, SWCNTs are considered as a great molecule including carbon atoms. Therefore, its potential energy function is expressed in the form of steric potential energy which depends solely on the relative position of nuclei of carbon atoms. The general form of a nanostructure force-field is expressed such as [9]:

$$U = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_w + \sum U_{wdw}$$
(4)

where U_r is the bond stretching, U_{θ} is bond angle bending, U_{ϕ} is dihedral angle torsion, U_w is out of plane torsion and U_{vdw} is the non-bonded Van der waals interactions in molecule.

Primarily, there are two kinds of potential energies in molecular mechanics that are mostly used by researchers in the area of SWCNT's continuum modeling based on their atomic structure. First, is the harmonic approximation for potential energy functions in molecular mechanics. This type of potential energy function is applied in molecular structural modeling method. Basically this method deems a linear behavior for carbon-carbon bonds and consequently results a linear trend for carbon nanotubes in their tensile properties.

Contrary to first mentioned method which is mostly used to examine the elastic behavior of nanotubes, second method namely molecular mechanics based on finite element method applied molecular mechanics relations to finite element method (FEM). This method is introduced to model the tensile behavior of nanotubes until the bond breakage. The second method is managed to observe each C-C bond as nonlinear based on its atomic properties using modified Morse potential energy. This method is broadly applied to simulate the stress-strain relation, strength evaluation and failure of CNTs in tensile loading.

In the following sections, modified Morse PEF and its capability to model the nonlinear behavior of nanotubes in tensile loading conditions of nanocomposites is specifically described.

B. Modified Morse Potential Energy Function

According to modified Morse PEF, the potential energy of carbon bonds in CNT is expressed as [13]:

$$E = E_{stretch} + E_{angle},\tag{5}$$

$$E_{stretch} = D_e \{ [1 - \exp(-\beta(r - r_0))]^2 - 1 \},$$
(6)

$$E_{angle} = (1/2) k_{\theta} (\theta - \theta_0)^2 [1 + k_{sextic} (\theta - \theta_0)^4]$$
(7)

where $E_{stretch}$ is the bond energy due to bond stretch, E_{angle} is the bond energy due to bond angle-bending, r is the length of the bond, θ is the current angle of the adjacent bonds and r_0 and θ_0 are the initial length and angle of bonds. The parameters corresponding to separation energy of 124 *kcal/mol* are as follows [13]:

$$D_e = 0.631 \text{ nN.nm}, \beta = 26.25 \text{ nm}^{-1}$$
 (8)

$$k_{\theta} = 1.42 \text{ nN.nm/rad}^2, k_{\text{sextic}} = 0.754 \text{ rad}^{-4}$$

C. Beam Element Definition

The beam elements in the frame structure are defined based on the above-mentioned PEF in software. By differentiating energy terms in (3) and (4), the force-bond length and moment bond angle relations can be derived as follows [14]:

$$F(\Delta r) = 2 \beta D_e (1 - \exp(-\beta \Delta r)) \exp(-\beta \Delta r)$$
(9)

$$M (\Delta \theta) = k_{\theta} \Delta \theta [1 + 3 k_{sextic} (\Delta \theta)]^4$$
(10)

where $\Delta \mathbf{r} = \mathbf{r} - \mathbf{r}_0$ and $\Delta \theta = \theta - \theta_0$.

Now it is possible to define the nonlinear elements in software based on above derived relations. As the effect of angle-bending potential is very small, only the bond stretching potential is considered, the same as Tserpes et al. did in their work [10].

First order three dimensional Timoshenko beam element with two nodes and 6 degrees of freedom (DOF) at each node was used to define each beam element in the structure. The length of element r selected equal to carbon bonds in CNT structure i.e. 1.42 \mathring{A} with aspect ratio of 14. The tensile behavior of elements is defined in software as each one has a force-displacement relation coincide with (9).

Beam elements are applied to a space-frame structure that is modeled geometrically through importing the coordinates of carbon atoms in its molecular structure. The coordinates are achieved by using a carbon nanotube modeling program and the end caps of nanotubes are neglected for convenience. After that, the beam elements are situated between two pertinent carbon atoms regarding the chirality of SWCNTs.

IV. ASSEMBLING REPRESENTATIVE VOLUME ELEMENT

The main principle in multi-scale material modeling of nanocomposites is to assemble a RVE as a representative of the material to be analyzed. One of the most referred techniques in multi-scale modeling of CNT/polymer nanocomposites is to embed a modeled CNT in a continuum material as polymer [8], [10]. Thus, CNT is modeled more precise in molecular mechanics regarding to its important role in composite behavior and the polymer in FEM by common solid elements.

In the present study, the polymer is deemed as a linear elastic material with Young's modulus of 2.5 GPa and Poisson's ratio of 0.3. Linear cubic 8 node elements with 6 DOF per each node in space are used to mesh the polymer portion in FEM.

In order to investigate the effect of CNT parameters, different arrangement of RVEs are modeled. The RVEs consist of two different diameters of Armchair and Zigzag CNTs embedded in diverse amount of polymer. CNTs are located at the middle of RVE with the same length as polymer. Therefore, volume fraction of CNT could be counted by means of cross section areas i.e. $V_f = \pi D^2/4a^2$ where **D** is the mean diameter of CNT considering its thickness and **a** is the edge length of square RVE. The thickness of CNT is supposed equal to the interlayer space in graphite sheets i.e. 0.34 nanometers. The length of RVEs are chosen in such a way that aspect ratio L/D in CNTs is greater than 10 (L is CNTs length). Fig. 3 shows a RVE including CNT and encircling polymer that is modeled in ABAQUS.

The interaction between CNT and surrounding polymer is a critical point in multi phase material modeling. Hence, "embedded element" as a capability in ABAQUS, is hired to model the interface in RVE. This ability is successfully used for reinforcing agents in multi phase structures [15].



Fig 3. The RVE consist of CNT and polymer in different scales.

In analyzing procedure, one end of each RVE was fully constrained and an incremental axial displacement is applied to another end until gaining 10% strain. Considering the nonlinearity of beam elements in CNT, the analysis is allowed to have nonlinear results in general. Normal stress is calculated based on total reaction forces in the fixed extremity and obtained from software outputs.

The results are converged successfully and verified with molecular mechanics modeling. Fig. 4 demonstrates the verification of results by comparing the stress-strain curve of a RVE that is assembled the same as in [6] with the reference curve.



V. RESULTS AND DISCUSSION

Twelve RVEs consisting two Armchair CNTs (12,12), (17,17) and two Zigzags (20,0), (30,0), each one in 4, 8 and 12 percent VF are analyzed in separate stepwise procedures. Its noticeable that (12,12) and (20,0) CNTs are two different kinds CNTs with nearly equal diameter length (9.4 Å). The same way is valid for two other mentioned CNTs in diameter length of about 23.25 Å. The volume fraction of CNT in RVEs is 8% unless specified otherwise in studying the effect of VF on tensile behavior part.

According to the nonlinear tensile behavior of nanotubes, secant moduli of RVEs are also derived from the results in order to investigate the nonlinearity of their tensile behavior. The secant modulus E_{SEC} is defined at a given value of strain $\bar{\epsilon}$ as follows [5]:

$$E_{SEC} = \frac{\sigma(\bar{\varepsilon}) - \sigma(0)}{\bar{\varepsilon}}$$
(11)

The Effect of CNT Diameter on tensile behavior of RVE



Fig 5. The effect of Armchair CNT diameter on the RVE tensile behavior.

In order to investigate the effect of embedded CNT diameter on tensile behavior of nanocomposites, Armchair and Zigzag CNTs were compared separately. Fig. 5 shows the stress-strain curves of RVEs including Armchair CNTs in

different diameters (both in same volume fraction). On the other side, Fig. 6 shows the same curves for inserted Zigzag CNTs in RVEs. It illustrates that using CNTs with lower diameter in RVEs will strengthen the nanocomposites in tension. A similar behavior also observed in Zigzag CNTs.



Fig 6. The effect of Zigzag CNT diameter on the RVE tensile behavior.

By a simple comparison between these stress-strain curves, the difference of nanocomposites strength caused by different types of embedded CNTs is clear. In next step, this significant parameter in nanocomposites design in the case of chirality effect is studied.

The Effect of Chirality on tensile behavior of RVE

In Fig. 7 the stress-strain curves of four RVEs in one diagram is presented. It is noticeable that the curves of RVEs including identical chirality of CNTs are in a same color and the curves of RVEs with equal diameter CNTs in same style.



Fig 7. The effect of CNTs chirality on tensile behavior of RVE.



Fig 8. Secant moduli of two kind of embedded CNTs in nanocomposites in two different diameters.

It can be concluded that using RVEs including Armchair CNTs results superior curves in nanocomposites. It means more strength and toughness in tensile loadings especially in higher strains (in both diameter ranges).

In order to evaluate the nonlinearity of modeled RVEs, the secant moduli of tensile analysis are shown in Fig. 8. It is

clear that in a same kind of inserted CNTs, the secant modulus decreases by raising the CNTs diameter. Also, in a same diameter of CNTs in RVEs, the secant modulus of Armchair included nanocomposites are in a higher range. (Curves with same shape in Fig. 8)

The Effect of Volume Fraction of CNT on tensile behavior of RVE

In Fig. 9 the stress-strain curves of 4, 8 and 12 percent VF of Armchair CNTs included RVEs, and in Fig. 10 for Zigzag CNTs included is depicted. The figures are expressing that higher amount of CNT in RVE will improve the tensile behavior of nanocomposite. It is clear that in a same VF using smaller diameter CNTs in RVE will result superior curves. The important point is that the improvement in tensile behavior of nanocomposites due to diameter of CNTs in higher VFs is greater. Thus, it could be deduced that the effect of CNT diameter on tensile behavior of nanocomposites is influenced by the amount of CNT in it.



Figure 9. The effect of Armchair volume fraction on RVEs tensile behavior



Fig 10. The effect of Zigzag volume fraction on RVEs tensile behavior.

In order to investigate the dependency of chirality effect to the volume fraction of CNT, stress-strain curves of two equal diameters Armchair and Zigzag CNTs are superposed in Fig. 11.

The diagram declares that the influence of chirality of CNT on tensile behavior of nanocomposite is not dependent to volume fraction of embedded CNT.



Fig 11. The effect of chirality and volume fraction of CNTs on tensile behavior of RVE.

VI. CONCLUSION

The effect of chirality, diameter and volume fraction of SWCNTs on tensile behavior of their nanocomposites is investigated. Multi-scale material modeling in ABAQUS software is used to simulate the tensile loading on a representative volume element of CNT/polymer nanocomposite. CNTs are modeled based on their atomic structures through modified Morse PEF in molecular mechanics as frame structures. Different amount of Armchair and Zigzag CNTs in different diameters are assembled by composing CNT and polymer in RVEs. The obtained nonlinear stress-strain curves of RVEs show the dependency of nanocomposites tensile behavior on volume fraction, chirality and diameter of embedded CNTs.

It is shown that using CNTs with lower diameter in RVEs will strengthen the nanocomposites in tension. In addition, using RVEs with Armchair CNTs results more strength and toughness in tensile loadings especially in higher strains. Moreover, inserting higher amount of CNT in RVE will improve the tensile behavior of nanocomposite. Finally, in a same amount of CNTs in RVES, using smaller diameter CNTs will result a significant strength in nanocomposites in tension, especially in higher volume fraction of CNTs.

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