Journal of Solid Mechanics Vol. 2, No. 3 (2010) pp. 248-256

Investigation of Vacancy Defects on the Young's Modulus of Carbon Nanotube Reinforced Composites in Axial Direction via a Multiscale Modeling Approach

M.R. Davoudabadi[1,*], S.D. Farahani[2]

[1]*Department of Mechanical Engineering, Semnan University, Semnan, Iran*
[2]*Department of Mechanical Engineering, University of Tehran, Tehran, Iran*

Received 16 September 2010; accepted 28 October 2010

ABSTRACT

In this article, the influence of various vacancy defects on the Young's modulus of carbon nanotube (CNT) - reinforcement polymer composite in the axial direction is investigated via a structural model in ANSYS software. Their high strength can be affected by the presence of defects in the nanotubes used as reinforcements in practical nanocomposites. Molecular structural mechanics (MSM)/finite element (FE) Multiscale modeling of carbon nanotube/polymer composites with linear elastic polymer matrix is used to study the effect of CNT vacancy defects on the mechanical properties. The nanotube is modeled at the atomistic scale using MSM, where as the interface we assumed to be bonded by Vander Waals interactions based on the Lennar-Jonze potential at the interface and polymer matrix. A nonlinear spring is used for modeling of interactions. It is studied for zigzag and armchair Nanotubes with various aspect ratios (Length/Diameter). Finally, results of the present structural model show good agreement between our model and the experimental work.

Keywords: Polymer matrix; Carbon nanotubes; Nonlinear spring; Multiscale modeling; Defect; Inter-phase; Finite element model.

1 INTRODUCTION

THE discovery of carbon nanotubes by Iijima (1991) opened up a new window in nano science [1]. Due to particular mechanical and electrical features of carbon nanotubes, this kind of nanostructure has come under close scrutiny by many researchers in recent decades. A very high Young's modulus and tensile strength combined with low density give these materials excellent mechanical properties [2-4]. Because of the need for specially prepared laboratories and particular conditions for experiments, experimental works in this context are very expensive. In addition to the experimental side, non empirical modeling and simulation of these nanotubes has also been a focus. The common computational methods for modeling and simulation of nanotubes include the ab initio method, the molecular dynamic (MD) method [5-7], and the tight binding method [8-10], which is a combination of the ab initio and MD methods. It is accepted that, in general, the ab initio method is more accurate than other methods [11].recently; CNTs have been produced in large-scale quantities with the development of different advanced production technologies at reasonable prices. Therefore researchers are now planning to use CNTs in polymer composites to increase simultaneously the strength and toughness of the composites.

As mentioned previously, several experimental investigations and numerical studies have been done to achieve the mechanical properties of CNTs and CNT-polymer composites. There are, however, some discrepancies between atomistic modeling and experimental results. Among the various factors that cause such a large difference, it seems

* Corresponding Author.
E-mail address: Davoudabadi.m@gmail.com

that the existence of defects in the structure of CNTs is the most effective one. We refer to defects in the board sense of the word to reflect deviation of the material from the regular atomic scale structure. Thus, in the case of CNTs, a defect is defined as a distortion of the perfect nanotube. The possible CNT defects can be classified into four main groups: incomplete bonding defects (vacancies), topological defects (introduction of ring sizes other than hexagons).

The majority of studies, CNTs have been treated as defect-free materials. However, experimental observations have revealed that vacancy defects are commonly present in the nanotube. Among the various types of defects in CNTs, vacancies have received much more attention than others. Vacancies result from missing carbon atoms in the walls, which can happen when CNTs are subjected to irradiation. Recently, a brief overview of the defects in CNTs has been given. Little work has been done to investigate the role of vacancy defects in CNTs on the mechanical properties of these nanostructures. In addition to experimental studies, a few simulation studies have been done to investigate the role of CNT vacancy defects. Although continuum methods work well for perfect materials, they cannot be directly applied to nanotubes with defects as these methods assume the material to be perfect. However, a combination of these methods and atomistic simulations can be used for evaluating elastic properties of defective CNTs. For example, by employing MD simulations and continuum theory. The objective of this work is to examine the effect of CNT vacancy defects on the Young's modulus of SWCNT-reinforcement polymer composites using a molecular structural mechanics/finite element Multiscale modeling approach. In this method, the nanotube is modeled at atomistic scale by the MSM method. The polymer matrix is at the macroscopic scale by the continuum FE method. The Nanotube and polymer matrix are assumed to be bonded by van der Waals interactions at the interface and nonlinear spring is used for simulating the Vander Waals interactions. This model is used to study the vacancies defects effects on SWCNT-polymer composite.

2 MODELING

Here, we use structural molecular mechanics to model the carbon nanotubes [12]. The element used for the covalent bonds is a uniaxial element with tension, compression, torsion, and bending capabilities and has six degrees of freedom at each node; three translations in *x*, *y*, *z* directions and three rotations about *x*, *y*, *z* axes. This element is defined by the cross sectional area, the moment of inertia, and the material properties. Based on the energy equivalence between local potential energies in the computational chemistry and elemental strain energies in the structural mechanics, the elastic constants for the equivalent beam are determined. The force field constants of the covalent bonds are used as follows:

$$\frac{EA}{L} = K_r, \qquad \frac{EI}{L} = k_\theta, \qquad \frac{GJ}{L} = k_\phi \tag{1}$$

where the force field constants K_r, k_θ and k_ϕ represent stretching, bending, and torsional stiffness of the covalent bonds [13]. Also, *E* and *G* denote module of elasticity and shear of the element, respectively. Moreover, *A* is the cross sectional area, I the moment of inertia, J the polar moment at Eq. (1). and *L* the length of the beam. The length of the element is assumed to be equal to the covalent distance of the carbon atoms ($L = a_{c-c} = 0.1421$ nm). Specific parameters of the element with a circular cross section could be obtained from the Eq. (1) .as follow [12]:

$$A = \frac{\pi d^2}{4}, \qquad I = \frac{\pi d^4}{64}, \qquad J = \frac{\pi d^4}{64} \tag{2}$$

where *d* is the cross-sectional diameter of the element. In the references of molecular mechanics, the units of the force constants K_r and k_θ are kcalmol^{-1}rad^{-2}, respectively. For the convenience of computation, we exchange them into nN nm^{-1} and nN nm rad^{-2}, respectively. These are well-known force field constants for modeling the carbon-carbon covalent bonds in CNTs and have been demonstrated successfully for modeling the static, dynamic, and thermal properties of carbon nanotubes and their composites. These values are listed as follow [12]:

$$K_r = 6.52\times10^{-7}\ \text{Nnm}^{-1}$$
$$K_\theta = 8.76\times10^{-10}\ \text{Nnmrad}^{-2} \quad (3)$$
$$K_\tau = 2.78\times10^{-10}\ \text{Nnmrad}^{-2}$$

As mentioned earlier, CNTs carbon atoms are bonded together with covalent bonds forming a hexagonal lattice. These bonds have a characteristic bond length C-C and bond angle in the 3D space. The displacement of individual atoms under an external force is constrained by the bonds. Therefore, the total deformation of the nanotube is the result of the interactions between the bonds. By considering the bonds as connecting load-carrying elements, and the atoms as joints of the connecting elements, CNTs may be simulated as space-frame structures. By treating CNTs as space-frame structures, their mechanical behavior can be analyzed using classical structural mechanics methods. In this work, a 3D FE model able to assess the mechanical properties of SWCNTs is proposed [12]. The 3D FE model is developed using the ANSYS commercial FE code. For the modeling of the bonds, the 3D elastic BEAM4 ANSYS element is used. The specific element is a uniaxial element with tension, compression, torsion and bending capabilities. It has six degrees of freedom at each node: translations in the nodal *x*, *y*, and *z* directions and rotations about the nodal x, y, and z-axes. The element is defined by two or three nodes as well as its cross-sectional area, two moments of inertia, two dimensions and the material properties. Prediction of material properties of nanotube, The Young's modulus of a material is the ratio of normal stress to normal strain as obtained from a uniaxial tension test. Following this definition, the Young's modulus of SWCNTs is been calculated using the following equation.

$$E_{cnt} = \frac{FL}{A_{cnt}\Delta L} \quad (4)$$

where F is the total applied force, A_{cnt}, the cross-sectional area, L the initial length and ΔL the elongation. A_{cnt} is equal to πDt where D is the mean diameter of the tube. It is shown in Fig.1. The nodes of the bottom end of the SWCNT have been fully constrain (zero displacement and rotation conditions), while the nodes of the upper end, are subjected to tensile forces. From the results it is clear that the wall thickness of CNTs significantly affect the calculation of Young's modulus of SWCNTs. The larger the wall thickness, the smaller the Young's modulus calculated. In the current work, energy equivalence between molecular and structural mechanics provides a wall thickness of 0.34 nm. The present Young's modulus of nanotube is in good agreement with the many previous theoretical predictions and experimental results [14-18]. Note that the currently existing theoretical and experimental values of the Young's modulus is quite scattered. The Young's modulus of nanotube ranges from 1 to1.05 TPa, from the different references. The Young's modulus of zigzag nanotube is greater than armchair nanotube modulus. The MSM model for prediction of the carbon nanotube can be adopted into a finite element model for prediction of the mechanical properties of nanotube reinforced composites. Continuum-based FE formulation is implemented to analyze the interphase layer and outer polymer matrix. Here, an isoparametric cubic element is used for modeling the matrix. The element is defined by eight nodes having three degrees of freedom per node: three *x*, *y*, and *z* directions. The polymer matrixes selected in this study are poly ethylene amorphous, crystalline poly ethylene. The Young's modulus of this isotropic amorphous polymer is assumed to be 3 GPa and Poisson's ratio is chosen as 0.3. The nanotube and matrix are assumed to be bonded by van der Waals interactions based on the Lennars-Jones (LJ) potential at the interface [19]. For modeling these forces, nonlinear spring elements are implemented in this work. The spring element used here is defined by two nodes and a spring constant.

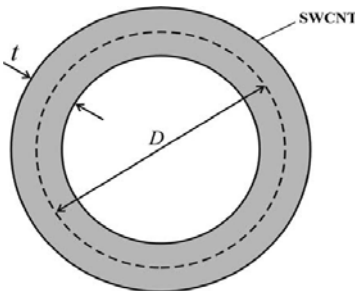

Fig. 1
Schematic of SWCNT Cross-section area .

To construct these elements, the distances between the nodes on CNT wall and the nodes on the inner surface of the polymer matrix are computed because of the matrix is continuum and each nodes on CNT connected to three node at inner wall of matrix we assumed that stiffness of equal spring is 3K. A spring element is inserted between every two nodes with their distance smaller than the cut off radius of LJ potential. It is a uniaxial tension - compression element with thee degrees of freedom at each node: three translations in the *x*, *y*, and *z* directions. No bending or torsion is considered in this element. The spring stiffness of this element is determined by the second derivative of the LJ potential [20], as follows:

$$V_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{5}$$

$$K = \frac{d^2 V_{LJ}(r)}{dr^2} = \frac{624\varepsilon\sigma^{12}}{r^{14}} - \frac{168\varepsilon\sigma^{6}}{r^{8}} \tag{6}$$

where r is the inter atomic distance and ε and σ are the LJ parameter. For carbon-carbon van der Waals interactions, these parameters are as follows:

$$r = \sqrt[6]{2}\sigma \tag{7}$$

$$\varepsilon_{c-ch_2} = 0.004556, \sigma_{c-ch_2} = 0.3825 \tag{8}$$

For obtaining the Young's modulus of polymer nanocomposite we considered two models one of them the long CNT through the polymer matrix and another is a short CNT with cap inside the polymer matrix. The thickness of the interphase layer is assumed to be 0.4293 nm, based on previous molecular mechanics works. The cross section of the unit cell is dependent on the CNT volume fraction in the representative volume element (RVE). The CNT volume fraction (V_f) is an important variable in determining the composite mechanical properties and can be defined [12]:

$$V_f = \frac{\pi\left(R_{cnt} + \frac{h_{vdw}}{2}\right)^2}{Acell} \tag{9}$$

where h_{vdw} is the equilibrium van der Waals separation distance between the CNT and the matrix and A_{cell} is the cross-sectional area of the unit cell. It can be expressed as:

$$A_{cell} = \pi(R_m^2 - R_{cnt}^2) \tag{10}$$

The Vander Waals separation distance depends on the nature of the CNT-polymer interfacial interactions and is assumed to 0.4293 nm. To study the effect of volume fractions and diameter and length of nano tube on the Young's modulus of the polymer nanocomposite, after constructing the RVE, we impose load in the RVE, and the macroscopic behavior of the RVE can be evaluated using the FE method. We applied the armchair and zigzag nanotubes through the polymer matrix. It is to be noted that the RVE used here is a continue RVE. After constructing the model, the macroscopic behavior of the RVE can be using the FE method. To study the effect of vacancy defects on the stability of the nanocomposite, after constructing the RVE, we impose the vacancy defects [21, 22]. This is done by removing the proper nodes and elements from the model in accordance with removed atoms and bonds that might.

3 RESULTS AND DISCUSSION

Using the MSM approach and nonlinear finite element method, computational modeling of a continuous CNT/polymer composite has been carried out in this work. This Multiscale modeling approach is implemented to

study the mechanical properties of the polymer matrix nanocomposite under axial tensile loading. When considering the tube as a solid shell body, from the classical elastic, we assumed the deformation of nanocomposite is Iso strain; the results are compared with Rule of mixture. The rule of mixture can be expressed as:

$$E_Z = E_f V_f + E_m (1 - V_f) \tag{11}$$

where E_f and E_m are in order to nanotube modulus and matrix modulus and V_f is volume fraction. Iso strain assumption led to:

$$\frac{F_m}{A_m E_m} = \frac{F_{cnt}}{A_{cnt} E_{cnt}} \tag{12}$$

where F_m is the load that exert on cross-section area of matrix and F_{cnt} is the load of nanotube, E_m is the Young's modulus of polymer matrix. By applying the elastic relation of displacement Fig. 2, we will have:

$$E_c = \frac{F_{total} L}{A_{eq} \Delta L} \tag{13}$$

where E_c is the Young's modulus of nanocomposite in the longitudinal direction, ΔL is elongation in z direction; F_{total} is the total load that exerted on nanocomposite that expresses by following Equation:

$$F_{total} = F_{cnt} + F_m \tag{14}$$

The A_{eq} is the nanocomposite cross section area .it can be expressed as:

$$A_{eq} = \pi (R_m^2 - R_{cnt}^2) + \pi D_{cnt} t \tag{15}$$

The Poisson's ratio in zx plane is obtained

$$\upsilon_{zx} = -\frac{\Delta R}{R} / \frac{\Delta L}{L} \tag{16}$$

For short nanotube inside the polymer matrix, after applying tension force Fig. 3, the displacement in z direction determined by traditional Finite element method, δ is the displacement and we will obtain the Young's modulus of composite part as follow:

a) b)

Fig. 2
Finite element macroscopic model for CNT/polymer composite. CNT through the RVE a) Isometric view b) left view.

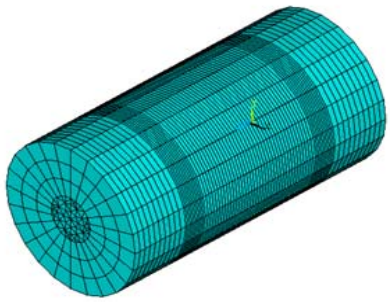

Fig. 3
Computational model for CNT/polymer composite.CNT inside the RVE

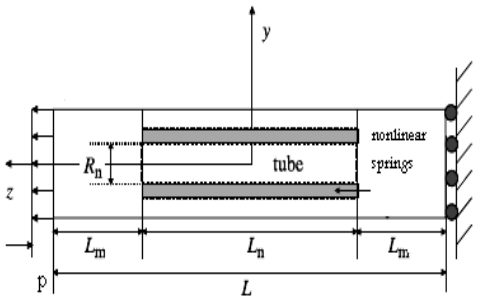

Fig. 4
For the case of the nanotube embedded inside the RVE.

$$\delta = \frac{P2L_m}{AE_m} + \frac{PL_n}{A_n E_c} \tag{17}$$

where L_m is the polymer matrix and p is tension force L_n is the composite part length, A_n and A are defined as:

$$A_n = \pi(R_m^2 - R_{cnt}^2), \qquad A = \pi R_m^2 \tag{18}$$

For the case of the nanotube embedded inside the RVE in Fig. 4 with the assumption of perfect bonding between the nanotube and matrix, [23] gave out the expression of the effective Young's modulus as follows:

$$\frac{1}{E_z} = \frac{2}{E_m}(\frac{L_m}{L}) + \frac{1}{E_c}(\frac{A}{A_n})(\frac{L_n}{L}) \tag{19}$$

After determining the properties of nanotube and nonlinear spring interaction between the nanotube and polymer matrix, the material properties of the nanotube reinforced composites can be predicted. Our numerical simulation is concentrated on the two case of polymer matrix reinforced with unidirectional short nanotubes inside the matrix and long nanotube through polymer matrix. This may be the ultimate goal for reinforcement. In this case, the RVE of our FEM model is shown in Fig. 2 for the polymer matrix, its Poisson ratio v_m is chosen as 0.3. The Young's modulus of polymer *Em* is quite scattered, depending on the various structures. Here, we take it as o.5 GPa in our Computation. In this study, we consider single, double, and triple vacancies in the nanotube structure as shown in Fig. 5. The models are under the tension loads and by using the above equation, the results is depicted in the Figs. 6-8. It is shown that Young's modulus in short length decrease under these defects but, at long length the effects of defect is negligible. The effect of third defect on the Young's modulus is most than others.

Next, an RVE for a short CNT in a matrix, as shown in Figs. 6 and 7 is studied. All dimensions for RVE are the same as in the previous, with the two hemispherical end caps. The material constants used for the CNT and matrix are the same as in the first example. Coupled DOF (degree of freedom) constraint is imposed for the surface under the axial load. Comparison of Young's modulus between defective zigzag and armchair CNTs indicates that the armchair CNT is more sensitive to vacancy defects. In addition, the mode shapes of defective nanotubes with a single vacancy and two opposite vacancies at the middle of the nanotubes are illustrated in Figs. 8.The mode shapes of the defective armchair CNT are not similar to those of the defective zigzag CNT. The main reason for this is the

different orientation of the vacancy defects .Another reason for this difference is due to orientation of the C-C bonds for zigzag CNTs that are in the load direction. Therefore, distribution of load on the carbon atoms for zigzag and armchair CNTs is uniform in the circumferential and axial direction, respectively [24].

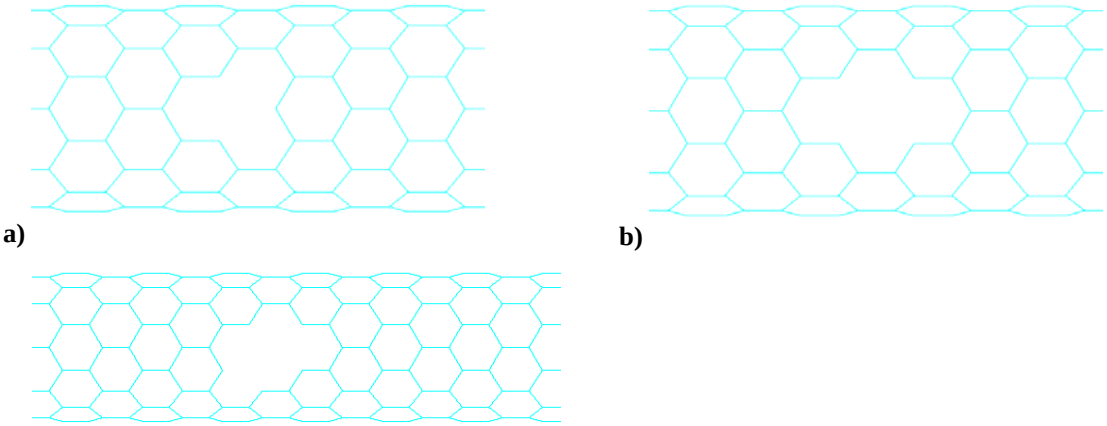

Fig. 5
Atomic networks of different single- wall CNTs with a) single b) double, and c) triple vacancies.

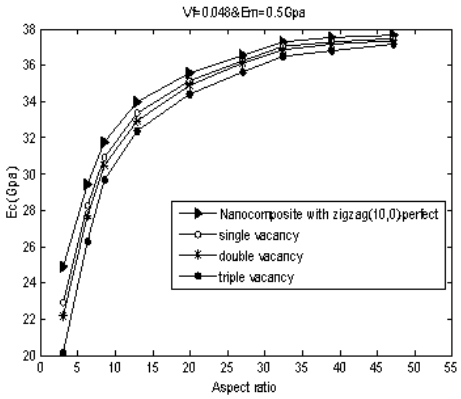

Fig. 6
Variations Young's modulus RVE for different types defects respect to aspect ratio and compare with zigzag (10,0) perfect model nanocomposite , (long CNT inside matrix, V_f =0.048and E_m=0.5 GPa).

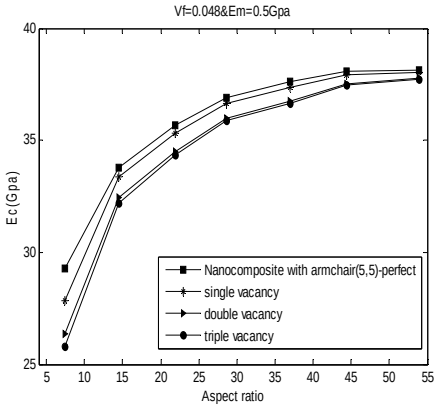

Fig. 7
Variations Young's modulus RVE for different types defects respect to aspect ratio and compare with armchair(10,10), perfect model nanocomposite, (long CNT inside matrix, V_f =0.048and E_m=0.5GPa).

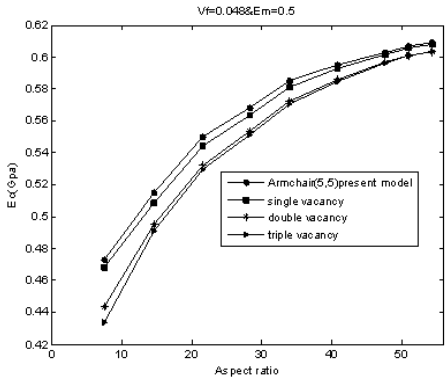

Fig. 8
Variations Young's modulus RVE for different types defects respect to aspect ratio and compare with armchair(5,5) perfect model nanocomposite, (short CNT inside matrix, V_f=0.048and E_m=0.5GPa).

4 CONCLUSIONS

In this article, a new MSM/FE Multiscale model of CNT-polymer composites under tension load was implemented to study the role of CNT vacancy defects on the stability of these nanocomposites. Using this model, we investigated the effects of these defects on Young's modulus. The results revealed that Young's modulus in short length decrease under these defects but, at long length the effects of defect is negligible. The effect of third defect on the Young's modulus is most than others. The present structural model can be used for prediction of the buckling behavior of CNT/polymer nanocomposite due to good agreement with the MD simulation.

5 ACKNOWLEDGMENT

The authors would like to acknowledge the Semnan University for supporting this research.

REFERENCES

[1] Iijima S., 1991, Helical microtubules of graphitic carbon, *Nature* 354- 568.
[2] Dresselhaus M.S., Dresselhaus G., Eklund P.C., 1996, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego.
[3] Nardelli M.B., Fattebert J.L., Orlikowski D., Roland C., Zhao Q., Bernholc J., 2000, Mechanical properties, defects and electronic behavior of carbon nanotubes, *Carbon* **38**: 1703–1711.
[4] Yakobson B.I., Avouris P., 2001, Mechanical properties of carbon nanotubes, *Carbon Nanotubes, Topics in Applied Physics*, edited by M.S. G. Dresselhaus, Dresselhaus, P. Avouris, Springer Verlag, Berlin/Heidelberg **80**: 287-329.
[5] Overney G., Zhong W., Tomanek D., 1993, Structural rigidity and low-frequency vibrational modes of long carbon tubules, *Zeitschrift Fur Physik D* **27**: 93-96.
[6] Lu J.P., 1997, Elastic properties of carbon nanotubes and nanoropes, *Physical Review Letters* **79**: 1297-1300.
[7] Chang T., Gao H., 2003, Size-dependent elastic properties of a single-walled carbon nanotube via a molecular mechanics model nanotubes, *Journal of the Mechanics and Physics of Solids* **51**: 1059-1074.
[8] Molina J.M., Savinsky S.S., Khokhriakov N.V., 1996, A tight-binding model for calculations of structures and properties of graphitic nanotubes, *Journal of Chemical Physics* **104**: 4652-4656.
[9] Hernandez H., Goze C., Bernier P., Rubio A., 1998, Elastic properties of C and B_x C_y N_z composite nanotubes, *Physical Review Letters* **80**: 4502-4505.
[10] Guzman de Villoria R.., Miravete A., 2007, Mechanical model to evaluate the effect of the dispersion in nanocomposites *Acta Materialia* **55** :3025-3031.
[11] Qian D., Wagner G.J., Liu W.K., Yu M.F., Rouff R.S., 2002, Mechanics of carbon nanotubes, *Applied Mechanics Review* **22**: 495-533.
[12] Tserpes K.I., Papanikos P., 2005, Finite element modeling of single-walled carbon nanotubes, *Composites Part B: Engineering* **36**: 468-477.
[13] Sakhaee-pour A., 2008, Vibrational analysis of single layered grapheme sheets, *Nanothechnology* **19**: 085702.
[14] Chopra N. G., Zettl A., 1998, Measurement of the elastic modulus of a multi-wall boron nitride nanotube, *Solid State Communications* **105**: 297-300.
[15] Krishnan A., Dujardin E., Ebbesen T.W., Yianilos P.N., Treacy M.M.J., 1998, Young's modulus of single-walled nanotubes, *Physical Review B* **58**: 14 013-14 019.

[16] Salvetat J.P., Bonard J.M., Thomson N.H., Kulik A.J., Forro L., Benoit W., Zuppiroli L.,1999, Mechanical properties of carbon nanotubes, *Applied Physics* A **69**: 255-260.

[17] Popov V.N., Van Doran V.E., Balkanski M., 2000, Elastic properties of single-walled carbon nanotubes, *Physical Review B* **61**: 3078-3084.

[18] Jin Y., Yuan F.G., 2002, Elastic properties of single-walled carbon nanotubes, in: *43rd AIA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*, April 22-25, Denver, Colorado, USA.

[19] Frankland S.J.V., Caglar A., Brenner D.W., Griebel M., 2002, Molecular simulation of the influence of chemical cross-links on the shear strength of carbon nanotube-polymer interfaces, *Journal of Physical Chemistry B* **106**: 3046-3048.

[20] Montazeri A., Naghdabadi R., 2009, Study the effect of Viscoelastic matrix model on the stability of CNT/polymer composites by Multiscale modeling, polymer composites, *Journal of the Brazilian Chemical Society* **20**(3): 466-471.

[21] Yu M.F., Lourie O., Dyer M.J., Moloni K., Kelly T.F., Ruoff R.S., 2000, Strength and breaking mechanism of multi walled carbon nanotubes under tensile load, *Science* **287**: 637-640.

[22] Krasheninikov A.V., Nordlund K., 2004, Irradiation effects in carbon nanotubes, *Nuclear Instruments and Methods in Physics Research Section B* **216**: 355-366.

[23] Li C., Chou T.W., 2003, A structural mechanics approach for the analysis of carbon nanotubes, *International Journal of Solids and Structures* **40**: 2487-2499.

[24] Sammalkorpi V.M., Krasheninnikov A.V., Kuronen A., Nordlund K., Kaski K., 2004, Mechanical properties of carbon nanotubes with vacancies and related defect, *Physical Review B* **1**: 1-8.