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New approach for modeling randomly distributed CNT reinforced polymer nanocomposite with van der Waals interactions

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Abstract. In this paper, using molecular and micromechanics methods, a new approach for the prediction of the stiffness of randomly distributed CNT/polymer nanocomposites with the van der walls interactions is presented. A multi-scale modeling technique was designed for CNT nanoparticles randomly embedded in the polymer using AMBER force field. This multi-scale model constitutes a representative volume element. The representative volume element consists of polymer, CNT nanoparticle, CNT-polymer interfacial region and van der waals bonds. A programming code was developed that randomly distributes nanoparticles according to the desired volume fraction. Python scripting language was used for the modeling technique performed in a finite element environment. By modeling the interfacial regions around randomly distributed CNTs, van der Waals bonds are modeled stochastically. In this study, the subject of interest is the number of CNTs positioned in the RVE according to the volume ratio. These numbers were determined at the level allowed by finite element equations and computational solvers and their effects were investigated by calculated stiffness behavior.

Introduction

With the discovery of nanomaterials, polymer nanocomposites are a new type of material whose advanced properties can be used in the polymer industry and new applications. Among nanomaterials, carbon nanotubes (CNTs) and graphene sheets are very important due to their superior mechanical, thermal and electrical superior and unique properties. Carbon nanotubes (CNTs) were discovered by Lijima in 1991 [2]. Carbon nanotubes have attracted the attention of scientists as reinforcement materials in nanocomposites with their low densities, high strength and high stiffness[3]. For example Qian et al.[4] when added only 1% by weight of carbon nanotubes to the polyester resin, they obtained a 35-42% increase in modulus of elasticity and a 25% increase in strength. In carbon nanotube-reinforced nanocomposites, the diameter and chirality of the carbon nanotube, its distribution, orientation and the general behavior of the polymer affect the properties of the nanocomposite. Therefore, modeling and simulations are very important in investigating the effect of adding carbon nanotubes to polymers. Epoxy polymers are well known for their excellent adhesion, significant mechanical and high electrical insulating properties, and relatively good chemical resistance. Epoxy is now widely used in various applications.

Tserpes et al. [5] investigated a multi-scale representative volume element for modeling the tensile behavior of carbon nanotube-reinforced composites. The RVE integrates nanomechanics and continuum mechanics, thus bridging the length scales from the nano- through the mesoscale. A progressive fracture model based on the modified Morse interatomic potential was used for simulating the behavior of the isolated carbon nanotubes and the FE method for modeling the matrix and building the RVE. The effect of interfacial shear strength on the tensile behavior of the

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nanocomposite was also studied. Stiffness was unaffected while tensile strength significantly decreased with decreasing the interfacial shear strength.

Khalili and Haghbin [6] to investigate the role of nanotube specifications on the nonlinear tensile behavior of nanocomposites, multi-scale material modeling was used. The effect of diameter, chirality and volume fraction of nonlinearly modeled. SWCNTs was studied on their nanocomposites. Multi-scale modeling was applied to assemble various RVEs composed of different SWCNTs embedded in a polymer. Continuum mechanics based on their atomic structures in the case of space frame structures were used to model nanotubes. Attained stress-strain curves of modeled nanocomposites revealed that using Armchair SWCNTs rather than Zigzags made nanocomposites tougher in tensile loading. Also, the diameter of CNT had an inverse effect on the stress-strain curve level. Using CNTs with smaller diameters, regardless of the chirality and type, made nanocomposites stronger in tension. Furthermore, the effect of diameter was more obvious in higher volume fractions of CNTs. Ayatollahi et al.[7] presented multiscale modeling for the nonlinear properties of a polymer/single wall carbon nanotube (SWNT) nanocomposite under tensile, bending and torsional loading condition. They used a finite element (FE) model based on the theory of molecular mechanics to predict the mechanical properties of both armchair and zigzag SWNTs. The equivalent beam element was then used to build a cylindrical representative volume element (RVE) where the effects of the interphase between SWNT and the polymer on mechanical response could be studied. The results showed that while the interphase had a small effect on the nanocomposite stiffness, the ratio of (SWNT length)/(RVE length) dramatically affected nanocomposite stiffness. For nano-structured materials a multi-scale model which is based on the equvalent continuum modeling technique was introduced by Odegard et al [8]. In their work the elastic parameters of the model were obtained through the same loading conditions in both the continuum model in finite element and the discrete model in molecular mechanics.

In this paper present a new multi-scale modeling approach including randomly-distributed carbon nanotube/epoxy nanocomposites with interfacial interactions to predic elastic properties and mechanical behavior of nanocomposites with single-walled carbon nanotube reinforcement. All modeling procedure and analyses were performed in ABAQUS finite element software [9].

Description of Multi-Scale Model

Geometry of Carbon Nanotubes

The CNT is a lattice of hexagonal bonds between carbon atoms, where each atom is bonded to the three nearest neighbors through very strong covalent bonds, 1.421 Å length. The mechanical and electrical properties of CNT depend on the direction and length of the vector, which describes the atomic arrangement of the bonds. This vector, in a word chirality vector or chirality index C_h, is produced from two vectors a_1 and a_2 of the unit cell in the CNT. The chiral vector consists of n units of $\vec{a}_1$ and m units of a_2 as seen in Figure 1.

$$C_h = n\vec{a}_1 + m\vec{a}_2 \text{ , } bn \geq m \quad (1)$$

Chirality index specified by (n,m), represents length and direction of chiral vector on a CNT. Three types of CNT are defined regarding the chiral index. Armchair geometry are defined by (n,n) ve Zigzag geometry by (n,0). Chiral CNT have different chirality indexes.

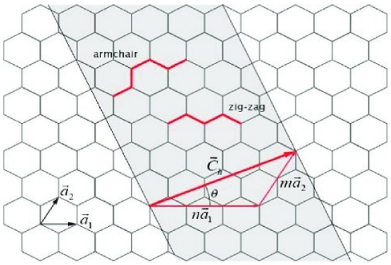

Figure 1. Schematic diagram of CNT geometry

The chiral vector with the length of L is rolled up and forms the nanotube circumference; the nanotube diameter can be obtained by the following equation [10]

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

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

Molecular Structural Mechanics Modelling

In computational nanomechanics, the energy of a system that includes hundreds of billions of atoms is evaluated by internal potential. The total potential energy function of an n-body structure is always clearly understood to address the configurational potential energy that can be the state of the coordinate of the constituent atom. The potential energy function explains as follows [10].

$$H_I = \frac{1}{2!}\sum_i \sum_{j\neq i} V_2(r_i, r_j) + \frac{1}{3!}\sum_i \sum_{j\neq i} \sum_{k\neq i,j} V_3(r_i, r_j, r_k) + \ldots \tag{3}$$

Where V_n, is n-body interatomic potential functions. The potentials are functions of atomic coordinates however these are stated in terms of interatomic distances in practice. Therefore, the potential energy depends on interatomic separation and the angle between bonds connecting individual atoms. The atomistic field of force consists of two basic potentials. These are potentials that occur between bonded atoms (V_{bonded}) and potentials that occur between atoms that are not bonded to each other ($V_{non\text{-}bonded}$). Figure 2 shows the atomic force field due to this work potential [10].

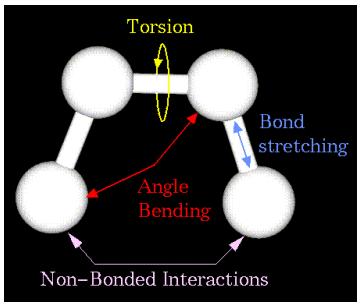

Figure 2. Atomic force field

$$U = U_{bonded} + U_{non\text{-}bonded} \tag{4}$$

In molecular mechanics, CNTs are acceptable as great molecules including carbon atoms. Thus, the potential energy function is expressed as steric potential energy, which depends only on the position of the nuclei of the carbon atoms. The general form of force field of a nanostructure explains such as [10]

$$U = \sum U_r + \sum U_\theta + \sum U_\emptyset + \sum U_W + \sum U_{vdw} \tag{5}$$

where represents the bonded interatomic potential, $\mathbf{U_r}$,is bond stretching, $\mathbf{U_\theta}$, is bond bending angle, $\mathbf{U_\emptyset}$ is dihedral torsion bending, $\mathbf{U_W}$, out of plane torsion and $\mathbf{U_{vdw}}$ is Van der Waals interactions potential between non-bonding atoms.

The molecular mechanical modeling method is intended to simulate the atomic properties of the CNT as a space framework in classical structural mechanics. Therefore, as seen in Figure 3 carbon atoms on CNT are acceptable as load-carrying beam elements. Simple harmonic functions and an Amber force field are applied to explain terms of potential energy in molecular mechanics [10].

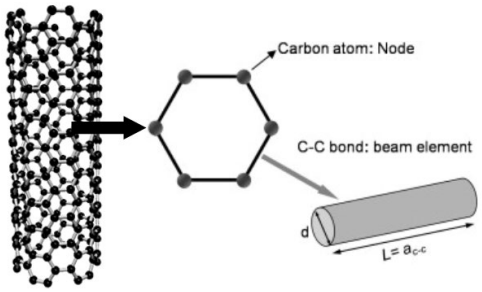

Figure 3. Model of CNT as a space-frame structure

$$\text{Bond Stretching Energy : } U_r = \frac{1}{2}k_r(r - r_0)^2 = \frac{1}{2}k_r(\Delta r)^2 \tag{6}$$

$$\text{Bond Angle Bending Energy : } U_\theta = \frac{1}{2}k_\theta(\theta - \theta_0)^2 = \frac{1}{2}k_\theta(\Delta\theta)^2 \tag{7}$$

$$\text{Bond Torsion Energy : } U_\tau = \frac{1}{2}k_\tau(\tau - \tau_0)^2 = \frac{1}{2}k_\tau(\Delta\tau)^2 \tag{8}$$

where, $\mathbf{k_r}$, $\mathbf{k_\theta}$, $\mathbf{k_\tau}$ are bond stretching force, bond angle bending force and torsional preventive constant, respectively, and the increase in these forces is expressed by the following symbols, respectively, $\Delta\boldsymbol{r}$, $\Delta\boldsymbol{\theta}$ and $\Delta\boldsymbol{\tau}$. In structural mechanics, the tensile energy of a regular beam element representing a carbon bond of length L due to deformations is expressed as [10]:

$$U_A = \frac{1}{2}\int_0^L \frac{N^2}{EA}dL = \frac{1}{2}\frac{N^2L}{EA} = \frac{1}{2}\frac{EA}{L}(\Delta L)^2 \tag{9}$$

$$U_T = \frac{1}{2}\int_0^L \frac{T^2}{GJ}dL = \frac{1}{2}\frac{T^2L}{GJ} = \frac{1}{2}\frac{GJ}{L}(\Delta\beta)^2 \tag{10}$$

$$U_M = \frac{1}{2}\int_0^L \frac{M^2}{EI}dL = \frac{2EI}{L}\alpha^2 = \frac{1}{2}\frac{EI}{L}(2\alpha)^2 \tag{11}$$

where $\mathbf{U_A}$, $\mathbf{U_T}$, $\mathbf{U_M}$ are the strain energies of a beam element due to axial force N, causing bending moment M, causing torsion T respectively. In relation to them, ΔL, α, Δβ are axial stretching deformation, rotating angle at the end of the beam and the relative rotation between the ends of the beam, respectively.

$$\frac{EA}{L} = k_r, \frac{EI}{L} = k_\theta, \frac{GJ}{L} = k_\tau, \tag{12}$$

Beam elements are expressed from a circular cross-section. Taking into account the molecular mechanical parameters from the amber force field, the beam elements E, G and diameter (d) are made available for application in structural mechanics modeling with the following relations:

$$d = 4\sqrt{\frac{k_\theta}{k_r}}, E = \frac{k_r^2 L}{4\pi k_\theta}, G = \frac{k_r^2 k_\tau L}{8\pi k_\theta^2} \quad (13)$$

Table 1. Amber Force Field Constants [10]

k_r ,	938 kcal mol^{-1} A^{-2}	6.52x10^{-7} N nm^{-1}rad^{-2}
k_θ ,	126 kcal mol^{-1}rad^{-2}	8.76x10^{-10} N nm rad^{-2}
k_τ ,	40 kcal mol^{-1} rad^{-2}	2.78x10^{-10} N nm rad^{-2}

The mechanical properties of the beam elements are as follows:

Table 2. Mechanical properties of beam elements

d	0.147 nm
E	5.49 TPa
G	0.87 TPa

This formulation was applied in the finite element method by solving the system of matrices that are derived for circular two-node beam elements. Each node has six degrees of freedom (DOF), three translational (x, y, z) and three rotational degrees of freedom (DoF).

Modelling of Carbon Nanotubes with Representative Volume Element (RVE)

In this study linear Euler-Bernoulli beam elements with six degrees of freedom are used for molecular mechanic modeling. This element, is based on known elastic parameters such as the Young Modulus (E) and shear modulus (G) and also on the diameter obtained by the molecular structural modeling method. Beam elements are applied to a space-frame structure which is modeled geometrically with coordinates of carbon atoms in its molecular structure. Coordinates are obtained by using a nanomaterial modeling program. After that, beam elements are placed between two carbon atoms respecting the chirality of CNT. ABAQUS finite element software was used to model CNT nanocomposites as shown in Figure 4.

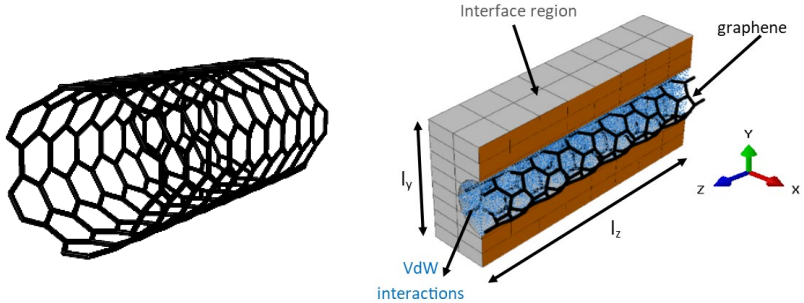

Figure 4. Carbon nanotube and RVE modeled in ABAQUS

Randomly Distributed Algorithm

The realistic behavior of CNT reinforced nanocomposite was modeled using a new random distribution algorithm proposed by this study. This algorithm was developed with the open-source programming language Python, in which the finite element code is also written. The random distribution algorithm of nanoparticles in a polymer matrix without intersecting each other was created with the following steps:

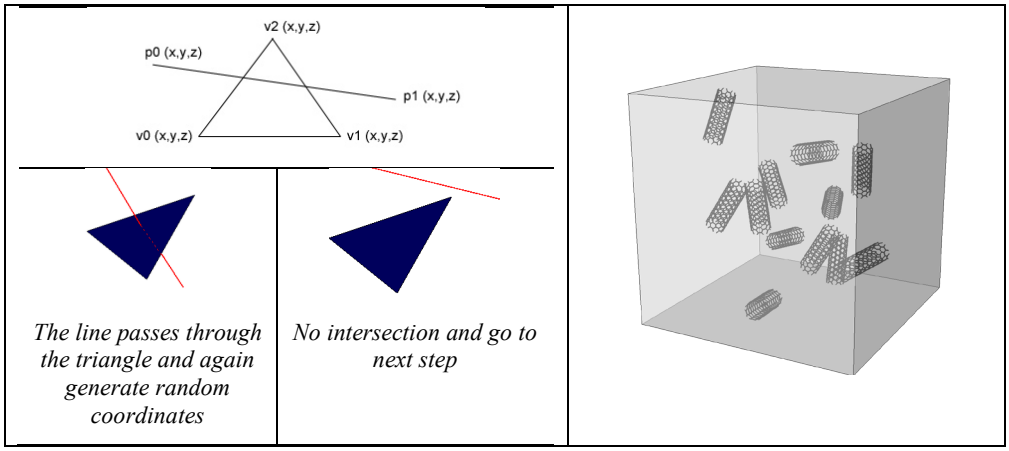

Figure 5. Checking intersection of a surface with a line, plotted core and transferred to finite element code

- Input step: Input information is needed for algorithm logic to work.
- Drawing step: According to the control volume dimensions received as input from the user, a center in 3-dimensional space is determined.
- Generating random coordinate step: In this stage, random coordinates need for the positioning of the drawn geometries within the control volume.
- Moving step: CNT particles in the center of the control volume are positioned according to randomly generated coordinates considering reference point in the center of the CNT.
- Checking intersection step: The steps of the developed algorithm up to this step include classical methods. After the CNT is positioned randomly within the control volume, it is necessary to check whether any of CNT cross-sections intersect with the control volume.
- Output step: The coordinates according to the written algorithm are imported into a text file.

Interactions Between CNT and Epoxy

Interfacial interactions between matrix and reinforcement have a great effect on the general properties of nanocomposites. Electrostatic interactions are negligible compared to Van der Waals interactions as the Van der Waals interaction contributes three orders of magnitude higher than electrostatic energy. Non-linear Van Der Waals force, with respect to interatomic distance, explained by the 6/12- Lennard-Jones equation [11];

$$F_{udW} = \frac{48e}{r}\left[-\left(\frac{\sigma}{r}\right)^{12} + 0.5\left(\frac{\sigma}{r}\right)^{6}\right] \quad (14)$$

Lennard-jones parameters, e and σ, are 0.4396 kJmol^{-1} and 0.3851 nm, respectively [12]. The interactions between the carbon atoms of the CNT and the nodes of the inner surface of the surrounding polymers, Van der Waals interaction will be modeled using the axial translation connector type (CONN3D2). These linear elements, which have different names in the finite element method, are named 'connector elements' in the ABAQUS software. In this way, only the Van der Waals interaction between the CNT node (atom) and the adjacent nodes of the polymer will be created. Van der Waals force is a non-linear force and can be neglected when the interatomic distance is greater than or equal to 0.85 nm as shown in Figure 5[12].

Between these nodes, a code would be written to form an element with distances less than 0.85 nm, and van Der Waals bonds would be formed only between the carbon atoms of the carbon nanotube or graphene and the inner surface of the polymer.

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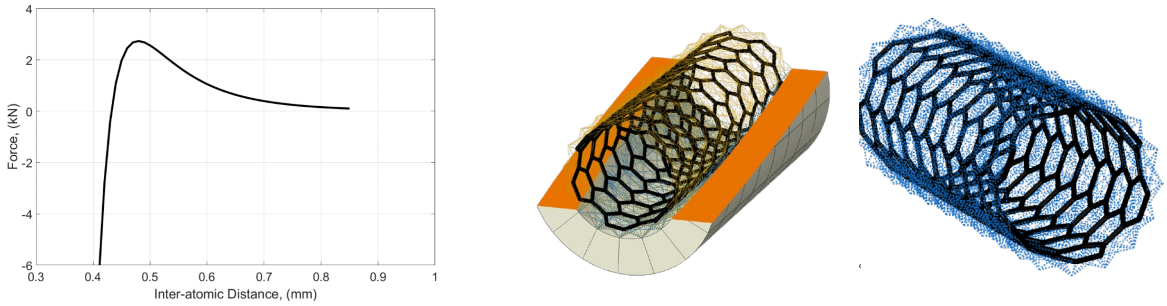

Figure 6. Van der Waals forces-interatomic distance variation

Stochastic RVE configurations

In this study, the polymer was considered as a linear elastic material with a Young's modulus of 2 GPa and a Poisson ratio of 0.35. Linear cubic eight-node elements with six degrees of freedom for each node in space were used to connect the polymer part in the finite element. CNTs were located in the middle of the representative volume element of the same length as the polymer interface. The CNT volume ratio was calculated by ABAQUS and the thickness of the CNT was taken to be equal to the interlayer space in the graphite sheets, i.e. 0.34 nm. Stochastic is an adjective that means variable, random, unpredictable. Stochastic processes are especially important in engineering. Transferring the stochastic process to numerical work is important for more accurate results. The stochastic process to be represented in this study is based on the unpredictable dispersal of CNT and the unpredictable Van der Waals interactions. At this point, there is another issue that makes the study more original and difficult. A bond was established between CNT atoms and polymer atoms, but these bonds form an interfacial layer on polymer atoms and the mechanical behavior of this interface region is different from the[13]. Interface material is also included in this unpredictable distribution. The interface material was modeled as embedded in the polymer material and included in the stochastic model. In the study, the transfer of mechanical properties from the interface material to the polymer was considered linear. This may result in transferring the high mechanical properties of nanomaterials to the polymer more than necessary. A description of the multi-scale model is given in Figure 7.

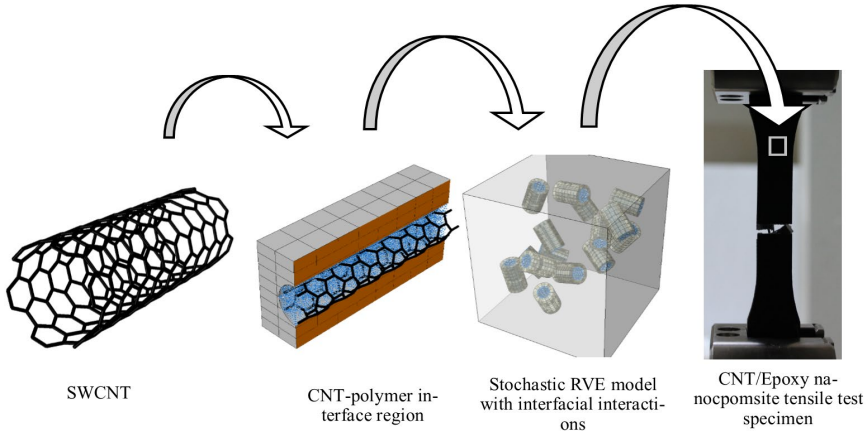

Figure 7. description of the multi-scale model

In this study, after the above-described tube processes have been carried out, there is only one point left to be decided. This situation constitutes the aim and originality of the study. The number of CNT to be used in the analysis according to the determined volume ratio is the first parameter that will affect the results. As this number increases, the interfaces and vdw interactions will also increase. Its solution is related to its solution capabilities. In this study, the case of randomly dispersed 5, 10 and 15 CNT in a representative volume element at 1% volume was investigated for all direction. Under these conditions, dimensions were formed according to the determined

volume ratio, CNT moved to randomly determined positions in the cubic volume element, interfacial phases were formed around them first, and van der walls interactions were formed for each CNT with its own phase under the specified conditions. This process is explained in detail in Figure 7 and the information about all RVE models were given in the table 3.

Table 3. Information about the RVE models

	Volume Fraction	CNT (Å)	CNT Volume (Å^3)	Epoxy (Å)	Number of VdW İnteractions
CNT-5	0.5, 1, 2 %	C_h(6x6)	5x835.21	75**x**75**x**75	22924
CNT-10		L_{CNT} =24	10x835.21	95**x**95**x**95	45844
CNT-15		$d_{(C-C)}$=0.735	15x835.14	108**x**108108	68768

Figure 8 shows the proposed RVE models for multi-scale **s**tochastic modeling of CNT nanocomposites. Along with investigating the effect of CNT number in RVE, the effect of CNT volume ratio on mechanical properties and modulus of elasticity was also investigated. For the tensile behavior of the CNT nanocomposite, the total force was calculated by applying 10% displacement to the RVE. The finite element model is shown in Figure 9.

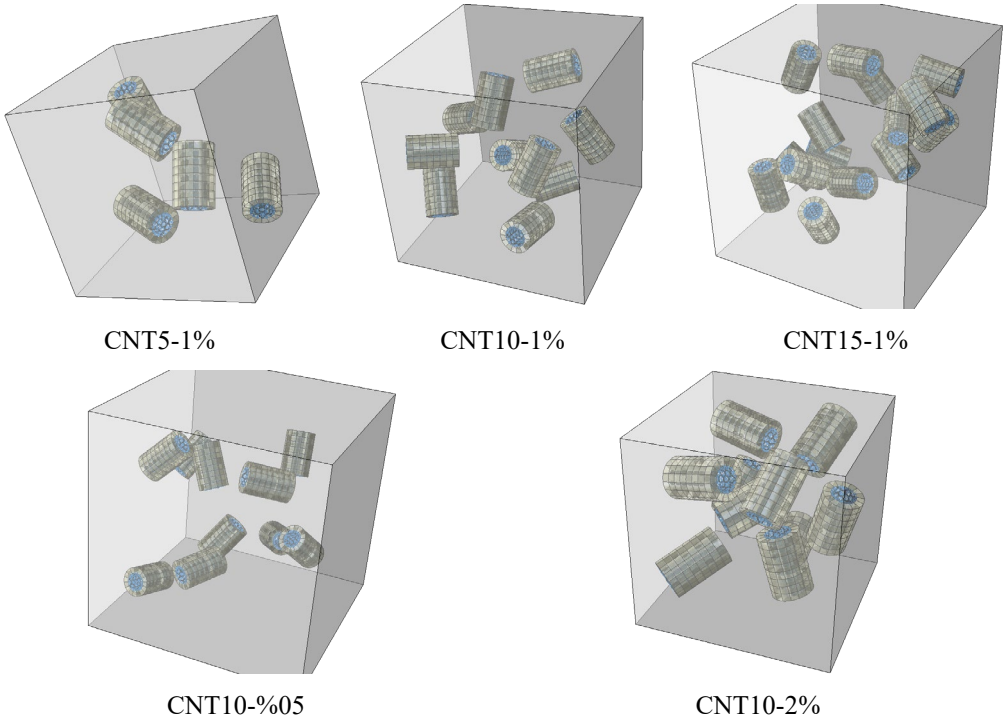

*Figure 8. Proposed RVE models for multi-scale **s**tochastic modeling of CNT nanocomposites*

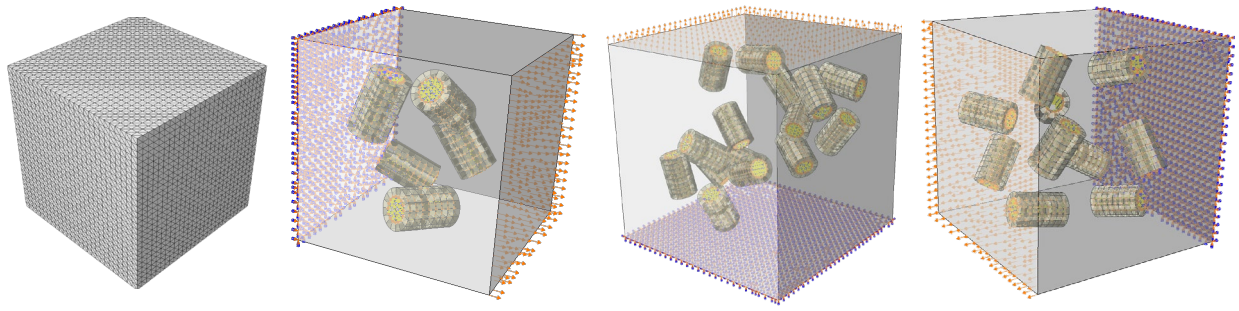

Figure 9. FE model of RVE

Results &Conclusion

Multi-scale material modeling with a stochastic approach with van der walls interaction was applied to investigate the effect of CNT quantity in an epoxy matrix, volume fraction and random distribution by direction of CNT. First, the effect of the number of CNTs in epoxy at the same volume fractions was investigated on RVEs under tensile load. Stress-strain curves and modulus of elasticity were calculated. Models named pure epoxy, CNT5, CNT10 and CNT15 were compared in the graphics. The general result in nanocomposites modeled at 1% volume ratio; the strength increases as the number of CNTs in the epoxy increases (Figure 10). The model with a CNT number of 5 showed approximately two times more resistance than pure epoxy. However, this increased rate decreased as the number of CNTs increased. With the increase in the number of CNTs in the models created to the extent of computational ability, the models will be able to give stable results. In order to examine the results of the random distribution effect, tensile loads were applied separately in 3 different axes, and the results were compared. Stress-Strain behaviors showed similar results. However, differences emerged in the Elasticity module. While the X and Y directions show similar results, the Z direction is calculated differently.

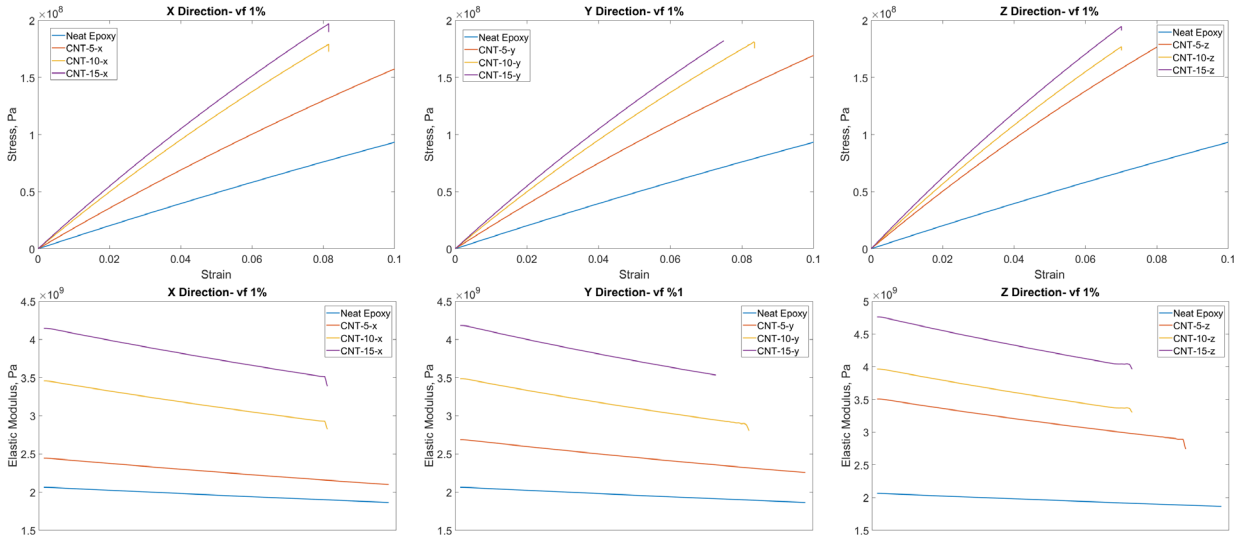

Figure 10. The effect of CNT quantity inside epoxy on the stress-strain behavior and elastic modulus for x, y and z direction.

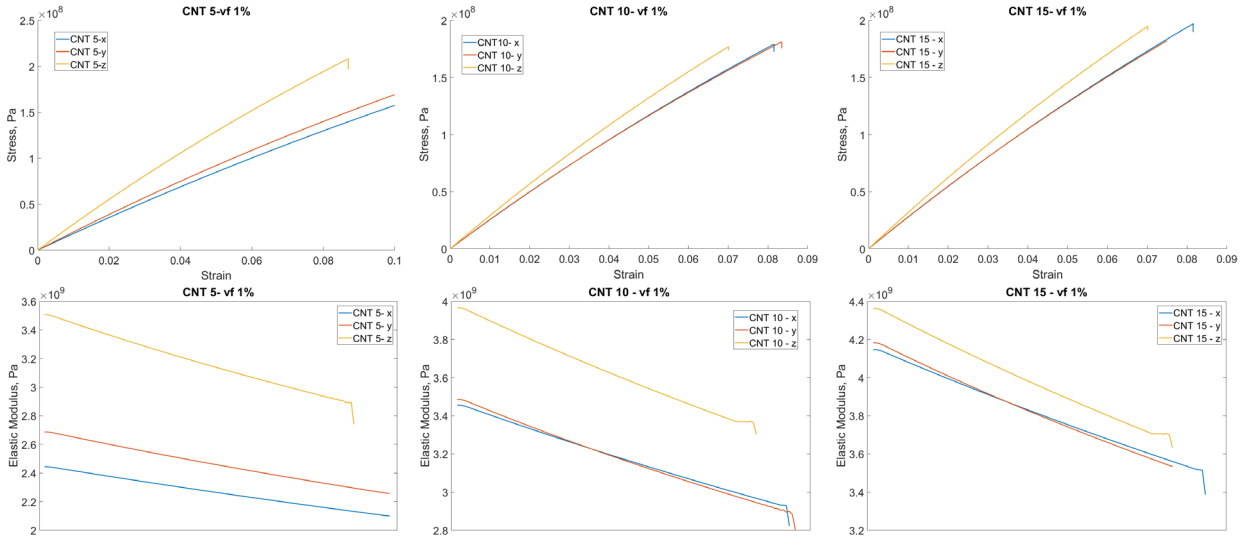

Figure 11. The effect of tensile direction on the stress-strain behavior and elastic modulus for different CNT quantity inside epoxy.

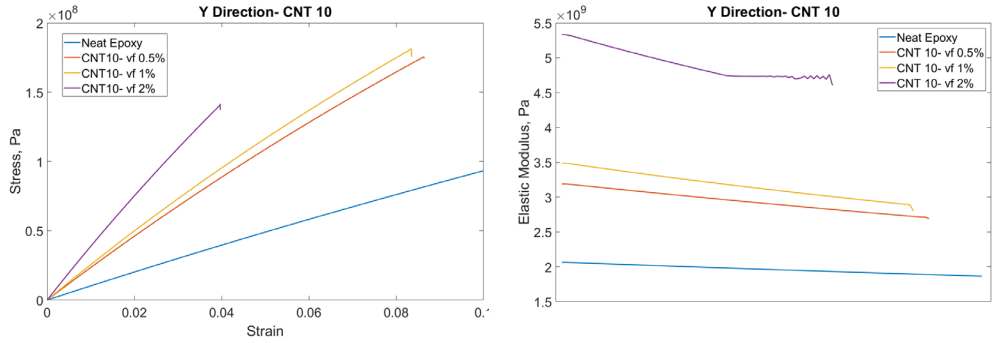

Figure 12. The effect of volume fraction of CNT nanocomposites on the stress-strain curve and elastic modulus variation.

In Figure 11, comparisons of the mechanical behavior of models with the same CNT number under loading in the x, y and z directions are given. Especially the distribution results in x and y directions were similar. The distribution results in the Z direction revealed higher stress levels and modulus of elasticity. In Figure 12, the results of the CNT volume ratio effect in the nanocomposite are given. The mechanical behavior of pure epoxy was improved with the use of CNT. 0.5% and 1 gave approximate results, while 2% gave very high results.

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References

[1] A. Hussein, B. Kim, Micromechanics based FEM study on the mechanical properties and damage of epoxy reinforced with graphene based nanoplatelets, Composite Structures, 215 (2019), 266-277. https://doi.org/10.1016/j.compstruct.2019.02.059

[2] S. Iijima, Helical microtubules of graphitic carbon. Nature, 354 (1991), 56-8. https://doi.org/10.1038/354056a0

[3] D. Qian, G. J. Wagner, W. K. Liu, M. F. Yu, R. S. Ruoff, Mechanics of carbon nanotubes, Applied Mechanics Reviews, 55(2022), 495-533. https://doi.org/10.1115/1.1490129

[4] D. Qian, E. Dickey, R. Andrews, T. Rantell, Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites, Appl Phys Lett, 76(2000), 2868-70. https://doi.org/10.1063/1.126500

[5] K.I. Tserpes, P. Papanikos, G. Labeas, and Sp.G. Pantelakis, Multi-scale modeling of tensile behavior of carbon nanotube-reinforced composites, Theoretical and Applied Fracture Mechanics, 49(2008), 51-60. https://doi.org/10.1016/j.tafmec.2007.10.004

[6] S.M.R. Khalili and A. Haghbin, Multi-scale modeling of nonlinear tensile behavior in single-walled carbon nanotube reinforced nanocomposites, International Journal of Modeling and Optimization,1(2011), 199-204. https://doi.org/10.7763/IJMO.2011.V1.35

[7] M.R. Ayatollahi, S. Shadlou and M.M. Shokrieh, Multiscale modeling for mechanical properties of carbon nanotube reinforced nanocomposites subjected to different types of loading, Composite Structures, 93(2011), 2250-2259. https://doi.org/10.1016/j.compstruct.2011.03.013

[8] G.M. Odegard, T.S. Gates, K.E. Wise, C. Park, E.J. Siochi, Constitutive Modeling of Nanotube-Reinforced Polymer Composites, Composites Science and Technology, 63 (2003), 671-1687. https://doi.org/10.1016/S0266-3538(03)00063-0

[9] ABAQUS/Standart, User's manual, Finite Element Software. www.simulia.com

[10] S.M.R. Khalili and A. Haghbin, Investigation on design parameters of single-walled carbon nanotube reinforced nanocomposites under impact loads, Composite Structures, 98(2013), 253-260. https://doi.org/10.1016/j.compstruct.2012.09.049

[11] L. Battezzati, C. Pisani, F. Ricca, Equilibrium conformation and surface motion of hydrocarbon molecules physisorbed on graphite J. Chem. Soc., Faraday Trans. 2: Mol. Chem. Phys., 71 (1975), 1629-1639. https://doi.org/10.1039/f29757101629

[12] Z. Shokrieh, M.M. Shokrieh, A new model to simulate the creep behavior of graphene/epoxy nanocomposites, Polymer Testing, 75 (2019), 321-326. https://doi.org/10.1016/j.polymertesting.2019.02.032

[13] Shokrieh, M., M., Rafiee, R. Investigation of nanotube length effect on the reinforcement efficiency in carbon nanotube based composites, Composite Structures, 92 (2010) (10), 2415-2420. https://doi.org/10.1016/j.compstruct.2010.02.018