

Investigation of CNT Defects on Mechanical Behavior of Cross linked Epoxy Based Nanocomposites by Molecular Dynamics

Farshid Aghadavoudi

Faculty of Engineering,
Shahrekord University, Iran
E-mail: farshid_ad@yahoo.com

Hossein Golestanian*, Yaghoub Tadi Beni

Faculty of Engineering,
Shahrekord University, Iran
E-mail: golestanian@eng.sku.ac.ir, / : tadi@eng.sku.ac.ir
*Corresponding author

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Abstract: Although carbon nanotubes (CNT) have been employed as reinforcements in nanocomposites, presence of nano scale defects such as Stone-Wales and vacancy defects in carbon nanotubes (CNT) weakens the mechanical properties of these materials. In this paper the effects of defects in CNTs on nanocomposite elastic behavior are investigated using molecular dynamics. Stiffness matrices of CNT and nanocomposite indicated the transversely isotropic behaviour of nanocomposite molecular model. Longitudinal and transverse Young's moduli for both perfect and defected CNT/epoxy nanocomposites are determined. A comparison between the results illustrates that the number and type of CNT defects have significant effects on mechanical behaviour of nanocomposite. Based on molecular dynamics results, CNT defects significantly affect the Young's modulus particularly in the transverse direction. Comparison between molecular simulation predictions and rule of mixtures results indicates that some correlation factors must be incorporated when using the micromechanical theories at nano scales.

Keywords: CNT, Defect, Nanocomposite, Stone-Wales, Vacancy

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Biographical notes: **H. Golestanian** received his PhD in Mechanical and Aerospace Engineering from University of Missouri-Columbia, USA in 1997. He is currently an Associate Professor at the Department of Mechanical Engineering, Sharekord University, Shahrekord, Iran. His current research interests include modelling of nanocomposites. **F. Aghadavoudi** is a PhD student of mechanical engineering at Sharekord University. **Y. Tadi Beni** received his PhD in Mechanical Engineering from Sharif University of Technology, Iran. He is currently an Associate Professor at the Department of Mechanical Engineering, Sharekord University, Shahrekord, Iran. His current research interest includes elasticity and nonlinear continuum mechanics.

1 INTRODUCTION

1.1 Background

Discovery of Carbon Nanotubes (CNTs) by Ijima [1] in 1991 has attracted great attention of researchers to use CNTs as a reinforcement in polymer nanocomposites. CNTs have exceptional thermal, electrical and mechanical properties such as: high longitudinal Young's modulus of about 1TPa and tensile strength up to 150 GPa [2-4]. These exclusive properties accompanied by light weight of CNTs make them suitable candidates for reinforcement in nanocomposites. CNTs could be added to brittle materials such as cured epoxy resins to improve the stiffness and toughness simultaneously [5].

Experimental tests for measuring the mechanical behaviour of nanocomposites are expensive, therefore several researches focus on predicting mechanical properties by conventional approaches such as micromechanical theory or finite elements [6-9]. Because of large value of surface to volume ratio in nano reinforcement, the material properties of nanocomposites are strongly dependent on atomistic structures and morphology of constituents [10]. This phenomenon is called nano effects in some literatures [11]. Consequently predictions of mechanical properties by classical approaches such as micromechanical theory are not reliable because these approaches are not sensitive to some issues such as morphology or atomistic structures [12].

Molecular Dynamics (MD) has become a powerful tool for modelling nanocomposites by considering the atomistic structures. Some researchers have applied MD to predict the behaviour of nanocomposites and CNTs during the past two decades [5,13-15]. Despite the success of molecular dynamics approach in modelling the nanocomposite structures, for achieving accurate results, some challenges must be overcome in molecular modelling of CNT reinforced polymer-based nanocomposites. These challenges include:

- i) Molecular modelling of thermoset polymers like epoxy resins is associated with some computational challenges due to cross linking between cured resin and curing agent. Accuracy of predicted mechanical properties depends on cross linking modelling [10].
- ii) The mechanical properties of CNTs and nanocomposites reported from simulation and experiments show substantial variations [16, 17]. These variations indicate that some issues have not been considered in modelling. CNT defects are one of the effective factors which could cause the scatter in the data reported for mechanical properties of nanocomposites.

1.2 Pervious works

The formation of defects in CNTs and their effects on material properties have been the focus of many researches. Mielke et al. found that removing one atom from CNT structures can reduce the fracture strength up to 26% [23]. They reported that both SW and vacancy defects reduce the CNT failure strength but SW influence on strength is less than vacancy defects. Lu and Bhattacharya [22] and Chandra et al. [17] in separate studies investigated the effect of SW defect on mechanical behaviour of CNTs. These researchers observed that CNT properties degraded due to SW defects. Lu and Bhattacharya employed a random function for describing the distribution of SW defects on CNT surface [22]. They used Morse potential function for interatomic forces for prediction of mechanical behaviour of defected armchair and zigzag CNT samples. They reported the mean values of stiffness and ultimate strength for defected CNT (6,6) and CNT(10,0).

Xiao and Hou studied the mechanical behaviour of CNTs with randomly located vacancy defects [26]. They used atomistic approach for modelling of one, two and cluster atom vacancy defects. In their study, the reconstructed structure for defected CNT was employed. They investigated the fracture, bending and torsion in defected nanotubes. Sammakorpi et al. studied the effects of non-constructed and reconstructed vacancy defects on mechanical properties of CNTs [25]. They derived analytic expressions for predicting Young's modulus of defected CNTs. Kuwar and Kamal used molecular dynamics for comparative investigation of SW and vacancy defects on mechanical performance of CNTs [27]. They reported that CNT Young's modulus weakened by 9% to 11% due to defects.

Although several evidences prove the presence and influence of defects in CNT structure, most researchers considered the pristine CNTs in modelling the nanocomposites [6-9]. Few works have been done on investigation of elastic behaviour of nanocomposites reinforced with defected CNTs. Mahboob and Islam simulated a defective CNT polyethylene based nanocomposite using molecular dynamics [28]. They constructed different nanocomposite models including several SW defected CNTs. They concluded that longitudinal Young's modulus is significantly dependent on the number of SW defects in CNTs. Davoudabadi and Farhani investigated the effects of vacancy defects on elastic behaviour of CNT/polymer nanocomposites using multiscale approach [29]. They used molecular structural mechanics and finite element modelling for determining the effects of defective CNTs with various aspect ratios on Young's modulus of nanocomposite. Their results showed a reduction of Young's modulus for short CNTs. They used non-constructed vacancy defect for modelling the

nanocomposite. Komuves et al. studied the effect of CNT defects on mechanical properties of CNT-epoxy nanocomposite [30]. They reported a reduction between 13% to 30% in the Young's modulus of nanocomposite with defected CNTs.

1.3 Objective of the Study

As mentioned in the previous section, few studies have been performed on defective CNT-reinforced nanocomposites. Epoxy based nanocomposites with cross linking structure as the matrix and defective CNT as the reinforcement have not been studied. The aim of this paper is to investigate the effects of carbon nanotube SW and vacancy defects on elastic properties of nanocomposites considering the cross linking in epoxy resin. Molecular dynamics (MD) has been used for simulation and predicting the nanocomposite mechanical properties. The main objectives of this investigation are quantifying the reduction in Young's modulus in: (i) SW defects, (ii) vacancy defects and (iii) cross linked epoxy based nanocomposite. In addition, the obtained results are compared with rule of mixtures predictions. In section 2 molecular structure and simulation details have been described. Obtained results are discussed in section 3. The results are validated in section 4. Finally, the concluding remarks are presented in section 5.

2 MATERIAL AND METHOD

2.1 CNT Defects

Mechanical behaviour of CNTs strongly depends on CNT specifications such as diameter, chirality and defects. It is noted that most of these specifications have not been considered in micromechanical simulation approach due to simplifications made in the models. Various types of defects were observed in the CNTs structure such as vacancies, Stone-Wales, heterogeneous atoms, metastable atoms, discontinuity of walls and distortion in CNT bundles [18]. These defects could form during the CNT manufacturing or purification processes. Some defects may form during composite production, mechanical loading or electronic irradiation. STM tests have showed that stable defects exist in 10% of CNT samples on the average [19]. Consequently researchers assume a random distribution for defects in CNT structures which is similar to experimental observations.

Stone-Wales (SW) defect is a point defect, which is created by converting four adjacent hexagons into two pentagons and two heptagons in CNT structures. As can be seen in Fig. 1, this defect is formed by rotating a sp^2 C-C bond by 90 degrees [20]. The resulted structure has a stable 5-7-7-5 topological defect. Experimental tests have shown the

presence of SW defect in CNTs [21]. Furthermore, most studies indicate that mechanical properties of CNTs are affected by SW defects [22].

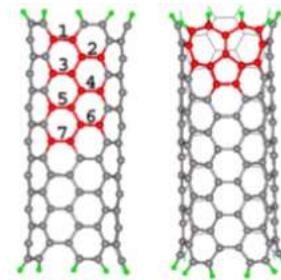


Fig. 1 Creation of Stone-wales Defect [20]

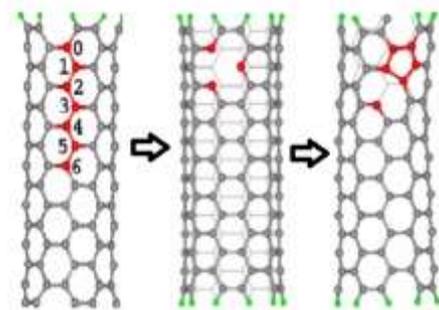


Fig. 2 Creation of single vacancy defect in nonconstructed configuration and transformation to reconstructed configuration [20]

Vacancy defects have the most influence on mechanical behaviour of CNTs among various types of defects [22, 23]. To create a vacancy defect, one or more atom(s) is removed from CNT structures. Vacancy defect is not stable and could be changed into a reconstructed structure by an annealing process. As can be seen in Fig. 2, a CNT with a single vacancy (one atom missing), which is called non-constructed configuration, transforms to a reconstructed configuration with more stability. Researchers believe that vacancy defects commonly are created by irradiation [24, 25].

2.1 Molecular Structures

In this paper, nanocomposite samples consisting of cross-linked epoxy resin and defected CNTs are simulated using molecular dynamics. A CNT with (6,6) armchair configuration and a length of 24 Å and a diameter of 8.14 Å is modelled in Materials Studio software. The epoxy matrix is composed of EPON 825 epoxy resin with DETA curing agent. The chemical structures of the molecules are shown in Fig. 3. In the curing process, the epoxy molecules can react with amine groups, based on the distance between reactive sites. The cross linking process has been described later.

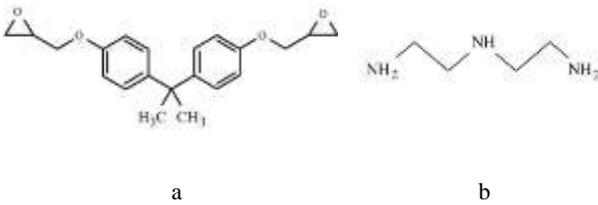


Fig. 3 Chemical Structure of a: EPON 825, and b: DETA

2.2 Forcefield

Forcefields are collections of parameters and equations that, in association with an atomistic model, allow a potential energy expression to be constructed for the model in hand. Selection of appropriate forcefield in molecular dynamics modelling is a challenging step. In this study Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS 27) forcefield has been selected for modelling the nanocomposites. COMPASS is the first ab-initio forcefield which successfully have been employed for predicting thermo-mechanical properties of polymers like epoxy resins [31, 32], CNT [33] and CNT/polymer nanocomposites [10, 14]. The COMPASS parameters for covalent molecules have been thoroughly validated using various calculation methods including extensive molecular dynamics simulations of liquids, crystals, and polymers. Moreover, the van der Waals parameters were optimized to fit the condensed-phase properties by refined Lennard-Jones 6-9 parameters. The potential energy function, E_{total} used in this field consists of the valence term, $E_{valance}$, cross term, E_{cross} , and non-bond term, $E_{non-bond}$ [28]. The cross term interacting energy, E_{cross} , includes several terms which calculate the energy of the variation of bond length and angle created by the surrounding atoms [28]. Non-bond interaction term, $E_{non-bond}$, represents the non-bonded coulomb and van der Waals intra-atomic potential energies.

2.3 Cross linking procedure

Cross-link is a covalent bond formed when epoxy molecules react with curing agent molecules. In crosslinking reactions of EPON 825 and DETA, as can be seen in Fig. 4, C-O bond within the epoxide group is broken, and the carbon end of the opened epoxy group reacts with nitrogen of the amine group in the curing agent molecule. Many researchers suggest some procedures to obtain cross-linked epoxy from neat resin and curing agent using MD simulations [34-36]. In this investigation, a dynamic approach is used to simulate the cross-linking process. The process includes a cyclic set of minimization, equilibration, and bonding to construct the final cross-linked structure. In

the equilibrium phase, NVT ensembles were conducted to the molecular model at a temperature of 600 K for 100 ps, followed by NPT ensemble at 300 K for 100 ps.

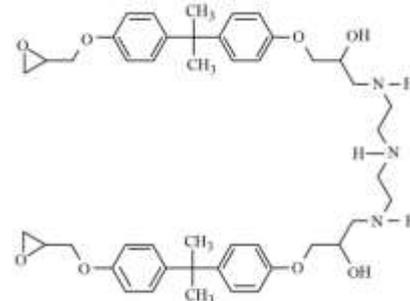


Fig. 4 Cross linked epoxy resin DGEBA/DETA

2.4 Modelling of Defects

The effects of two types of defects on nanocomposite mechanical properties have been investigated in this paper: Stone-Wales (SW) defect and vacancy defect. For investigation of SW defects, several models were constructed with different number of SW defects. The SW defects locations have been selected along the CNT molecular model with a random strategy. Moreover, care is taken to locate the defects in the greatest possible distance from each other and from the CNT ends. Two SW defected CNTs, with 2 and 4 SW defects, are modelled as shown in Fig. 5.

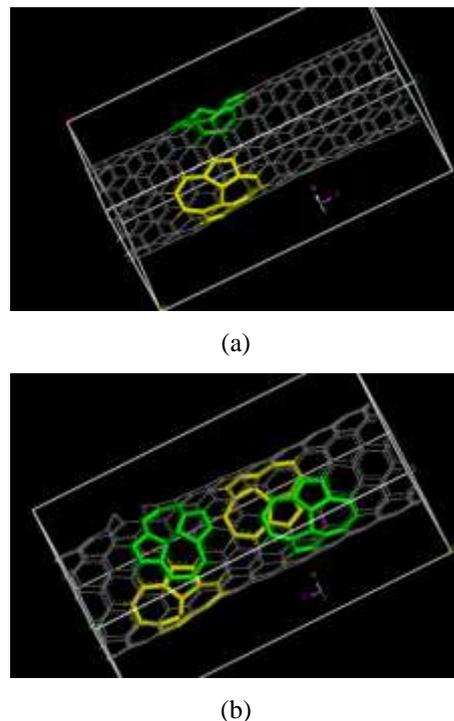


Fig. 5 Two SW defected CNT with: (a) 2 SW defects and (b) 4 SW defects

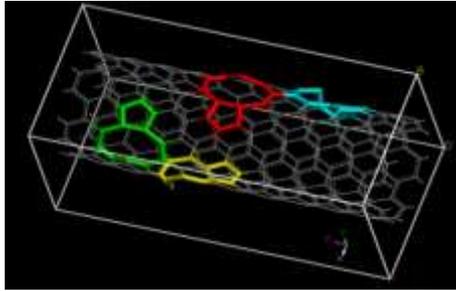


Fig. 6 Defected CNT with 4 reconstructed vacancy defects

Vacancy defects result from missing carbon atoms. In this study, only the single vacancy defects were considered. Similar to SW molecular modelling discussed above, a variety of CNT samples with different number of single vacancies are created. The vacancies are distributed in the CNT structures in a random manner. These non-constructed configurations are metastable and dangling carbon atom may bond with the surrounding media such as polymer matrix [37]. These structures could be annealed to stable reconstructed structures. In this study, two types of vacancy defects including non-constructed and reconstructed have been investigated. In Fig. 6 defected CNT with 4 reconstructed vacancy defects is shown.

2.5 Mechanical Properties

Constant-strain minimization method was used on all unit cells to determine nanocomposite Young's modulus using molecular simulations. Three dimensional normal strains and shear strains were applied along three principal axes of the unit cell with equal magnitudes. The maximum strain magnitude was set at ±0.003 to avoid nonlinearity of nanocomposite due to large strains. The measured stress, which is called virial stress in atomistic level, is the average atomic stresses in the volume of the model. Therefore the stress components of each model were calculated for each strain increment using the following relation [28]:

$$\sigma_{ij} = -\frac{1}{V} \sum_{\alpha} \left(M^{\alpha} v_i^{\alpha} v_j^{\alpha} + \sum_{\beta} F_i^{\alpha\beta} r_j^{\alpha\beta} \right) \tag{1}$$

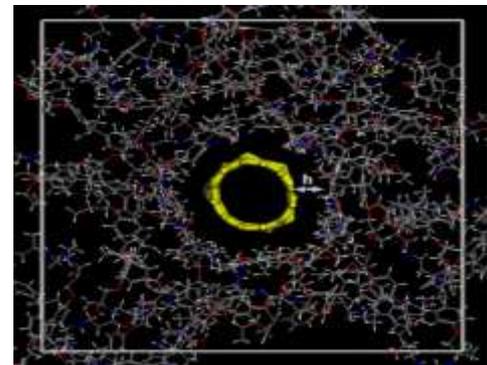
where, M^{α} indicates the mass of atom α and V^{α} denotes the un-deformed atom volume. v_i^{α} and v_j^{α} are the i^{th} and j^{th} components of atom velocity. $F_i^{\alpha\beta}$ is the i^{th} component of the force between atoms α and β and $r_j^{\alpha\beta}$ is the j^{th} component of the separation distance between atoms α and β . Based on Hooke's law for elastic material, using Voigt notation, the stiffness matrix components, C_{ij} , can be calculated using [9]:

$$\sigma_{ij} = C_{ij} \epsilon_j \quad (i, j = 1, 2, 3) \tag{2}$$

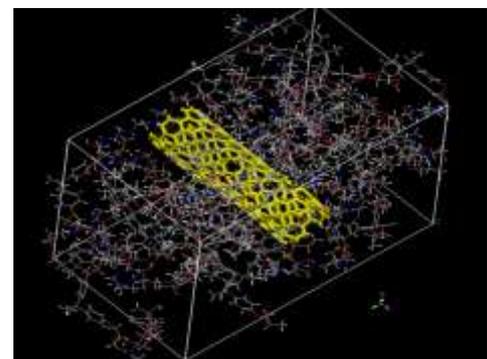
Where σ_i are the 6 independent components of the stress tensor, and ϵ_j are the three strain components. The stress components are calculated using Eq. (1) and are substituted in Eq. (2) to determine the stiffness matrix components, C_{ij} , for a specific strain vector. Next, the Young's and shear moduli can be calculated by solving the resulting algebraic linear system of equations.

2.6. Simulation details of nanocomposite

To reduce the simulation time, one representative molecule was selected from the cross linked epoxy resin model to construct the samples. Molecular models of defected and pristine CNTs (6, 6) have been built and, after equilibrium process, the stiffness matrix was computed for each model using constant-strain minimization method. Then amorphous cell, packing module of Materials Studio was used for constructing the polymeric matrix around the CNT. The mole ratio of epoxy resin and curing agent molecules is 2:1, based on experimental results [38, 39]. The thickness of the lattice along CNT axis is 24Å. The length of the lattice was assumed to be 40Å.



(a)



(b)

Fig. 7 Molecular model of the defected CNT-reinforced epoxy a: cross sectional model, an arrow (marked h) shows van der Waals separation distance, b: three dimensional molecular model

The dynamic process and optimization subjected to the system can be divided into the following steps:

- Geometry optimization and energy minimization were applied to molecular structures by Smart algorithm which is a cascade of the steepest descent, ABNR, and quasi-Newton methods.
- The system was equilibrated using NVT (isothermal-isochoric) dynamic simulation for 100 ps at a temperature of 600 K (above curing temperature). The initial density was set at 1g/cm^3 in this step.
- NPT (isothermal-isobaric) ensemble was used to reach the nearest local equilibration for 100ps at a pressure of 1atm and a temperature of 300K.

In NVT and NPT ensembles, Berendsen thermostat and barostat were used. In NVT and NPT ensembles, Berendsen thermostat and barostat were used for all simulation boxes and periodic boundary conditions were applied to eliminate the surface effects. A sample nanocomposite molecular model is shown Fig. 7. The van der Waals separation distance between epoxy molecules and CNT is measured about 2.8\AA in Fig. 7-a. A three dimensional view of molecular model is presented in Fig 7-b.

3 RESULTS AND DISCUSSION

After constructing the models and applying the equilibrium process, stiffness matrices were determined for all case studies. In addition, mechanical properties of pristine CNT and cross linked epoxy are determined using molecular simulations independently. The results of these analyses are presented in this section.

3.1 Mechanical properties of Defected CNT's

Mechanical properties of pristine and defected CNT molecular samples were predicted using the constant strain method. The stiffness matrix of pristine CNT (6,6) is given below.

$$C_{ij}(\text{GPa}) = \begin{bmatrix} 62.07 & 45.02 & 20.70 & 0.04 & 0.14 & 0.01 \\ 45.02 & 61.84 & 20.80 & 0.29 & 0.27 & 0.00 \\ 20.70 & 20.80 & 812.14 & 0.02 & 0.04 & -0.06 \\ 0.04 & 0.29 & 0.02 & -2.7 & 0.00 & 0.02 \\ 0.14 & 0.27 & 0.04 & 0.00 & -2.8 & 0.03 \\ 0.01 & 0.00 & -0.06 & 0.02 & 0.03 & 8.8 \end{bmatrix}$$

The above matrix indicates that the CNT is nearly transversely isotropic since $C_{11} \sim C_{22}$ and $2C_{66} \sim (C_{11} - C_{12})$. Moreover C_{33} is much larger than the other diagonal components [12]. Using these results, CNTI on longitudinal and transverse Young's modulus were

determined. These results are listed in Table1 for pristine and defected CNTs. As can be seen in this table, defected CNTs have lower Young's modulus than pristine CNT. Moreover, CNTs with more defects show a larger decrease in stiffness. Presence of the defects results in a reduction of 26 to 36% in the CNT elastic properties. Similar results have been reported by other researchers for SW defects and vacancy defects [22, 28].

Table 1 Predicted longitudinal (E_L) and transverse (E_T) Young's moduli for pristine and defected CNT (6, 6), SW: Stone-Wales, V(n.c): Vacancy nonconstructed, V(r.c): Vacancy reconstructed

Defect type	No. of Defects	E_L (GPa)	E_T (GPa)
-	-	804.20	29.20
SW	2	637.62	15.15
SW	4	598.84	13.50
SW	6	592.70	12.02
V(n.c)	1	645.80	14.50
V(n.c)	2	622.20	13.09
V(n.c)	4	571.50	13.02
V(n.c)	6	519.42	11.50
V(r.c)	4	618.46	15.02
V(r.c)	6	597.16	13.01

3.2 Young's modulus of cross linked epoxy

After constructing the molecular model of cured epoxy resin, followed by 100 ps NVT and NPT ensembles, elastic constants of the cured epoxy were calculated. It is noted that molecular dynamics simulation of polymer structures is much more complex than solids or crystals and significantly time consuming. Because of the isotropy of epoxy resin, Young's modulus values along the three principal axes turned out to be nearly equal. The mean value of the three Young's moduli was determined to be about 2.8GPa. Young's modulus reported for epoxy resin is 2.4-3.4 GPa. [40, 41]. Thus, our results are in good agreement with that reported in the references.

3.3 Elastic constants of defected CNT/epoxy nanocomposite

Unit cells consisting defected CNT and cross linked resin molecules were subjected to constant strains and the stiffness matrix elements for the nanocomposite were determined. As an example, the stiffness matrix of 2 SW defected CNT/epoxy nanocomposite is presented below. Referring to the matrix elements, note that the nanocomposite is transversely isotropic. That is, C_{11} and C_{22} is much smaller than C_{33} . The elastic constants for nanocomposites obtained from molecular models are presented in Table 2.

$$C_{ij} (GPa) = \begin{bmatrix} 4.55 & 0.95 & 2.20 & -0.09 & -0.03 & -0.79 \\ 0.95 & 1.80 & 0.86 & -0.56 & -0.22 & -0.70 \\ 2.2 & 0.86 & 56.86 & 0.14 & -0.34 & -0.99 \\ -0.09 & -0.56 & 0.14 & -0.28 & 0.26 & 0.04 \\ -0.03 & -0.22 & -0.34 & 0.26 & 2.32 & 0.13 \\ -0.79 & -0.70 & -0.99 & 0.04 & 0.13 & 1.93 \end{bmatrix}$$

As can be seen in this table, CNT strengthening effect is obvious since the longitudinal Young's modulus in all cases is larger than 2.8 GPa, matrix Young's modulus. It is clear that the type and the number of defects have significant effect on nanocomposite Young's modulus. To investigate the extent of this influence, several models were created and analysed. The ratios of nanocomposite Young's moduli for nanocomposites reinforced with pristine CNT to those reinforced with defected CNT are presented in Figs. 8 and 9. Note in these figures that nanocomposite moduli decrease as the number of defects in the CNT increases. Note in Fig. 8 that the influence of vacancy defects on nanocomposite longitudinal Young's modulus is more than the influence of SW defects.

The decrease in nanocomposite longitudinal Young's modulus due to vacancy defects is about 18 to 67%. Whereas, SW defects have weakened the longitudinal Young's modulus by about 14% to 23%. This differences are also reported by other researchers [28, 29]. It should be noted that if the reconstruction conditions are assumed for vacancy defects, this weakening effect is reduced compared to non-constructed defects. Researchers believe that the reconstruction of these defects is more probable when CNTs are used in nanocomposites [25]. A comparison between Figs. 8 and 9 suggests that defects have a larger effect on nanocomposite transverse modulus than on the longitudinal modulus. The transverse modulus drops by about 60 percent when only one vacancy defect exists in the CNT.

4 VERIFICATION OF THE RESULTS

For validation of the molecular simulation results, rule of mixtures (RM) theory was used to calculate nanocomposite mechanical properties [13]. Nanocomposite longitudinal and transverse moduli were determined using the following equations:

$$E_{L-comp} = V_{CNT} E_{L-CNT} + V_{epoxy} E_{epxy} \quad (3-a)$$

$$E_{T-comp} = \frac{E_{T-CNT} E_{epxy}}{E_{T-CNT} V_{epoxy} + V_{CNT} E_{epxy}} \quad (3-b)$$

Where V_{CNT} and V_{epoxy} are the volume fractions of CNT and cross linked epoxy resin, respectively. E_{T-CNT} , E_{L-CNT} and E_{epxy} in the above equations are

longitudinal and transverse moduli of CNT and cured epoxy resin, respectively. For increasing the accuracy, in rule of mixtures equations E_{T-CNT} and E_{L-CNT} values listed in Table 1 were used. Also, E_{epxy} was taken to be 2.8GPa. All of these values were obtained from molecular simulations. The volume fraction of CNT can be estimated using the following equation [5, 13]:

$$V_{CNT} = \frac{\pi(R_{CNT} + h_{eq}/2)^2}{A_{Cell}} \quad (4)$$

Where R_{CNT} is the CNT radius and h_{eq} is equilibrium van der Waals separation distance between CNT and epoxy molecules. This distance was taken to be 2.8Å based on molecular models. A_{Cell} is the cross sectional area of the simulation box. V_{CNT} was calculated to be about 0.09 with substituting the above values in Eq. (9). Table 3 presents the rule of mixtures (RM) and molecular dynamics (MD) predictions for nanocomposite moduli.

As can be seen in this table, longitudinal modulus values predicted by MD and RM are approximately equal. However, in transverse modulus results, great differences are observed for both pristine and defected CNT reinforced nanocomposites. These differences are due to perfect bonding assumption considered in RM formulations. It is notable that the RM results for nanocomposites are not accurate because these results are independent of geometry distribution and shape of reinforcements [42].

Table 2 Predicted longitudinal (E_L) and transverse (E_T) Young's modulus for nanocomposite reinforced by pristine and defected CNT (6, 6), SW: Stone-Wales, V(n.c): Vacancy non-constructed, V(r.c): Vacancy reconstructed

Defect type	No. of Defects	E_L (GPa)	E_T (GPa)
-	-	63.70	5.75
SW	2	55.50	3.05
SW	4	52.56	1.51
SW	6	51.48	0.82
V(n.c)	1	53.71	2.20
V(n.c)	2	51.21	2.00
V(n.c)	4	50.43	1.16
V(n.c)	6	38.12	0.87
V(r.c)	4	54.43	3.15
V(r.c)	6	52.31	3.01

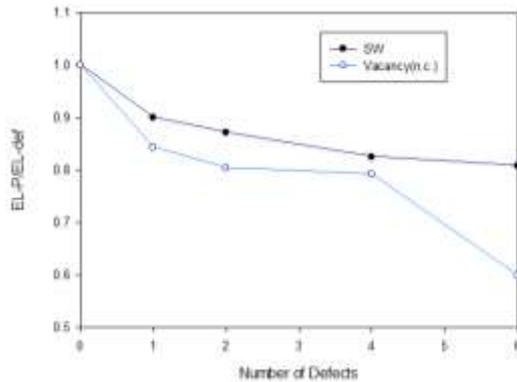


Fig. 8 Ratio of longitudinal Young's modulus of nanocomposite reinforced with pristine CNT (EL-P) to longitudinal Young's modulus of nanocomposite reinforced with defected CNT (EL-Def)

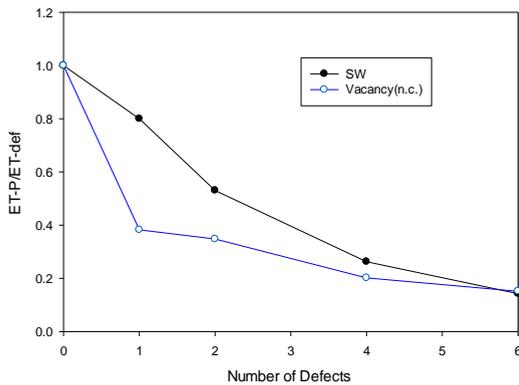


Fig. 9 Ratio of transverse Young's modulus of nanocomposite reinforced with pristine CNT (ET-P) to transverse Young's modulus of nanocomposite reinforced with defected CNT (ET-Def)

Table 3 Comparison of Young's moduli of defective CNT reinforced nanocomposite predicted by molecular dynamics (MD) and rule of mixtures (RM)

Defect type	No of Def.	E_L (GPa)			E_T (GPa)		
		RM	MD	Diff.%	RM	MD	Diff.%
-	-	77.04	63.70	20	3.05	5.75	46
SW	2	61.57	55.50	10	3.03	3.05	0
SW	4	57.90	52.56	10	3.02	1.51	100
SW	6	57.40	51.48	11	3.01	0.82	267
V(n.c)	2	60.18	51.21	17	3.02	2.00	50
V(n.c)	4	55.45	50.43	9	3.01	1.16	159
V(n.c)	6	50.63	38.12	32	3.01	0.87	245

5 CONCLUSIONS

Defects including Stone-Wales or vacancy, which are generally present in CNT structures, affect the mechanical properties of polymer based nanocomposites. In this investigation, molecular modelling was used to investigate the effects of defects on nanocomposite properties.

The results indicate that nanocomposite stiffness reduces by increasing the number of defects in the CNT. The reduction in nanocomposite modulus was more pronounced in the transverse direction. Non-constructed vacancy defects have the most effect on mechanical behaviour of nanocomposites. Nanocomposite Young's moduli were also determined using rule of mixtures formulations. CNT and resin properties used in the rule of mixtures formulations were determined using molecular dynamics models. Comparison between MD and RM results showed that rule of mixture equations must be modified to account for CNT defects, if these formulations are to be used to predict nanocomposite properties more realistically.

REFERENCES

- [1] Iijima, S., "Helical microtubules of graphitic carbon", nature, 354(6348), 1991, pp. 56-58.
- [2] Wong, E.W., Sheehan, P.E., and Lieber, C.M., "Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes", Science, 277(5334), 1997, pp. 1971-1975.
- [3] Treacy, M.J., Ebbesen, T., and Gibson, J., "Exceptionally high Young's modulus observed for individual carbon nanotubes", 1996.
- [4] Yu, M. F., "Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties", Physical review letters, 84(24), 2000, pp. 5552.
- [5] Zhu, R., Pan, E., and Roy, A., "Molecular dynamics study of the stress-strain behavior of carbon-nanotube reinforced Epon 862 composites", Materials Science and Engineering: A, 447(1), 2007, pp. 51-57.
- [6] Thostenson, E.T. and Chou, T., "On the elastic properties of carbon nanotube-based composites: modelling and characterization", Journal of Physics D: Applied Physics, 36(5), 2003, pp. 573.
- [7] Asadi, E. and Jam, J., "Analytical and Numerical Buckling Analysis of Carbon Nanotube Reinforced Annular Composite Plates", International Journal of Advanced Design and Manufacturing Technology, 7(2), 2014, pp. 35-44.
- [8] Ghahfarokhi, Z.M. and Golestanian, H., "Effects of nanotube helical angle on mechanical properties of carbon nanotube reinforced polymer composites", Computational Materials Science, 50(11), 2011, pp. 3171-3177.
- [9] Moradi-Dastjerdi, R., Sheikhi, M., and Shamsolhoseinian, H., "Stress distribution in functionally graded nanocomposite cylinders reinforced by wavy carbon nanotube", International Journal of Advanced Design and Manufacturing Technology, 7(4), 2015, pp. 43-54.

- [10] Yu, S., Yang, S., and Cho, M., "Multi-scale modeling of cross-linked epoxy nanocomposites", *Polymer*, 50(3), 2009, pp. 945-952.
- [11] Quaresimin, M., Salviato, M., and Zappalorto, M., "Strategies for the assessment of nanocomposite mechanical properties", *Composites Part B: Engineering*, 43(5), 2012, pp. 2290-2297.
- [12] Shi, D. L., "The effect of nanotube waviness and agglomeration on the elastic property of carbon nanotube-reinforced composites", *Journal of Engineering Materials and Technology*, 126(3), 2004, pp. 250-257.
- [13] Frankland, S., et al., "The stress-strain behavior of polymer-nanotube composites from molecular dynamics simulation", *Composites Science and Technology*, 63(11), 2003, pp. 1655-1661.
- [14] Arash, B., Wang, Q., and Varadan, V., "Mechanical properties of carbon nanotube/polymer composites", *Scientific reports*, 4, 2014.
- [15] Odegard, G., "Constitutive modeling of nanotube-reinforced polymer composites", *Composites science and technology*, 63(11), 2003, pp. 1671-1687.
- [16] Sears, A. and Batra, R., "Macroscopic properties of carbon nanotubes from molecular-mechanics simulations", *Physical Review B*, 69(23), 2004, pp. 235406.
- [17] Chandra, N., Namilae, S., and Shet, C., "Local elastic properties of carbon nanotubes in the presence of Stone-Wales defects", *Physical Review B*, 69(9), 2004, pp. 094101.
- [18] Banhart, F., "Irradiation effects in carbon nanostructures", *Reports on progress in physics*, 62(8), 1999, pp. 1181.
- [19] Ouyang, M., et al., "Atomically resolved single-walled carbon nanotube intramolecular junctions", *Science*, 291(5501), 2001, pp. 97-100.
- [20] Ding, F., "Theoretical study of the stability of defects in single-walled carbon nanotubes as a function of their distance from the nanotube end", *Physical Review B*, 72(24), 2005, pp. 245409.
- [21] Ebbesen, T. and Takada, T., "Topological and sp³ defect structures in nanotubes", *Carbon*, 33(7), 1995, pp. 973-978.
- [22] Lu, Q. and Bhattacharya, B., "Effect of randomly occurring Stone-Wales defects on mechanical properties of carbon nanotubes using atomistic simulation", *Nanotechnology*, 16(4), 2005, pp. 555.
- [23] Mielke, S.L., et al., "The role of vacancy defects and holes in the fracture of carbon nanotubes", *Chemical Physics Letters*, 390(4), 2004, pp. 413-420.
- [24] Xiao, S. and Hou, W., "Fracture of vacancy-defected carbon nanotubes and their embedded nanocomposites", *Physical Review B*, 73(11), 2006, pp. 115406.
- [25] Sammalkorpi, M., et al., "Mechanical properties of carbon nanotubes with vacancies and related defects", *Physical Review B*, 70(24), 2004, pp. 245416.
- [26] Hou, W. and Xiao, S., "Mechanical behaviors of carbon nanotubes with randomly located vacancy defects", *Journal of nanoscience and nanotechnology*, 7(12), 2007, pp. 4478-4485.
- [27] Kuwar, M. and Kamal, S., "Molecular Dynamics Simulation Study of Novel Properties of Defect Full Single Walled Carbon Nanotubes".
- [28] Mahboob, M. and Islam, M.Z., "Molecular dynamics simulations of defective CNT-polyethylene composite systems", *Computational Materials Science*, 79, 2013, pp. 223-229.
- [29] Davoudabadi, M. and Farahani, S., "Investigation of Vacancy Defects on the Young's Modulus of Carbon Nanotube Reinforced Composites in Axial Direction via a Multiscale Modeling Approach", *Journal of Solid Mechanics* Vol, 2(3), 2010, pp. 248-256.
- [30] Komuves, F., et al., "Prediction of Mechanical Properties of EPON 862 (DGEBF) cross-linked with Curing Agent W (DETDA) and SWCNT using MD Simulations", 52nd AIAA Structural Dynamics and Material conference, 2011.
- [31] Tack, J.L. and Ford, D.M., "Thermodynamic and mechanical properties of epoxy resin DGEBF crosslinked with DETDA by molecular dynamics", *Journal of Molecular Graphics and Modelling*, 26(8), 2008, pp. 1269-1275.
- [32] Wu, C. and Xu, W., "Atomistic molecular simulations of structure and dynamics of crosslinked epoxy resin", *Polymer*, 48(19), 2007, pp. 5802-5812.
- [33] Duan, W., "Molecular mechanics modeling of carbon nanotube fracture", *Carbon*, 45(9), 2007, pp. 1769-1776.
- [34] Li, C. and Strachan, A., "Molecular simulations of crosslinking process of thermosetting polymers", *Polymer*, 51(25), 2010, pp. 6058-6070.
- [35] Tam, L.-h. and Lau, D., "A molecular dynamics investigation on the cross-linking and physical properties of epoxy-based materials", *RSC Advances*, 4(62), 2014, pp. 33074-33081.
- [36] Yang, S. and Qu, J., "Computing thermomechanical properties of crosslinked epoxy by molecular dynamic simulations", *Polymer*, 53(21), 2012, pp. 4806-4817.
- [37] Krasheninnikov, A., et al., "Formation of ion-irradiation-induced atomic-scale defects on walls of carbon nanotubes", *Physical Review B*, 63(24), 2001, pp. 245405.
- [38] Shokuhfar, A. and Arab, B., "The effect of cross linking density on the mechanical properties and structure of the epoxy polymers: molecular dynamics simulation", *Journal of molecular modeling*, 19(9), 2013, pp. 3719-3731.
- [39] Sundararaghavan, V. and Kumar, A., "Molecular dynamics simulations of compressive yielding in cross-linked epoxies in the context of argon theory", *International Journal of Plasticity*, 47, 2013, pp. 111-125.
- [40] Morgan, R.J., "The effect of thermal history and strain rate on the mechanical properties of diethylenetriamine-cured bisphenol-A-diglycidyl ether epoxies", *Journal of Applied Polymer Science*, 23(9), 1979, pp. 2711-2717.
- [41] Brown, E.N., White, S.R., and Sottos, N.R., "Microcapsule induced toughening in a self-healing polymer composite", *Journal of Materials Science*, 39(5), 2004, pp. 1703-1710.
- [42] Giannopoulos, G., Georgantzinos, S., and Anifantis, N., "A semi-continuum finite element approach to evaluate the Young's modulus of single-walled carbon nanotube reinforced composites", *Composites Part B: Engineering*, 41(8), 2010, pp. 594-601.