9th ANKARA INTERNATIONAL AEROSPACE CONFERENCE AIAC-2017-128
20-22 September 2017 - METU, Ankara TURKEY

MOLECULAR DYNAMICS SIMULATIONS OF CARBON NANOTUBE REINFORCED POLYMER COMPOSITES

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ABSTRACT

Aim of this study is to investigate the elastic properties of carbon nanotube (CNT) reinforced PEEK (Poly-Ether-Ether-Ketone) composites. For this purpose, first the elastic properties of CNTs are examined at temperatures 0 K and 300 K using Molecular Dynamics (MD) simulation technique. Then the physical and mechanical properties of PEEK bulk matrix are investigated once again with the MD approach. Having studied the CNT and the PEEK separately, the CNT-PEEK interface is examined by using both the Density Functional Theory (DFT) and MD methods.

INTRODUCTION

CNTs are 1D allotropes of carbon and they can simply be described as rolled up graphene sheets. Radius and length of a typical CNT structure are in the order of nanometers and microns, respectively. CNTs, much like their parent material graphene, are characterized by high strength, high Young's modulus, durability and tunable electronic behavior. As a result of their superior properties, CNTs, have gained considerable interest in the material research communities in recent years. Also, in the aerospace industry, CNTs have a great potential to replace traditional carbon or glass fibers in fiber reinforced composites. CNTs are divided into three types; zigzag, armchair and chiral according to the rolling direction of the graphene sheet as shown in Figure 1 (a), and divided into two types according to their wall number; single-walled (SWCNT) and multi-walled (MWCNT)as shown in Figure 1 (b) [Thostenson et al., 2001].

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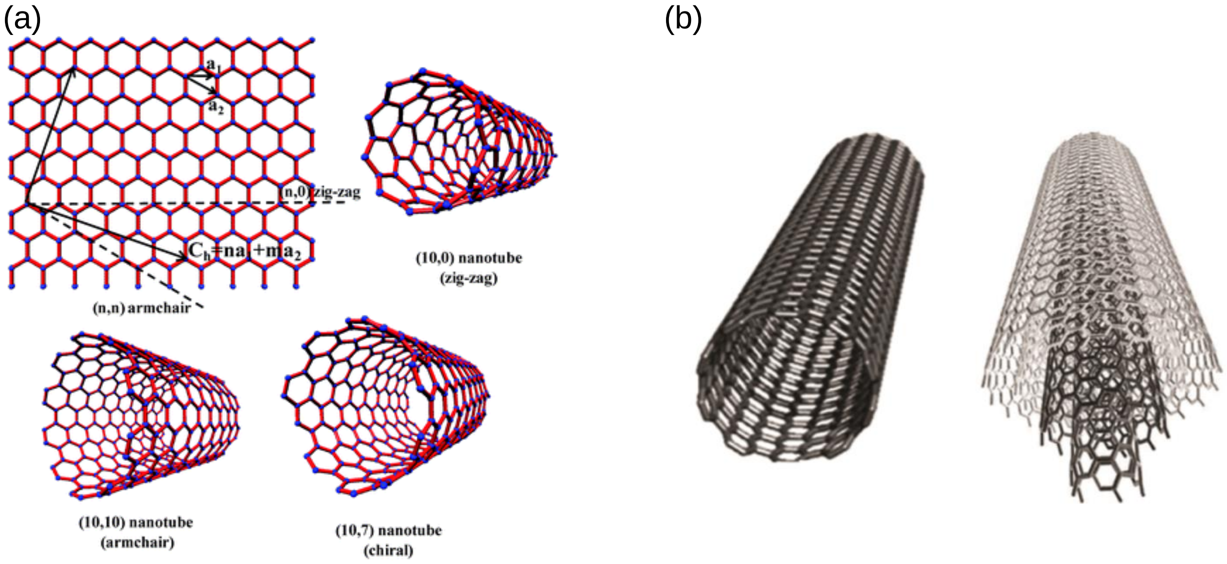

Figure 1: Types of CNTs (a) according to chiral vector [Retrieved from http://machinedesign.com, 2016] and (b) according to wall number (right)[Retrieved from http://www.nanoscience.com]

Chirality which defines the Rolling direction of a CNT, is described by the chiral vector, shown in the Figure 1 (a)

$$\overrightarrow{C_h} = n\overrightarrow{a_1} + m\overrightarrow{a_2}$$

When $m = 0$, CNTs are called as zigzag$(n, 0)$ and when $n = m$, CNTs are called as armchair(n, n). Otherwise, i.e, $n \neq m$, they are called chiral.

PEEK polymer is a semi-crystalline thermoplastic that has remarkable mechanical properties with elastic modulus of 3.6 GPa and a rather high melting point (370 ºC). When it is reinforced with CNTs, its melting point can reach up to 390 ºC [Brydson, 1999]. Because of relatively high stiffness and high melting temperature, in this study, PEEK is chosen as the matrix material of the CNT reinforced polymer composite.

METHOD

The testing, manipulating and design of viable mixtures of nanotubes and polymers present challenges from an experimental point of view. For this reason, numerical modeling at the atomistic scale of CNT reinforced polymers is crucial for the design of future CNT reinforced systems. Computer simulations act as a bridge between the theory and the experiment and provide a powerful insight about the systems [Allen, 2004]. Molecular Dynamics (MD) is a computer simulation technique to study time evolution of a system of interacting particles (i.e. N-body simulation technique). It is basically based on the Newtonian mechanics. MD simulations solve numerically the Newton's equations of motions to predict the trajectory of the system and calculate force on each particle by using inter-atomic potentials.

In our calculations, we used MD technique to investigate mechanical properties of CNTs, PEEK polymer and CNT/PEEK interface. MD simulations performed in a classical molecular dynamics code called LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) developed by Sandia National Laboratories [Plimpton, 1995]

RESULTS

At the beginning of the study, elastic properties of CNTs with different chiralities and lengths are calculated. In order to find an inter-atomic potential that can model both CNT and polymer accurately, we tested two different potentials. AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) [Stuart et al., 2000] and ReaxFF (Reactive Force Field) [Van Duin et al., 2001] inter-atomic potentials are used at 0K and 300K temperatures.

For the calculation of the Young's modulus, a CNT is compressed and stretched in the axial direction. While the behavior of CNT is linear in the strain range between -2% to +2%, it shows non-linear response beyond these limits. Due to this reason, in the simulation results, data corresponding to axial strain of -2% to +2% are taken into account and fitted to 2nd order polynomial as shown in Figure 2 (a) and (b). By using the second derivate of strain versus energy per unit volume graph the Young's modulus is obtained:

$$E = \frac{1}{V}\frac{\partial^2 U}{\partial \varepsilon^2}$$

The Poisson's ratio ν is calculated from the strain ε versus radius change graph given in Figure 2 (c) again for the same ranges by using the following formula:

$$\nu = -\frac{1}{\varepsilon}\frac{R - R_0}{R_0}$$

where the results are given in Table 3 R and R_0 are the current and initial radii, respectively. The Young’s modulus and the Poisson’s ratio results of (10, 0) zigzag and (10, 10) armchair CNTs with AIREBO and ReaxFF potentials at 0 Kand 300 K are given in Table 1 and Table 2, respectively.

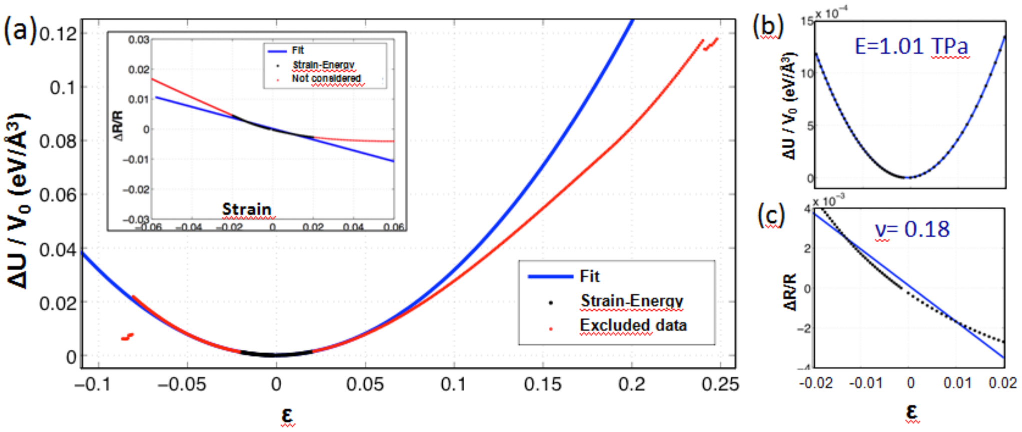

Figure 2 : (a) The graph of strain versus energy per volumeand strain versus radius change. Black line shows the taken data, blue line shows polynomial fit and red line shows the excluded data.(b) Zoomed view of strain versus energy per volume of a (10,0) CNT with AIREBO potential at 0K. (c) Zoomed view of strain versus radius change of a (10,0) CNT with AIREBO potential at 0K.

Table 1: Young's modulus and Poisson's ratio of (10,0) and (10,10) zigzag CNTs with length 10 nm at 0K

CNT	**AIREBO**		**ReaxFF$_{C2013}$**	
	E [TPa]	**ν[-]**	**E [TPa]**	**ν[-]**
(10,0)	1.013	0.185	0.763	0.532
(10,10)	0.917	0.273	0.775	0.538

Table 2: Young's modulus and Poisson's ratio of (10, 0) and (10,10) zigzag CNTs with length 5 nm at 300K

CNT	**AIREBO**		**ReaxFF$_{C2013}$**	
	E [TPa]	**ν[-]**	**E [TPa]**	**ν[-]**
(10,0)	0.95	0.15	0.835	0.60
(10,10)	0.99	0.19	0.754	0.56

The Young's modulus and the Poisson's ratio results for these two potentials are compared with the literature and they are found to be consistent with previously reported values of CNTs [Jensen et al., 2016 and Bialoskorskive et al., 2012].

For the shear modulus of CNT, both ends of a CNT are twisted with specific angles relative to each other as shown in Figure 4 while keeping center of the CNT is fixed. The shear modulus is calculated by using the classical torsion formulation for circular tubes as

$$G = \frac{L}{2\pi h R_0 \left(R_0^{\,2} + \frac{h^2}{4} \right)} \frac{d^2 U}{d\theta^2}$$

Here $h = 0.34$ nm represents the wall thickness of the circular tube.The computed shear moduli and torsional rigidities are given in Table 3.

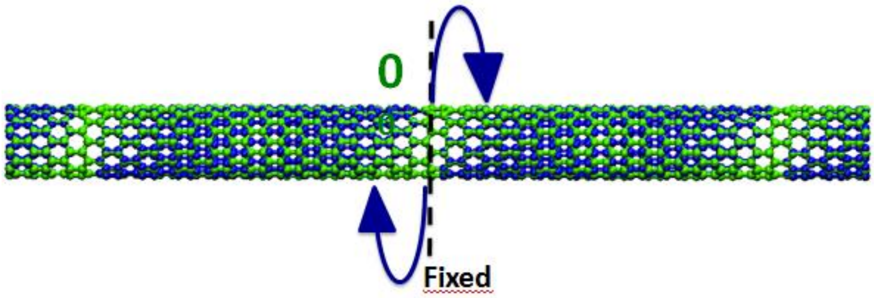

Figure 3: Applied torsion type

Table 3: Shear modulus and torsional rigidity of CNTs with different chiralities by using AIREBO potential at 0 K

CNT	Radius[nm]	G [TPa]	GJ[TPaÅ^4]
(5,0)	0.199	0.212	61.74
(8,0)	0.319	0.212	190.29
(10,0)	0.399	0.225	358.24
(12,0)	0.479	0.233	618.32

The shear modulusand the torsional rigidity results are also consistent with the literature and they increase with the increasing radius [Pereira, et al., 2015].

In order to calculate the mechanical properties of PEEK, first PEEK matrix is created by nanoHUB Polymer Modeler tool [Madhavan et al., 2013] as shown in the Figure 4 (b) and the initial system is brought to equilibrium at the desired temperature under the MD conditions specified by our calculations.

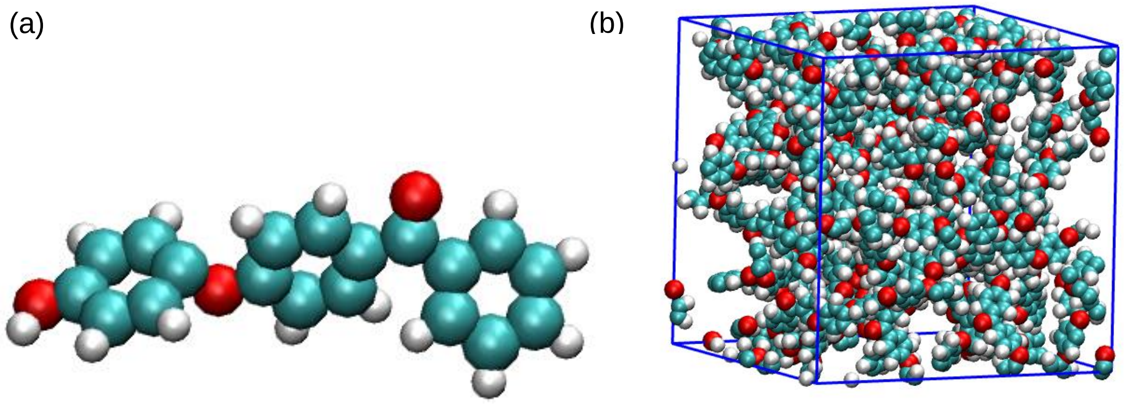

Figure 4: (a) PEEK monomer and (b) initial simulation box of PEEK

In theoretical studies, the polymeric materials are generally examined using classical force field potentials. Even if they can model the system properly and give accurate predictions about mechanical properties of systems, they cannot give any insight about material failure. Unlike these force fields, bond-order ReaxFF can model polymer systems better and provides understanding about material failure [Pisani et al., 2016]. In our simulations ReaxFF potential with London dispersion corrections is preferred because it gives more accurate prediction of elastic properties of polymeric materials [Liu et al., 2011].

In MD simulations, thermostat and barostat choices are also important when modeling such complex systems. In our calculations, Berendsen thermostat and barostat are used to control temperature and pressure. This thermostat and barostat often preferred in simulations of polymers. Berendsen thermostat suppresses fluctuations of kinetic energy and instantaneous temperature is pushed towards the desired temperature by scaling the velocities at each step. Berendsen barostat rescales volume of the system and the coordinates of atoms within the simulation box at each time step and controls the pressure of the system at desired pressure.

In this study, a PEEK simulation cell with14 chains each consisting of 7 monomers (having 3360 atoms in total) is created by nanoHUB Polymer Modeler (see Figure 4(b)). The initial density of simulation cell is 0.5 g/cm^3. It is brought to equilibrium at desired temperature by using ReaxFF potential within the following well-defined succession of NVT and NPT calculations: first, the system is slowly equilibrated in an NVT ensemble by using the Berendsen thermostat and then NPT simulation is performed at 1 atm with a 0.1 fs time-step by using Berendsen barostat as shown in Figure 5 (a). After the desired density is reached (1.30 g/cm^3 density of PEEK stated in experimental studies), strain is applied along x-direction over 100 ps resulting in 25% strain. The stress-strain graph in Figure 5(c) indicates that after 10% strain, structure gives non-linear response. Due to this reason, the data is excluded after %10 strain and the Young's modulus is calculated from the slope of remaining data. The Poisson's ratio of the polymer is also obtained from the average ratio of the transverse strain to the axial strain.

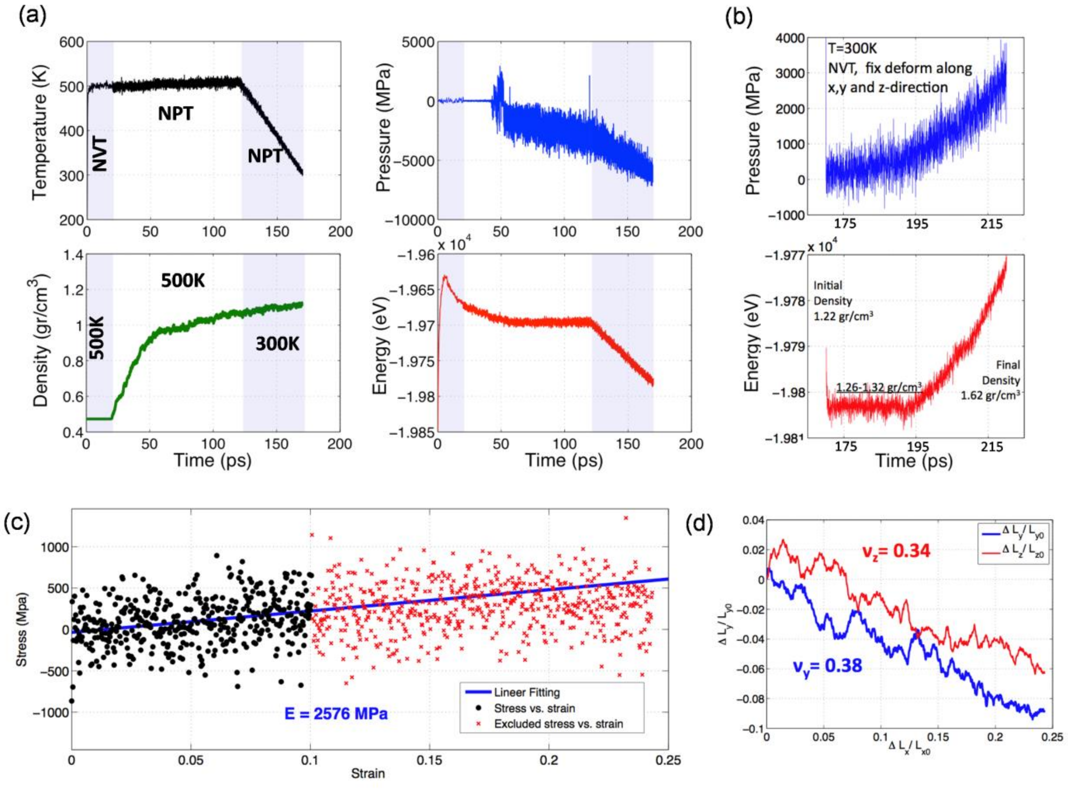

Figure 5: MD results of PEEK for 14 chains of 7 monomers: (a) Initial structure is thermalized at 500K within well-defined consecutive simulations of NVT and NPT using the ReaxFF force field. Temperature is also lowered from 500K to 300K at 1 atm using NPT ensemble in an additional step (b) Resulting polymer of (a) is densified with simulations using axial tensile straining at 300K (NVT ensemble). During the densification, equilibrium state of PEEK is determined from energy and pressure profiles. Potential energy is minimum and smooth, where density of PEEK is around 1.30 gr/cm^3 (c) Stress-strain data along the x-axis and (d) Poisson ratios are shown.

Our preliminary results of PEEK are given in Table 4 and they are in good agreement with recently reported conclusions of MD simulations [Pisaniet al., 2016].

Table 4: Mechanical properties of PEEK polymer

	ReaxFF	Pisani et al.(2016)
Density [gr/cm^3]	1.30	1.30
Young's modulus [MPa]	2576	3620±943
Poisson's ratio [-]	0.36	0.387±0.153

To understand the nature of surface properties of CNT and polymer, the interaction between PEEK and graphene is investigated as a benchmark study. For the sake of calculation, PEEK monomer is placed on a graphene sheet and binding energy of monomer is obtained by using two different methods: Density Functional Theory (DFT) [Berland et al., 2014] and MD method based on ReaxFF potential. In this study, DFT calculations are performed Quantum ESPRESSO software distributed free under GNU public licence [Giannozzi et al., 2009].

The binding energy of PEEK on graphene is obtained by following equation:

$$E_b = E_{total} - E_{gr} - E_{molecule}$$

where E_{total}, E_{gr} and $E_{molecule}$ are total energy of system, the total energy of pristine graphene and single molecule energy, respectively. Our results, given in Table 5, show that the result of ReaxFF matches reasonably well with those of DFT.

Table 5: Binding energy results of PEEK by using DFT and MD methods

	DFT	MD(ReaxFF)
Binding Energy [eV]	-1.43	-1.75

In our calculations, the interaction between CNTs and PEEK is also examined using ReaxFF potential. 3 monomers of PEEK are placed on (8,8) armchair and (5,10) CNTs. As shown in Figure 6, different configurations of PEEK chain have been explored and the binding energy of each shape has been calculated. After geometric optimization at T=0K, four possible configurations of PEEK chain on CNTs are obtained: L-shaped, V-shaped, M-shaped and S-shaped. Once again, the binding energies of these configurations are calculated by MD method and results are given in the Table 6. Our results indicate that all configurations are possible, however V-shaped is favorable on (8,8) and V-shaped is more likely on CNT of (5,10).

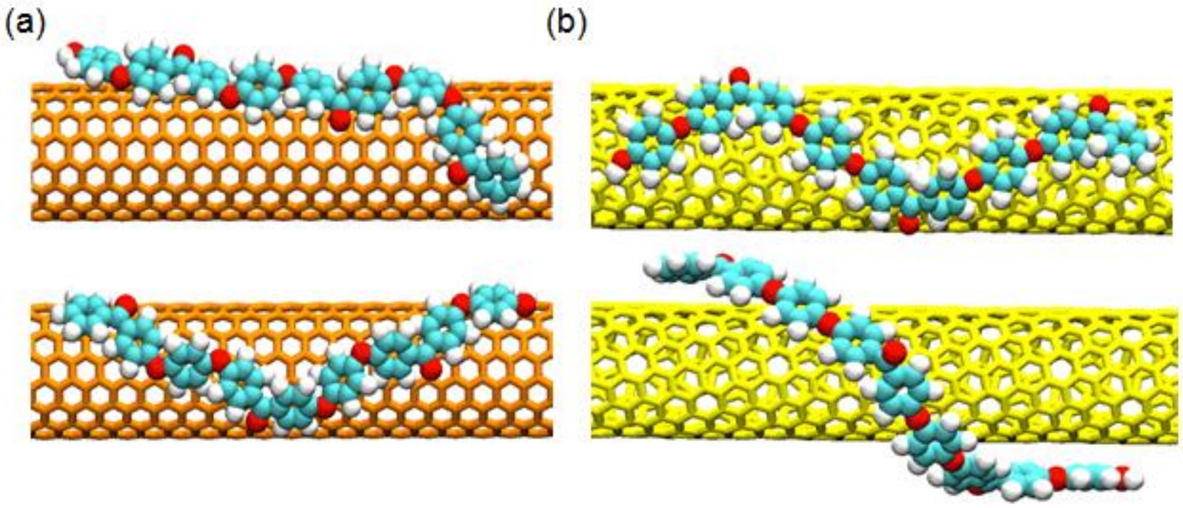

Figure 6: (a) L-shaped (top) and V-shaped (bottom) PEEK on (5,10) chiral CNT (b) M-shaped(top) and S-shaped(bottom) PEEK on (8,8) armchair CNT

Table 6: Binding energies of PEEK configurations on (8,8) armchair and (5,10) chiral CNT. It can be seen that favorable configuration is V-shape for (8, 8) CNT and L-shaped for chiral one.

3-PEEK on CNT(8,8)	**E_b[eV]**	**3-PEEK on CNT(5,10)**	**E_b[eV]**
V-shaped	**-3.87**	**L-shaped**	**-3.77**
L-shaped	-3.83	M-shaped	-3.66
S-shaped	-3.53	S-shaped	-3.52

These calculations help us to understand the nature of bonding between CNT/PEEK interface. Our results indicate that CNT and PEEK interaction occur via van der Waals forces and there is no sign of chemical bonding.

Acknowledgment: This work is supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK), Grant No. 115M550.

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