



Research Article

Crosslinking and interfacial behavior of carboxylic functionalized carbon nanotube Epon nanocomposites: a molecular dynamic simulation approach

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Abstract

We implemented molecular dynamics simulations to study the effect of single-walled carbon nanotube (SWCNT) and carboxylic (–COOH) functionalized SWCNT on the crosslinking and interfacial behavior of Epon 862 nanocomposite. Results showed that the introduction of control SWCNT in the Epon system reduced the crosslinking by 8–12% in comparison to control system (without CNT). The molecules of Epon 862 and Epikure-W changed their conformation and aligned themselves in the direction parallel to the surface wrapping the nanotubes. Also, no interfacial bonding was found between the polymer and SWCNT. However, the introduction of the –COOH functional groups on the surface of SWCNT lead to increase in crosslinking and resulted in a strong bond formation between the polymer and nanotube interphase. A significant increase in energy was found in Epon/COOH-SWCNT systems that lead to an increase of 33% in interfacial strength in comparison to Epon/SWCNT counterpart. The pullout simulations of Epon/SWCNT samples showed separation at the interphase with no polymer atoms attached to CNT. In contrast, bond stretching and breakage were observed in the polymer chain, whereas, a strong interphase was observed in Epon/COOH-SWCNT samples. This study reveals the nanolevel interactions between the nanotubes and polymers which otherwise not possible through experimental techniques, and lead to cognize that the functionalization of SWCNT with –COOH groups can establish a strong network with the epoxy chain and significantly enhance the interfacial properties particularly for applications where the interphase is critical.

Keywords Polymers · Carbon nanotubes · Computational mechanics · Crosslinking · Interfacial strength

1 Introduction

Prediction of mechanical properties and modeling the mechanical behavior of the CNT reinforced polymeric composites (RPCs) has attracted great attention [1–3] especially considering their unique structural and electronic properties [4, 5]. High strength, large aspect ratio and low density of CNTs have made these particles an ideal reinforcement candidate in polymeric composites

for next generation applications such as in aerospace, packaging, automotive and civil industries. However, a number of experimental investigations in the literature reported contradicting crosslink density and macroscopic mechanical properties considerably lower than the theoretically predicted values [6–8]. It is well known that the macroscopic properties of CNT RPCs are directly depends on the extent of crosslinking between the epoxy resin and its curing agent, CNT dispersion and its interfacial bonding

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with the epoxy system. Also, the interfacial strength, a key property responsible for maximizing the load transfer has been investigated using the fiber pull-out or push-out tests [9, 10]. Fiber pull-out from a matrix is usually characterized by the critical shear stress to debond the CNT/polymer interface and the subsequent interface friction of the CNT and polymer. Results demonstrated that the magnitude of interfacial bonding is limited and thus the load transfer ability in CNT RPCs is weak because of the atomically smooth, non-reactive nature of the nanotube outer surface [11, 12]. The load transfer between CNTs and polymer matrix takes primarily due to weak Van der Waals forces. However, the authors and other researchers showed recently through macroscopic experimental techniques that a strong covalent bonding between the CNTs and polymer was formed by making the outer surface of CNTs reactive through chemical functionalization with carboxylic (COOH) or amino (NH₂) groups [13–17]. As a result, the mechanical and thermal properties enhanced significantly due to improved interfacial bonding and better crosslinking between the CNTs and polymer. However, no microscopic level experimental testing proving the improvement in interfacial bonding between the functionalized CNT and matrix such as fiber pull-out are conducted, whereas, only a few studies are reported on non-functionalized CNT RPCs [18, 19].

In addition, the crosslinking of epoxy molecules and its interaction with the CNT is a nanolevel phenomenon. The interface region between the CNT and epoxy molecules is reported to be less than 5 nm. Due to the complexity and lack of microlevel experimental techniques, researchers over the years have extensively focused on theoretical methods for predicting the properties of CNT RPCs. It is recognized that atomic simulations based on high-fidelity forcefields models can provide a better understanding of interfacial bonding and load transfer mechanism between the CNTs and the polymer matrix [20, 21]. Currently, Molecular dynamics (MD) simulation technique has been widely used for studying these properties due to its accuracy, flexibility, and various force fields [1, 22–25]. Liao and Li [26] evaluated the interface of a CNT reinforced polystyrene composites. However, no chemical bonding was considered in their simulation, and thus the interfacial adhesion primarily resulted from weak Van der Waals interaction and mismatch in the coefficient of thermal expansion.

On the other hand, several researchers studied the influence of chemical crosslinks between a single-walled carbon nanotube (SWCNT) and a polymer matrix and reported that forming few crosslinks between CNT and polymer, the crosslinking and interfacial strength increased significantly. However, the simulations in these studies were performed on uncured epoxy models. In recent years, MD simulations to predict interfacial

bonding/stresses were extended further by considering the cured epoxy model with and without the SWCNT reinforcement which is more realistic than uncured CNT/polymer model [26–28]. However, again, no chemical crosslinking was considered between nanotubes and polymer in these studies and the pullout simulations were based on weak Van der Waals interaction.

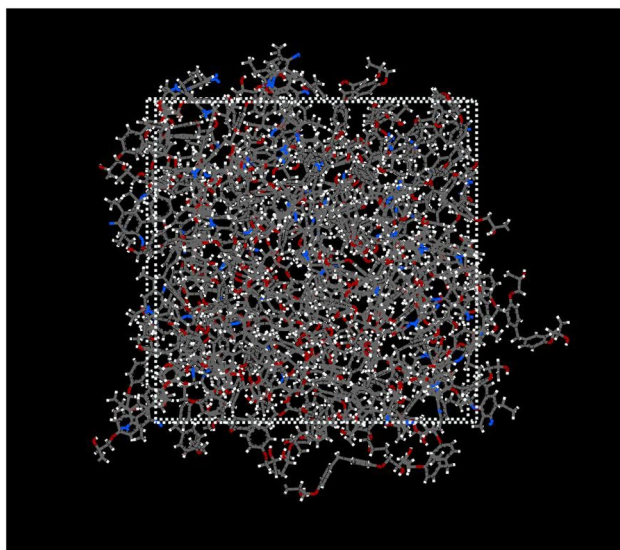
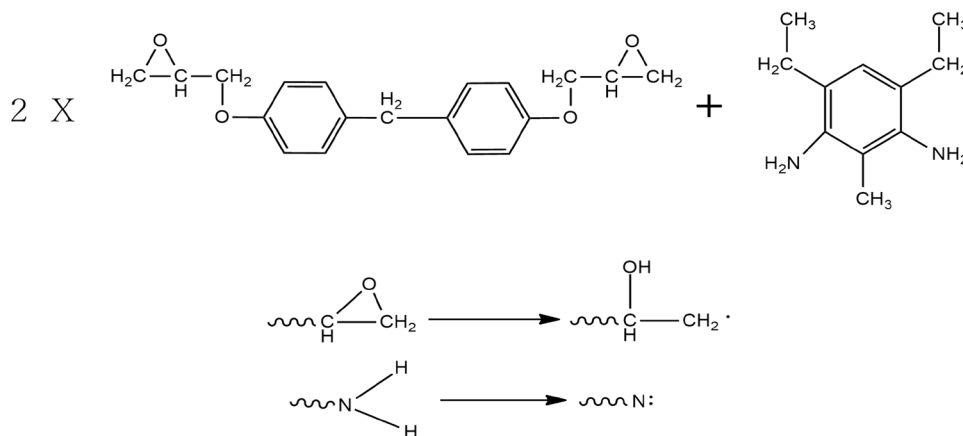
Although to the best of our knowledge, a considerable MD simulation study is done to understand the interfacial bonding between the CNT and polymer matrix, many of these investigations were performed by considering the weak Van der Waals interactions and by considering the uncured/cured polymer models. Thus, a huge variation in interfacial strength of CNT RPCs is reported in these studies [1, 22–28]. The variation in interfacial strength may be acceptable due to the fact that the simulations were performed on various polymers and with different model set-up. However, the predictions based on weak Van der Waals forces are questionable, specifically when polymer is modified with functionalized nanotubes. Modification of CNTs induces strong covalent bonds with matrix [13–17], thus predicting the interfacial bonding based on the Van der Waals interaction will not yield dependable results.

Therefore, in this work, a comprehensive fundamental MD simulations was performed to understand the variation in crosslinking behavior with the introduction of SWCNT and carboxylic (–COOH) functionalized SWCNT, and compared with the neat Epon composites. Also, the interfacial strength of non-functionalized and –COOH functionalized RPCs was investigated by performing the CNT pull-out simulations.

2 Simulation method: crosslinking procedure

Large-scale atomic/molecular massively parallel simulator (LAMMPS) was used to carry MD simulations. The simulations were performed mimicking the RPCs processing procedure suggested by the manufacturer using a mixing ratio of Epon 862 (resin) and Epikure-W (curing agent) as 100:26.4. Initially, non-crosslinked Epon 862 and Epikure-W molecules were packed into an amorphous cell. Initial parameters like density of 1.17 gm/cc³ and a temperature of 393 K was applied. The crosslinking simulations were then performed using Dreiding forcefield and LAMMPS software. Systems of 100 molecules of Epon 862 and 50 molecules of Epikure-W were used to create structures. The diameter and length of carbon nanotubes were 6.78 Å and 27 Å respectively.

The molecular model of cured Epon resin was developed using MAPS software following the same procedure reported by Varshney et al. [28]. Initial system

Fig. 1 Activation of Epon 862 and Epikure-W atoms**Fig. 2** Crosslinking of Epon 862 and Epikure-W atoms

was equilibrated using NPT simulations at 300 K and atmospheric pressure for 100 ps. The temperature was controlled using Nose–Hoover thermostat and barostat, and the possibility of any surface effects was minimized by applying 3D periodic boundary conditions. The crosslinking was performed after equilibrating the system using several steps which includes optimization, relaxation and then multistep algorithm which created new bonds after each cycle. Cyclic process of crosslinking continued until a specified target was achieved or there was no more possibility of crosslinking left or the reactive sites moved far away. Figure 1 shows the system model system and activation steps of reactive sites. Consequently, the final cured model of neat Epon system is shown in Fig. 2.

The cured model of Epon/SWCNT was developed using the similar crosslinking procedure followed for

the neat Epon system shown in Fig. 3. The Epon 862, Epikure-W and SWCNT were allowed to react in amorphous cell. However, for the Epon/COOH-SWCNT system, at first, one-side of SWCNT surface was functionalized by manually placing the $-\text{COOH}$ groups at random position. The functional groups were then activated and placed in an amorphous cell with activated Epon 862 and Epikure-W molecules. The surface of the SWCNT was modified with $-\text{COOH}$ groups which tend to form strong covalent bonding with the epoxy groups of the Epon 862 system shown in Fig. 4. During the curing reaction, hydrogen atoms in the amine (NH_2) groups of a cured epoxy molecule reacts with the COOH groups of SWCNT as shown in Fig. 4b, c. Finally, multistep algorithm was performed to create bonds between the activated reaction sites of Epon 862, Epikure-W and COOH-SWCNT. The final cured model of Epon/COOH-SWCNT system showing bonds formation at the interface is represented in Fig. 5.

3 Interfacial properties

The interfacial bonding energy of Epon/SWCNT and Epon/COOH-SWCNT systems were determined using pullout simulations by applying a displacement controlled load on the CNT. Interaction energy of the system was estimated from the energy difference, i.e. between the total energy of system and sum of energies of Epon and SWCNT system using Eq. 1.

$$\Delta E = E_{total} - (E_{nanotube} + E_{polymer}) \quad (1)$$

where E_{Total} is the total energy of Epon/SWCNT system, $E_{nanotube}$ is the energy of CNT and $E_{polymer}$ is the energy of polymer.

In this study, the SWCNT was set free, while the polymer and amorphous cell were fixed. Energy required to

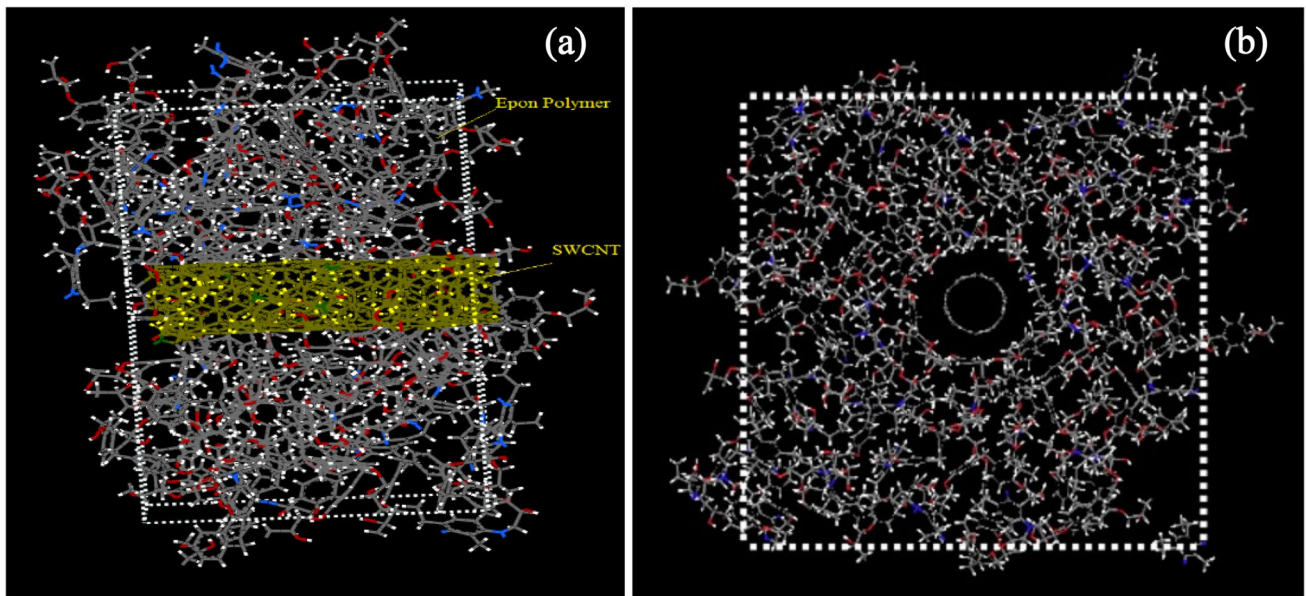


Fig. 3 Final cured model of Epon 862/SWCNT system, **a** side view, and **b** front view

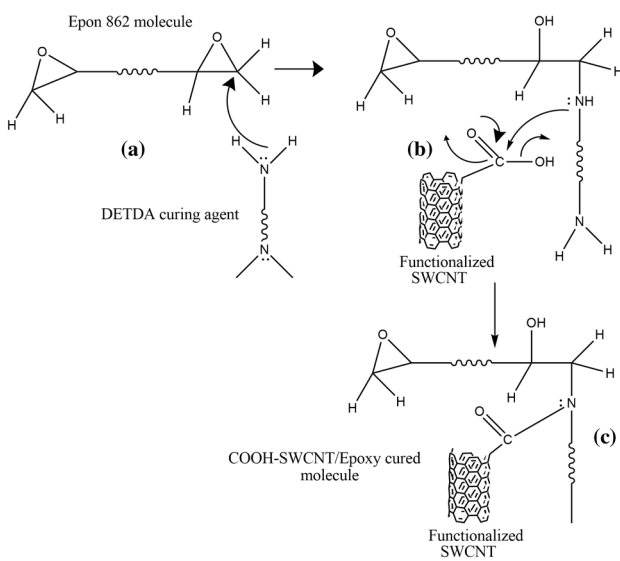


Fig. 4 Schematic of the crosslinking reaction of SWCNT-COOH and Epon 862 systems

completely pullout the CNT from the system was calculated using Eq. 2.

$$E_{pullout} = E_2 - E_1 \tag{2}$$

where E_1 and E_2 are the initial and final energy during pullout.

Finally, the interfacial shear stress (τ_i) was determined using Eq. 3.

$$\tau_i = \frac{E_{pullout}}{\pi r L^2} \tag{3}$$

where r and L are the radius and length of nanotube.

Steered molecular dynamics (SMD) simulations were employed to simulate the pullout of the SWCNT from the Epon 862 system. The potential mean force was calculated from non-equilibrium process such as SMD. By applying a moving spring force to the center of mass of the SWCNT's atoms, the SWCNT was pulled along z-axis at a constant speed, while all other sides were constrained.

4 Results and discussion

4.1 Epon system crosslinking

Crosslinking algorithms were continued upto 10 iterations for a time length of 1 ns. The amount of crosslinking was recorded with every iteration. Once the crosslinking process of neat Epon system started, the simulations continued until all the maximum possible activated reactive sites were crosslinked or the system completed the set 10 iterations. At this point, to confirm the accuracy of the crosslinked neat Epon system, the glass transition temperature (T_g) was predicted with the annealing method and compared with the experimental, simulated and manufacturer reported T_g . The temperature of the system was raised from 300 K to 520 K and the T_g was determined from the density versus temperature response shown in Fig. 6. Result showed a T_g of 397 k or 122.85 °C calculated using the discontinuity in the graph is in good agreement with the reported value of 120–135 °C [29, 30].

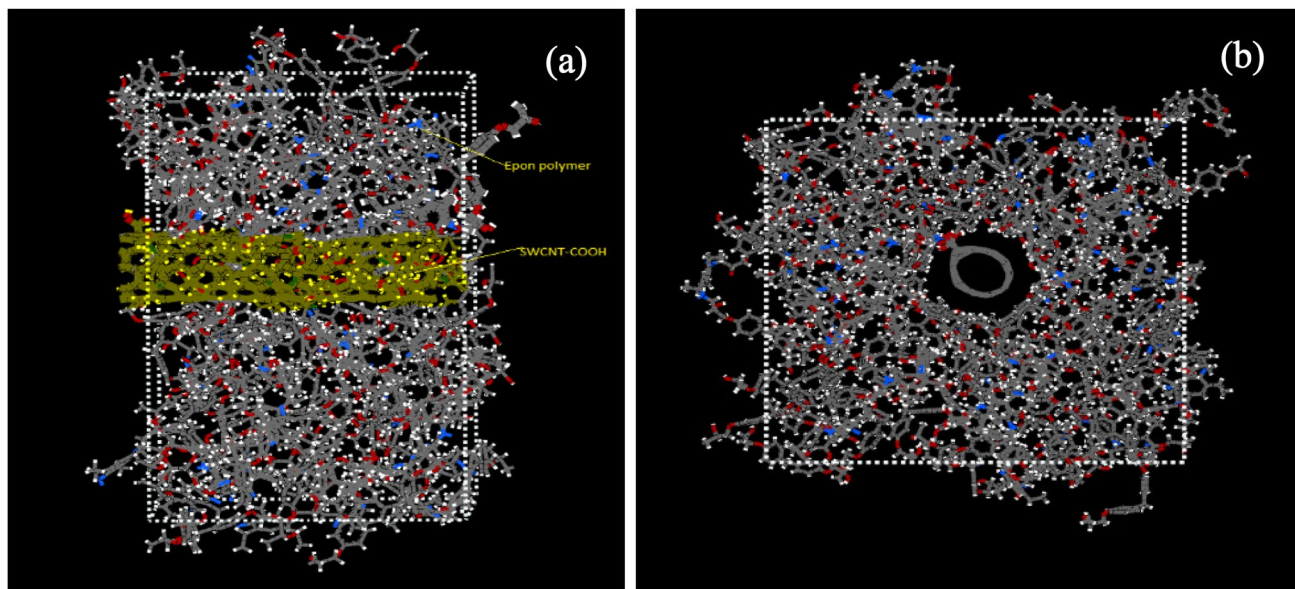


Fig. 5 Final cured model of Epon 862/COOH-SWCNT system, **a** side view, and **b** front view

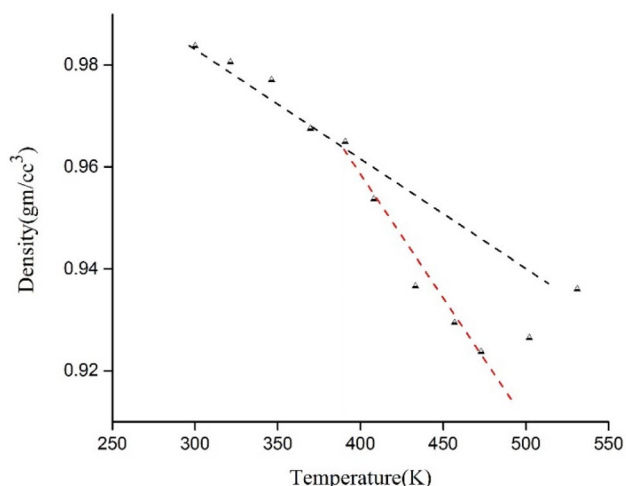


Fig. 6 Predicted glass transition temperature versus density response of neat Epon 862 system

After assuring the accuracy of the neat system, identical crosslinking algorithm were continued for Epon/SWCNT system, and the initial and final crosslinking densities were measured. The initial crosslinking density of this system after first iteration was reduced by 5% in comparison to neat Epon system. Also, the Epon/SWCNT system reached its maximum crosslink density of 72–75% within the set number of iterations which is 11% lower in comparison to neat counterpart shown in Fig. 7. The decrease in crosslink density of Epon/SWCNT can be attributed to the presence of SWCNT itself, which is not only non-reactive with the Epon system, but also found to block and

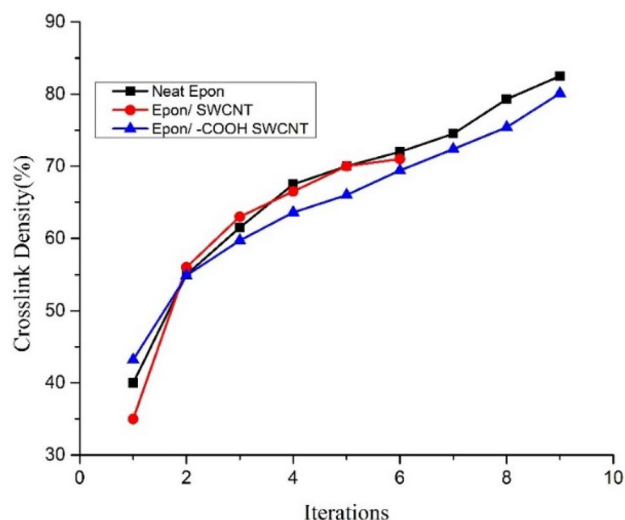


Fig. 7 Crosslink density versus iterations response of neat, Epon/SWCNT, and Epon/COOH-SWCNT systems

move away the reactive sites of Epon 862 and Epikure-W molecules as shown in Fig. 3b. Another interesting phenomenon observed in our simulation is the polymer wrapping around SWCNT shown in Fig. 8. The aromatic rings of Epon 862 and Epikure W were found to gradually align parallel and wrap the nanotube surface. Also, due to the absence of functional groups on SWCNT, no interfacial bonding was observed with Epon862 system's reactive sites as shown in Fig. 3b. Eventhough, the desired higher crosslink density and interfacial bonding between the SWCNT and Epon system was not found in this study,

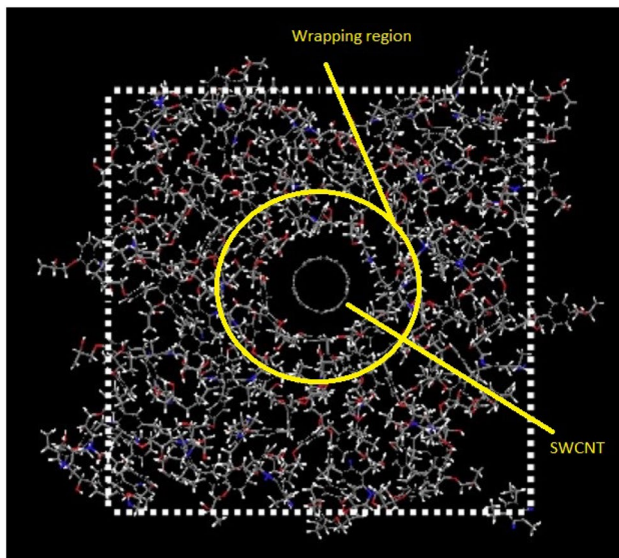


Fig. 8 MD simulation snapshot of wrapping of SWCNT by an Epon862 and Epikure-W chain

the improvements in mechanical properties reported by other researchers through experiments and simulations could be due to the polymer wrapping of CNTs surface

and strong inherent tensile strength and elastic modulus of CNT itself. The polymer wrapping around the CNT surface is helpful in preventing them from aggregating into bundles and improving their dispersion in a epoxy composite.

On the otherhand, the initial and maximum crosslink density of neat Epon and Epon/SWCNT-COOH systems were found higher than the Epon/SWCNT counterpart. The higher crosslinking density in the neat system could be attributed to the availability of more Epon and Epikure-W reactive sites that were blocked or moved away by the presence of SWCNT in the Epon/SWCNT system. In contrast, for the Epon/COOH-SWCNT system, even though the reactive sites were blocked similar to Epon/SWCNT system, the presence of -COOH functional groups on CNT surface established a strong bonding with the reactive sites of polymer as shown in Fig. 5 and illustrated in Fig. 4, respectively.

4.2 Interfacial properties

Snapshots of SWCNT and SWCNT-COOH being pulled from the Epon system are shown in Figs. 9 and 10. It can be seen from Fig. 9, that the surface of SWCNT after

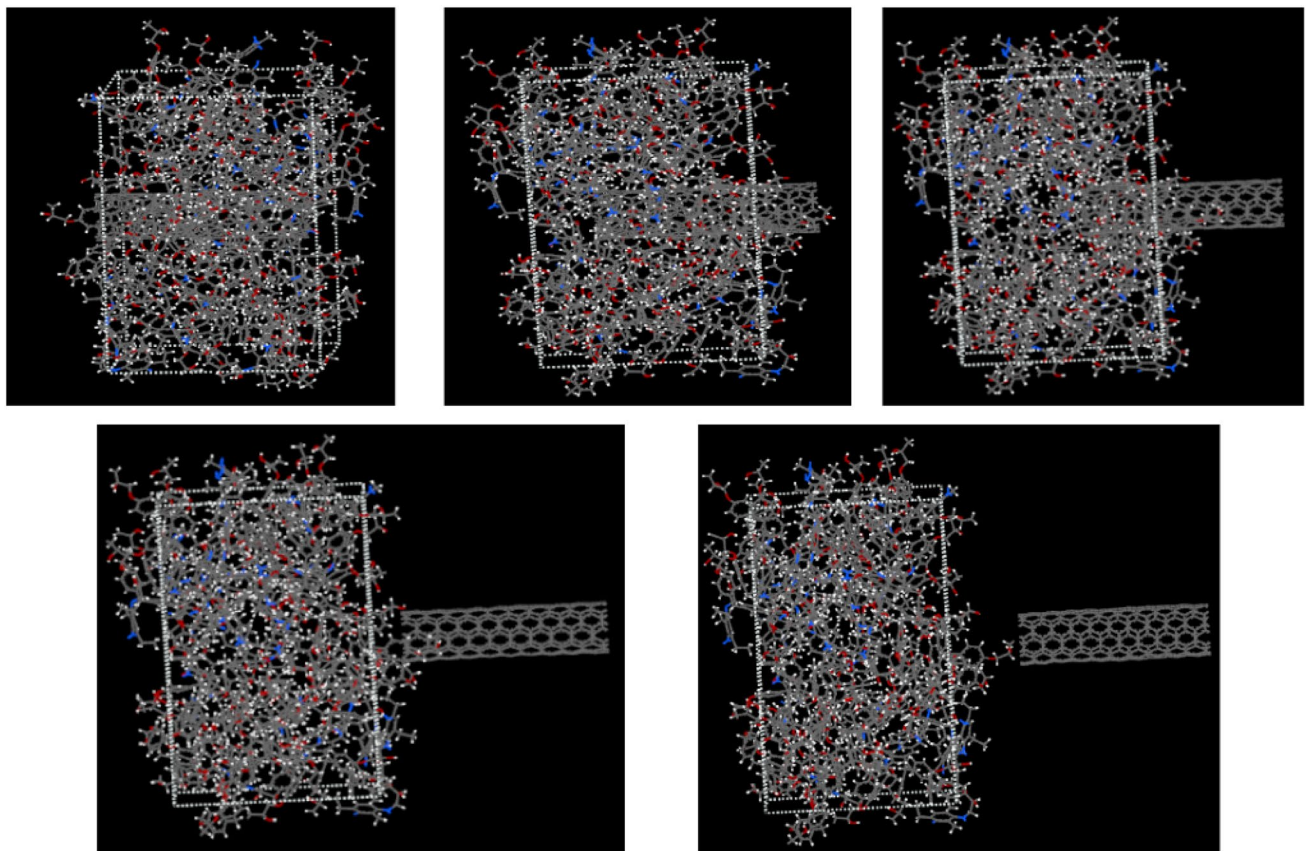


Fig. 9 MD simulation snapshot of SWCNT pullout from Epon system

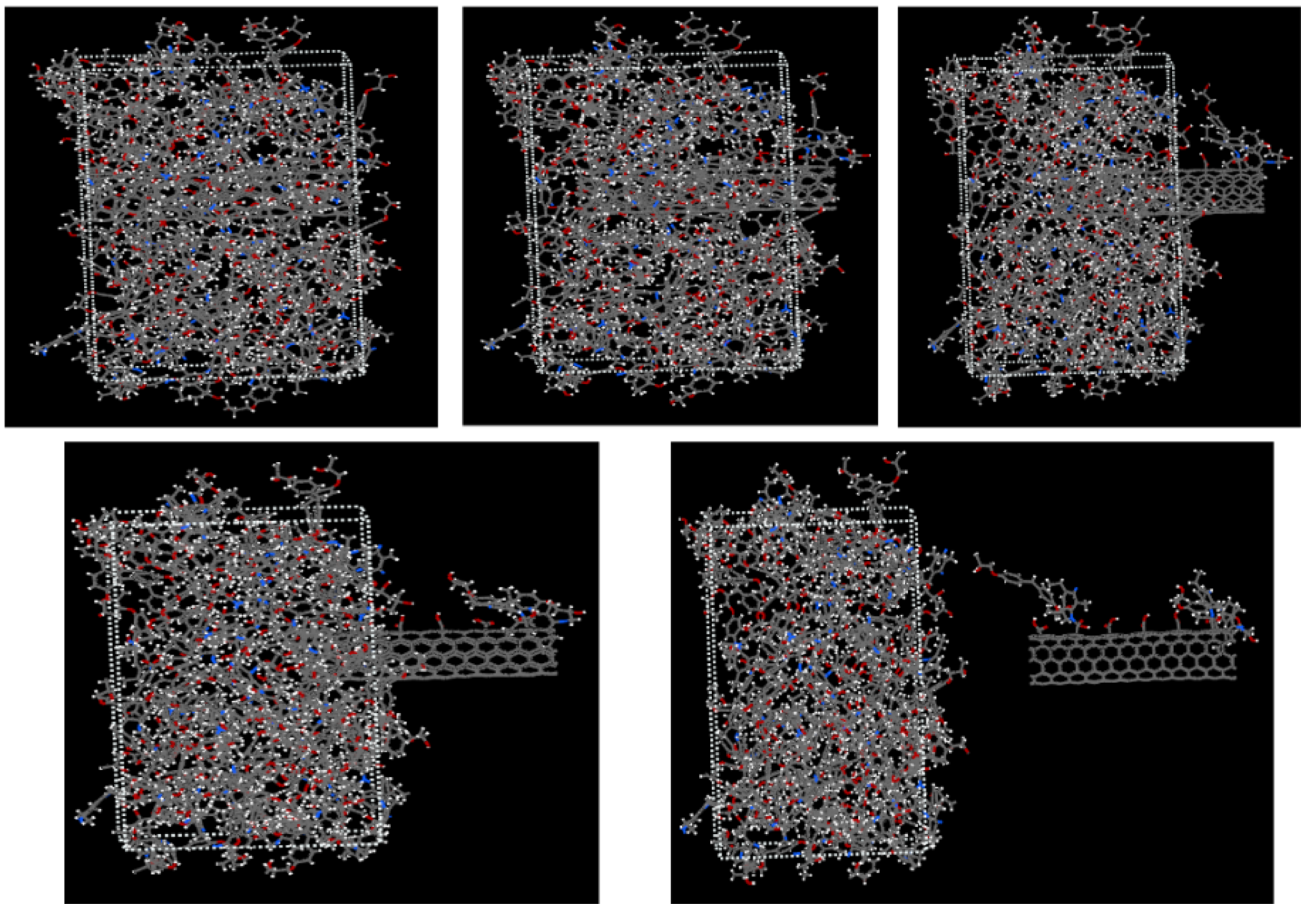


Fig. 10 COOH functionalized SWCNT pullout from Epon system

pullout was very smooth with no polymer attached to it indicating no interfacial bonding. Therefore, the only interaction between the SWCNT and Epon system expected is may be due to the weak Van der Waals forces considered by other researchers [22–24, 26–28] However, in Epon/COOH-SWCNT system, when higher pull-out force were applied, no separation was observed at the interface between SWCNT and polymer. Instead, the friction/shearing was initiated in the polymer molecules, and lead to complete breakage of polymer chain bonds, while a strong interphase was found between between the Epon/COOH-SWCNT evident from Fig. 10. Similar higher pull-out forces for a capped CNT than that of the corresponding open-ended CNT was reported by Li et al. implying a significant contribution from the CNT cap to the interfacial properties [31].

The energy trend in the systems monitored during the pull-out is shown in Fig. 11. The initial and final energy in Epon/SWNCT and Epon/COOH-SWCNT measured during the pullout was 13,500 kcal/mol and 12,000 kcal/mol, and 15,200 kcal/mol and 13,200 kcal/mol, respectively. A significantly higher initial and final energy was

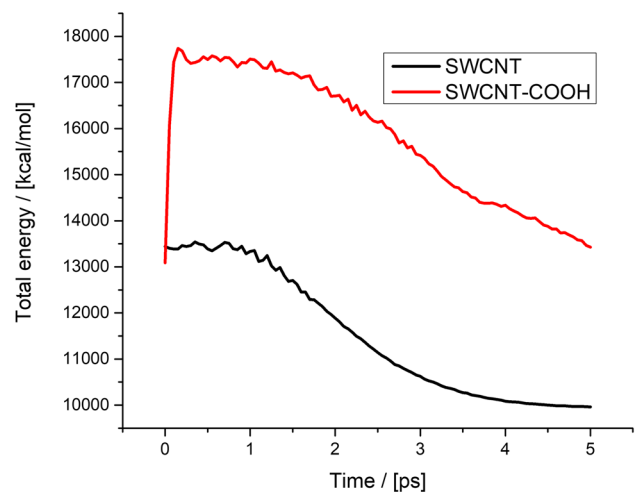


Fig. 11 Energy versus time response during CNT pullout from Epon system

found in the Epon/COOH-SWNCT system in comparison to Epon/SWCNT counterpart. Similarly, the interfacial shear strength in these system was found 97.84 MPa and

130.46 MPa, with a increase of 33% in the Epon/COOH-SWNCT system. These significant enhancements in the system energy and interfacial shear strength in Epon systems reinforced with –COOH functionalized SWCNT could be attributed to the formation of a strong covalent bond at the interface. It is to be noted that in this study, the carboxylic functional groups were placed on one side of CNT surface. We expect the enhancement of these properties in the nanotube RPCs to be even significantly higher than neat composites.

5 Conclusion

In this study, MD simulations was successfully utilized to predict the crosslinking behavior and interfacial properties of Epon 862 systems reinforced with non-functionalized and –COOH functionalized SWCNT.

The crosslinking density reduced when SWCNT was introduced into the neat Epon system as a result of reactive site blockage and no interface bonding between nanotubes and polymer. Another interesting phenomenon observed was polymer wrapping, which could potentially reduce the re-agglomeration of CNTs in the epoxy system, depending on the uniformity of dispersion, percentage of CNT concentration, and the carbon–carbon attraction energy. Hence, the enhancements in mechanical properties reported by the researchers in epoxy systems at lower concentrations of non-functionalized CNTs could be due to the inherent properties of CNTs combined with polymer wrapping and weak Van der Waals forces at the interphase.

In contrast, the surface functionalization of SWCNT with –COOH groups established a strong interfacial bonding with the Epon system that lead to significant enhancement in crosslink density and interfacial strength. Pull out simulations showed polymer chain sliding, shearing and finally leading to breakage instead of separation at the interphase in Epon/COOH-SWCNT systems. This results indicated that by functionalizing nanotubes with compatible functional groups such as carboxylic, amine etc., a highly crosslinked system with stronger interface can be developed which could be potent than the crosslinking of base polymer molecules chain itself.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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