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Effect of defect and functionalization of CNTs on the interphase characteristics of CNT-epoxy nanocomposites

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Abstract: The interphase region of nanoparticle-polymer nanocomposites plays an important role in their property enhancement. In this paper, the interphase characteristics including interaction strength and effective thicknesses of epoxy nanocomposites with either defective or functionalized CNTs are determined using molecular dynamics (MD) simulation. CNTs with monovacancy and trivacancy are created by removing one- and three-bonded carbon atoms from a pristine CNT, respectively. In addition, amine was chosen as the functional group being end-grafted to the sidewall of CNTs. The different concentration of amine was applied to identify the best functionalization for reinforcing the CNT-epoxy nanocomposites. The atomic density profiles of epoxy atoms were determined to characterize the density gradient along the radial direction from CNT long axis in the interphase region and quantify the effective interphase thicknesses. The calculated interaction energies between CNTs and epoxy matrix confirm that the strong adhesion strength exists between CNT and polymer matrix and the values of predicted interphase thickness are reasonable compared to those in literatures.

1. Introduction

In the past two decades, carbon nanotube (CNT) has received tremendous attention in both scientific and industrial communities due to its extraordinary mechanical, thermal and electrical properties such as the tensile strength of 50-100 GPa and the elastic modulus of 1.4 TPa [1]. Carbon nanotube-reinforced composites with various polymers (e.g., thermoplastics, thermoset plastics, elastomers) have been widely reported, which demonstrated that carbon nanotubes offer outstanding opportunities in materials development [2, 3]. Epoxy is a thermoset polymer that has received great interests because of its superior properties (e.g., thermal, mechanical, electrical, dimensional stability, chemical resistance) and wide applications (e.g., aircraft, aerospace, boat, automobile). In spite of its great advantages, epoxy has some inherent limitations (e.g., high brittleness, easy delamination, low fracture toughness). Some strategies have been employed to overcome these limitations, including chemical modification, increase in molecular weight, decrease in cross-link density, and reinforcement with tougher fillers [4]. Reinforcing epoxy matrix with nano-sized fillers like carbon nanotubes represents a new development strategy for property enhancement of epoxy [5, 6].

To further develop CNT-epoxy nanocomposites with better properties, understanding the complex interphase interactions between nanotube and polymer is critical. This is because when the particle size is in the nanometre scale, there is a large fraction of interphase [7]. Some studies have taken into account the effect of such interphase on the reinforcement of mechanical properties of CNT-polymer nanocomposites [8-14]. It is widely recognized that the experimental techniques are still difficult to determine the characteristics of such interphase because of the unclear boundaries and the nanoscale nature of the interphase. Thus further research is needed to shed light on the structural development in the interphase region [7]. In the past years, many theoretical and numerical efforts have been made to improve the understanding of the relationship between interphase structure and properties of CNT-

polymer nanocomposites [15-20]. For instance, Guru et al. [8] applied MD simulations to calculate the interphase thickness and interphase stiffness and then study their effects on elastic properties of nanocomposites. Their study showed that an interphase stiffness of 18.79 GPa can be achieved and an interphase thickness of 0.3 nm exists around the CNT filler.

Simply mixing pristine CNTs with epoxy matrix may result in poor reinforcement because of the weak covalent bonding and load transfer between the matrix and CNTs. To promote the crosslinking between CNTs and epoxy matrix, both defects and functionalization of CNTs are explored. The two types of defects are: monovacancy and trivacancy. Both defects are realised by removing one- and three-bonded carbon atoms from pristine CNTs, respectively. For functionalization, amine groups are introduced into pristine CNTs to increase the covalent bonding between CNTs and epoxy matrix, with four different concentrations of amine groups including 1%, 3%, 5% and 8% of the pristine CNTs. The present objective is to employ MD simulation to determine the effect of defects and functionalization of CNTs on molecular interactions in the interphase between CNTs and epoxy polymer chains, and thus predict their interphase thickness of the nanocomposites.

2. Simulation method

2.1. Molecular structures of CNTs and epoxy

All simulations were carried out using MATERIALS STUDIO 2016, a commercial software (Biovia Co.), specifically the Amorphous Cell module for model construction and Forcite module for MD simulation. The pristine CNT used is armchair (10,10) single wall carbon nanotube (SWCNT) with an outer diameter of 13.56 Å. The parameters of MD simulation cell for CNT-epoxy nanocomposites are a=b=c=50Å and α=β=γ=90˚. Fig.1 represents three molecular structures of CNTs, two with defects, i.e., monovacancy and trivacancy and the third with functionalization of amine group ($-CH_2-CH_2-NH_2$) by grafting them onto the sidewall of the CNT. Monovacancy and trivacancy are generated by removing one- and three-bonded carbon atoms from the pristine SWCNTs, respectively. Specifically, CNTs with 6 monovancies, 6 trivacancies, and amine functional group of 1%, 3%, 5% and 8% are considered. All vacancies and functionalization are randomly located in the pristine SWCNTs.

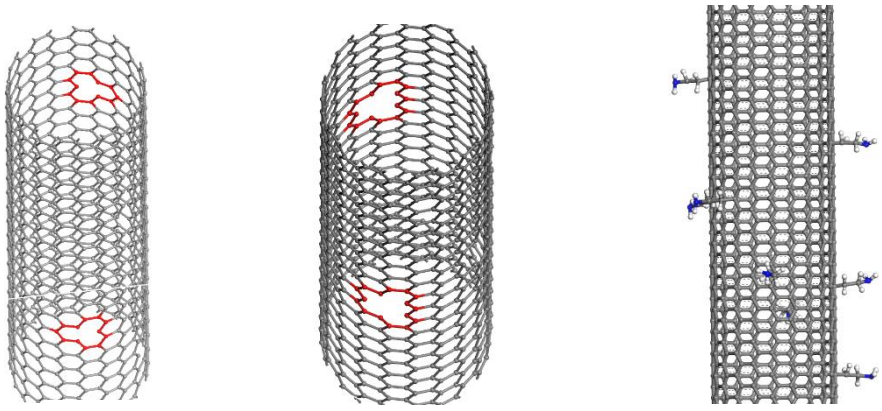


Fig.1 Molecular structures of a single CNT with (a) monovacancy, (b) trivacancy, and (c) amine group functionalization. Colour: hydrogen atom in white; carbon atom in grey; and nitrogen atom in blue.

The polymer matrix was cross-linked epoxy resin which composed of epoxy monomer bisphenol A diglycidyl ether (DGEBA) and its curing agent triethylenetetramine (TETA). Chemical structures of DGEBA and TETA are shown in Fig. 2. To obtain the cured epoxy system, the mixture of DGEBA and TETA with a ratio of 6:1 is firstly packed into a simulation cell containing a single CNT (e.g., pristine CNT, monovacancy or trivacancy defected CNT, or CNT with 1%, 3%, 5% and 8% amine functional group) with a targeted density of 1.09 g/cc. Then the mixture is cured by running a cyclic set of minimization, equilibration and dynamics simulations to reach a cross-linked structure by

forming covalent bonds between hydrogen atoms from amine groups of TETA and epoxide groups of DGEBA [21-25]. The cured epoxy system is then minimized using the method of conjugate-gradient [26] with a convergence criteria of 0.0001kcal/mol.

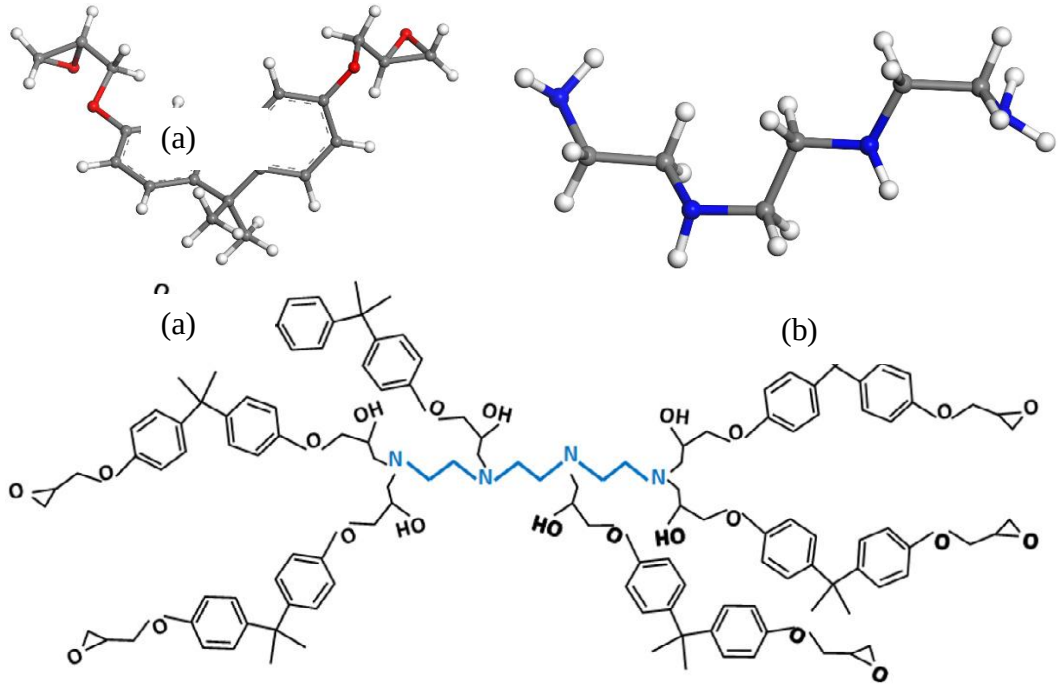


Fig. 2 Chemical structures of (a) DGEBA, (b) TETA and (c)cured epoxy oligomer consisting of 6 DGEBA chains connected by 1 TETA chain. Colour: hydrogen atom in white; carbon atom in grey; nitrogen atom in blue; and oxygen atom in

2.2 Construction of CNT-epoxy nanocomposites

Models of epoxy nanocomposites reinforced with a pristine CNT, monovacancy or trivacancy defect CNTs, or CNT of 1%, 3%, 5% and 8% amine functional group are constructed in Amorphous Cell module. The model of CNT with 5% amine functional group is shown in Fig. 3.

2.3 Simulation method and conditions

The minimized CNT-cured epoxy system is initially performed by applying a NVT MD simulation at an elevated temperature of 400 K for 500 ps to achieve an ideal mixing of CNT and cross-linked epoxy chains. Then the temperature is cooled down to 298 K by multiple stages, with each stage cooling for 25 K and a simulation time of 20 ps. After that, the mixture is subjected to a further NVT simulation at 298 K for 500 ps to achieve an equilibrium state. Finally, data of the last 200 ps is collected and analysed.

The condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) forcefield is applied in all MD simulations. The Forcite module is employed to run all MD simulations. The time step of integration is set to 1 fs. The van der Waals and Coulomb forces are calculated by the Ewald summation method. Anderson method is used to control the temperature. Periodic boundary conditions are adopted in all MD simulations.

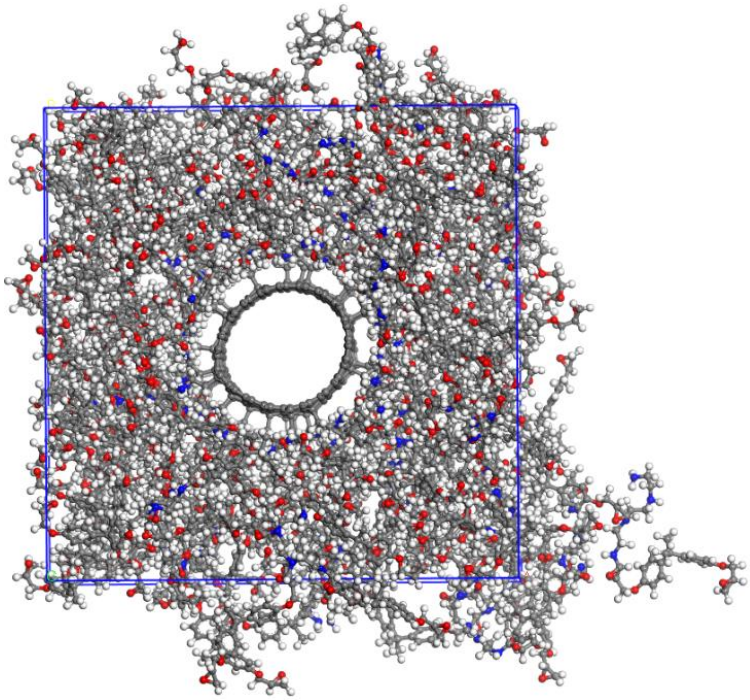
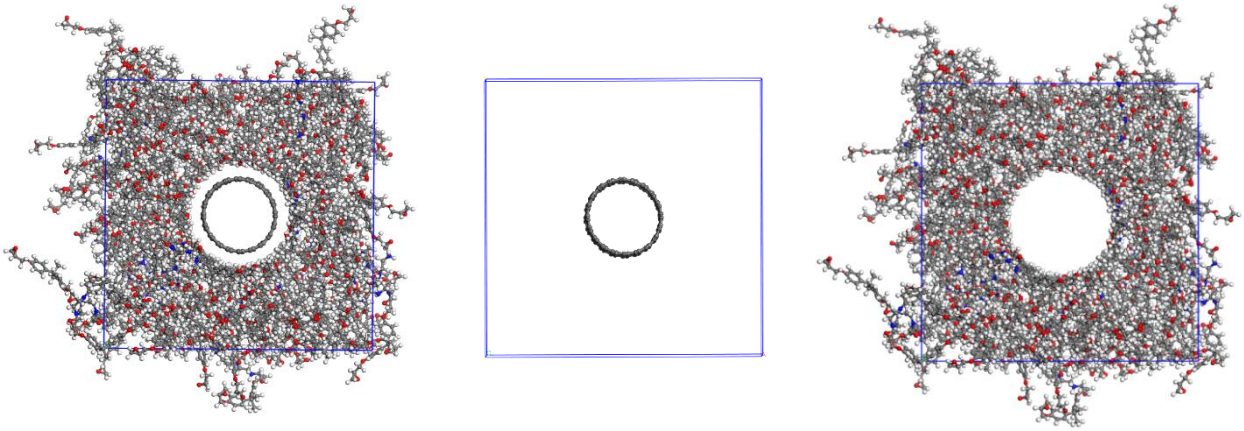


Fig.3 Model of a CNT-epoxy nanocomposite with 5% amine functional group. Colour: hydrogen atom in white; carbon atom in grey; nitrogen atom in blue; and oxygen atom in red.

2.4 Analysis method

In this study, the interaction energies between CNT and epoxy polymer in all cases are quantified on the basis of the average of final MD snapshots. A final snapshot of a pristine CNT-epoxy nanocomposite and the extracted CNT and epoxy matrix is shown in Fig. 4.



(a) (c)

Fig. 4 An equilibrium structure of a pristine CNT-epoxy nanocomposite: (a) nanocomposite (b) extracted CNT, and (c) extracted epoxy matrix. Colour: hydrogen atom in white; carbon atom in grey; nitrogen atom in blue; and oxygen atom in red.

The total interaction energies as well as the contributions from electrostatic and van der Waals interactions between the CNT and epoxy matrix are calculated according to the following equation [27].

$$E_{CNT-epoxy} = E_{total} - E_{CNT} - E_{epoxy} \qquad \text{(b)}$$

where $E_{CNT-epoxy}$ is the interaction energy (in Kcal) between the two components, E_{total} is the potential energy of the nanocomposite, E_{CNT} and E_{epoxy} are the potential energies of the extracted CNT and epoxy, respectively.

Interphase thickness is a crucial characteristic in nanocomposites. Such thickness can normally be defined as the distance from nanoparticle surface to the point where the atomic properties (e.g., atomic density profile) are different from those in bulk matrix systems [7]. From atomic density profiles, the effective thickness of these nanocomposites is analysed by two different approaches. The first method is based on the relative ratio of atomic density profiles and the average atomic density of bulk epoxy. Specifically, a distance is identified in the profile where the atomic density is close to that of bulk epoxy, normally showing a sharp transition point into flat curve [11]. The second approach is based on the full width at half maximum (FWHM) value of the first peak from CNT surface along the radial direction from CNT long axis in the above atomic density profiles.

3. Results and discussion

3.1Interaction strength at the interphase

The overall interaction between CNTs and epoxy matrix (Table 1) is attractive. Such attractive interaction for nanocomposites with defected CNTs is slightly weaker than that of pristine nanocomposite. However, nanocomposites with amine-functionalized CNTs show stronger attraction than that of pristine nanocomposite. Such attractive interaction increases with the concentration of functional groups. This is because of a strong connection between amine functional groups and TETA repeat units in epoxy which also contains amine groups. Moreover, the more amine functional groups attached to CNT, the stronger the interaction. This conclusion can be validated from the radial distribution function (RDF) profiles of N atoms in both amine functional groups and TETA repeat units as well as the RDF profiles of N atoms in amine functional groups and C atoms in epoxy matrix of nanocomposite with CNT functionalized by 5% amine groups (Fig. 5). It is clearly noticed that there is a closer connection between amine groups and the TETA than that of amine groups and C atoms in epoxy.

3.2 Effective thickness of the interphase

Fig. 6 shows the atomic density profile along the radial direction from CNT axis) of epoxy matrix in nanocomposites with pristine CNT, monovacancy or trivacancy defected CNTs, or CNTs functionalized with 1%, 3%, 5% and 8% amine groups, respectively.

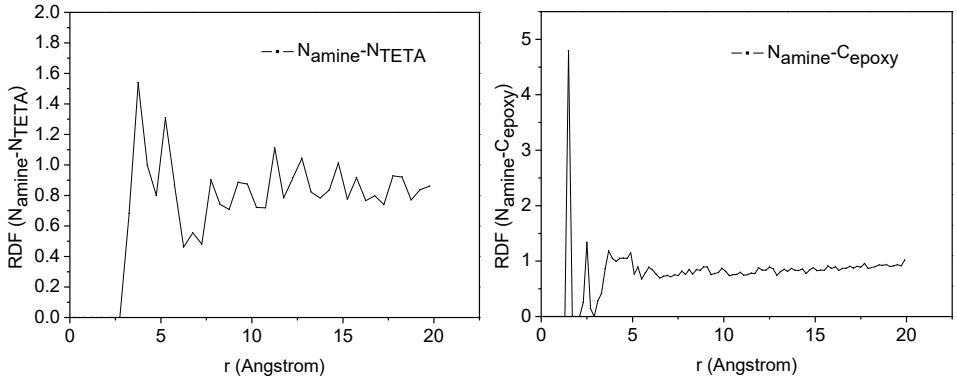


Fig. 5 RDF profiles of N atoms in amine functional group and epoxy TETA repeat units of the nanocomposites with 5% amine group (left) as well as the RDF profiles of N atoms in amine functional groups and C atoms in epoxy matrix (right).

Table 1. Interaction energies (Kcal) between CNT and epoxy matrix in pristine, defective and functionalized CNT-epoxy nanocomposites.

CNT	Electrostatic	vdW	Total
Pristine	-0.005	-793.605-	-866.012-
monovacancy defected	-0.832	778.878	851.863
trivacancy defected	-10.477	-750.486	-832.398
functionalized with 1% amine group	-24.887	-796.587	-895.661
functionalized with 3% amine group	-53.594	-806.798	-940.294
functionalized with 5% amine group	-106.229	-805.385	-994.594
functionalized with 8% amine group	-110.385	-807.885	-1006.963

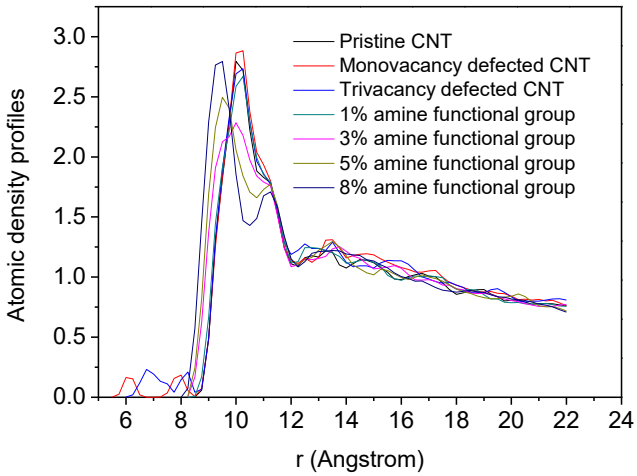


Fig. 6 Atomic density profiles of epoxy atoms in nanocomposites with pristine CNT, defected, and functionalized CNT of various amine concentrations.

Table 2. The average atomic density of bulk epoxy matrix and calculated interphase thickness in nanocomposites with pristine CNT, monovacancy and trivacancy defected CNTs, and functionalized CNT with 1%, 3%, 5% and 8% amine groups

	Pristine CNT	defected CNT		CNT with amine functional group			
		monovacancy	trivacancy	1%	3%	5%	8%
ρ (g/cm^3)	1.02	0.95	0.95	0.94	0.93	0.91	0.90
t_1 (Å)	3.72	3.97	3.72	3.72	3.72	3.97	3.97
t_2 (Å)	2.26	2.29	2.39	2.48	2.96	3.06	3.00

Note: t_1 is the effective thickness calculated by the first method, and t_2 is the effective thickness calculated by the second method

The average atomic density of bulk epoxy and the calculated interphase thickness based on the first method are shown in Table 2. From Table 2, it is clearly noticed that the effective interphase thickness ranges from 3.72 Å for epoxy nanocomposites with pristine CNT and low level of functionalization to 3.97 Å in nanocomposites with high level of functionalized CNT amine groups. These significant

values of interphase thickness assure the existence of interphase in the CNT-epoxy nanocomposites [10]. From the second approach, the effective interphase thickness ranges from 2.26 Å in pristine CNT-epoxy nanocomposites to 3.06 Å in CNT nanocomposites with 5% amine functional groups. The values of interphase thickness calculated from the second method are slightly lower than those from the first method. Nevertheless, the values of interphase thickness from both methods are in the range of 2.26-3.97 Å, which are reported by Alian et al. [28] It is also noteworthy that both calculation results show that both defect and functionalization can slightly increase the interphase thickness of nanocomposites. This is attributed to a better crosslinking between CNT and epoxy matrix [9, 12]. It is believed that the results from the second approach should be more reliable than those from the first method because FWHM is an apparent index in the atomic density profiles. On the other hand, the sharp transition point into flat curve in atomic density profiles of nanocomposites may not be clear as well and therefore the first method may not be as accurate as the second method.

4 Conclusions

In this work, molecular interactions as well as interphase thickness of defective and functionalized CNT-epoxy nanocomposites are studied using MD simulations. The simulation results show that the overall interactions between amine functionalized CNT and epoxy matrix are slightly larger than that of defective CNT and epoxy matrix. The interphase thickness of defective and functionalized CNT-epoxy nanocomposites is calculated by two approaches. The results show that both defects and functional groups in CNT can significantly increase the interphase thickness of nanocomposites. Moreover, with the increase in the level of amine functional groups, the interphase thickness increases.

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