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Characterizing nanotube–polymer interaction using molecular dynamics simulation

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ABSTRACT

Theoretical characterization of the interaction between Carbon nanotube (CNT) and surrounding polymer is presented in this article using molecular dynamics simulation. Firstly, isolated non-defected and defected CNTs are simulated. The reduction level in Young's modulus of CNT is analyzed due to the induced vacancy defects in CNT nanostructure. Then, embedded CNT in polymer is simulated focusing on the CNT and polymer interaction. The effect of chemical functionalization on mechanical properties of nanocomposites is discussed at micro level. Stochastic analysis is conducted treating numbers of established covalent bonds between CNT and polymer and their positions as random parameters. Young's modulus of the interphase region as an intermediate phase between CNT and polymer for continuum modeling is extracted. It is revealed that increasing numbers of transverse covalent bonds between CNT and polymer, Young's modulus of the nanocomposites decreases arisen from induced vacancy defects in CNT. Although functionalization can improve the interfacial shear strength between CNT and polymer, it has a disadvantage in reducing Young's modulus of the interphase region leading to weak stress transferring from resin to CNT.

1. Introduction

Thanks to high strength and modulus, low density, large aspect ratio and remarkable electrical and thermal properties, Carbon nanotubes (CNTs) have attracted significant attention among other nano-fillers for reinforcing polymers [1–3]. Experimental observations imply on considerable growth in mechanical properties of nanocomposites by adding low amount of CNT to polymers [4,5]. Besides the supreme mechanical properties of CNT originated from strong covalent bonds of its nano-structure, the stress/load transferring mechanism from matrix to CNT is a crucial issue in defining CNT capability for reinforcing polymers. The interaction between CNT and surrounding polymer which occurs at the intermediate region between CNT and polymer (interphase) accounts for reinforcing efficiency of CNT at micro/nano level. The interphase region between CNT and polymer naturally consists of weal van der Waals (vdW) interactions owing to SP^2 hybridized carbons in CNT. This will be resulted in poor load transferring from resin to CNT. Therefore, some researchers have tried to improve the load transferring mechanism from matrix to CNT by establishing transverse covalent link between CNT and surrounding polymer [6–10]. The process recognized as functionalization has a main drawback of inducing vacancy defects to the CNT nanostructure. As a result, it is substantially important to analyze how functionalization affects overall properties of the nanocomposites relying on the role of interphase region. It is very well known that functionalization will improve mechanical properties of CNT-based composites at macro level due to reduction of aggregate formation; but the main drawback of functionalization attributed as the induced structural defects in CNT nano-structure should be also investigated.

Recently, Rahmat and Hubert [11] have comprehensively reviewed the performed studies on interaction between CNT and polymer in literature. Measuring techniques which are divided into experimental observations and atomistic modeling have been explained and discussed. More recently, Rafiee et al. [12] have extensively reviewed atomistic and continuum modeling methods for investigating the CNT–polymer interactions. They have outlined challenges of each modeling category. Limited theoretical studies have been concentrated on the influence of functionalization on mechanical properties of CNT/polymer nanocomposites.

Performing a review on literature, it can be seen that mainly two different approaches as continuum and atomistic modeling have been used by researchers to study the interaction between CNT and polymer [12]. While atomistic modeling is able to accurately address the real nature of the interactions between CNT and polymer, it is suffering from complex formulations, intensive computational efforts and its limitations of small length scale.

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Alternatively, continuum modeling techniques are able to overcome aforementioned obstacles, but the accuracy of continuum modeling in capturing the actual behavior of CNT and/or interphase at nano-scale has to be carefully investigated.

Rafiee and Pourazizi [13] used continuum modeling to study the influence of vacancy defects induced by functionalization on mechanical properties of a representative volume element (RVE) containing functionalized CNT, interphase and surrounding polymer. They have used 3D Finite Element (FE) modeling method assuming both numbers of defects and defects locations as random parameters. CNT was modeled as a lattice structure while polymer was modeled as continuum medium. Non-linear spring elements were employed for capturing vdW interactions and beam elements were used to simulate covalent transverse bonds between CNT and polymer representing interphase. Performing a stochastic analysis, they have shown that functionalization procedure will reduce the Young's modulus of the RVE at nano/micro scale [13]. Pourakbar et al. [14] have studied the effect of functionalized CNT on the properties of RVE. Constructing a 2D model, they have replaced CNT with a solid member. Beam elements were used to simulate covalent bonds between CNT and resin. It was reported that higher population of covalent bond will be led to the improvement in stress transferring efficiency from matrix to CNT [14].

Frankland et al. [15] modeled an embedded single armchair CNT in polymer using MD. The results show an increase in the Interfacial Shear Strength (ISS) by establishing less than 1% cross-links between CNT and polymer [15]. Chowdhury and Okabe [16] reported that ISS increases from 310 MPa to 1630 MPa for a functionalized (5, 5) CNT with four chemical cross links using MD simulation on the basis of Tersoff–Brenner force field.

In this article, the influence of interphase region on the mechanical properties of CNT-based composites is investigated using MD simulation. Both non-modified CNT and functionalized CNT embedded in a polymer are analyzed concentrating on the interphase region. For the case of functionalized CNT, stochastic approach is employed taking into account the location and number of defects as random variables. CNT and interphase region is replaced with an equivalent fiber on the basis of obtained results. Therefore, the mechanical properties of the intermediate region between CNT and polymer which can be used for continuum modeling are extracted accordingly. In other words, the novelty of this article is placed behind the developed bridging approach that the required mechanical properties of the interphase region for continuum modeling will be obtained using MD simulations.

The remaining of the article is organized as follows: Firstly, the modeling procedures of isolated CNT in both non-defected and defected forms are studied. Then, the representative volume elements (RVEs) of CNT-based composites at micro scale consisting of CNT, interphase and polymer are studied resembling non-modified and functionalized CNTs. Mechanical properties of equivalent fiber and virtually continuum medium of interphase region are obtained afterwards.

2. Modeling CNT

A computer code is written in the platform of LAMMPS to perform MD simulations [17]. The total interactions in a CNT nanostructure system is a combination of bond stretching, bond-angle bending, improper dihedral-angle bending and inversion-angle bending as below [18]:

$$E_{\text{Total}} = E_{\text{stretching}} + E_{\text{bending}} + E_{\text{dihedral}} + E_{\text{inversion}} \tag{1}$$

The first two terms of Eq. (1), i.e. bond stretching and bond bending, are the most dominant ones in comparison with the remaining ones. Consequently, two-body potential energy function is used for modeling CNT.

The non-linear REBO [19] potential accounting for bond-stretching of Carbon–Carbon (C—C) interaction is used and expressed as below:

$$V^{\text{REBO}}(r_{ij}) = f_c(r_{ij})[V^R(r_{ij}) + \bar{\bar{b}}_{ij} V^A(r_{ij})] \tag{2}$$

$$V^R(r_{ij}) = f_c(r_{ij})\left[1 + \frac{Q_{ij}}{r_{ij}}\right] A_{ij} e^{-\alpha_{ij} r_{ij}} \tag{3}$$

$$V^A(r_{ij}) = -f_c(r_{ij}) \sum_{n=1,3} B_{ijn} e^{-\beta_{ijn} r_{ij}} \tag{4}$$

$$f_c(r_{ij}) = \begin{cases} 1 & r_{ij} \leqslant 1.8 \\ \frac{1}{2} + \frac{1}{2}\cos\left[\frac{\pi(r_{ij}-1.8)}{2.1-1.8}\right] & 1.8 \leqslant r_{ij} \leqslant 2.1 \\ 0 & r_{ij} \geqslant 2.1 \end{cases} \tag{5}$$

Non-linear bond-bending interaction is expressed using below equation [18]:

$$H(\cos(\theta)) = E(\cos(\theta) - \cos(\theta_0))^2 \tag{6}$$

where E is 67.1383 kcal mol^{-1} and $\cos\theta_0$ is taken as -0.5 for C—C bonds [18].

One end of CNT is fixed and the other end is subjected to a constant strain by applying a constant velocity using below equation:

$$\varepsilon = \frac{N_s \times dt \times V}{L} \tag{7}$$

where ε is the strain, N_s is the number of steps, V is the velocity and L is the length of CNT.

An increasing trend of Young's modulus with respect to the CNT diameters has been observed [20]. When CNT diameter is larger than 1 nm, the CNT modulus approaches extreme values of 777 GPa and 882 for Armchair and Zigzag CNTs, respectively. The reduction level in the Young's modulus of CNT arisen from vacancy defect is studied, accordingly. Both number and position of defects are taken into account as random variables. Therefore, stochastic MD simulations are conducted.

Increasing number of vacancy defects, the Young's modulus of defected CNTs experience a linear decreasing trend. It was evident that the Young's modulus of a defected CNT containing six vacancy defects is reduced 10% [20]. A detailed study on the stochastic modeling of defected CNT is conducted by the same author in another article [20]. Moreover, a comparison between the results obtained using TB or REBO is carried out and it was revealed that using TB potentials higher values of Young's modulus is obtained for CNT than that of REBO.

3. Modeling neat polymer

There are a various types of polymeric resin in polymer matrix nano composites. Among them, Epoxy has received more attention due to its proper mechanical, chemical and thermal properties [21]. The molecular structure of Epoxy with two chains is shown in Fig. 1.

The covalent bond stretching in polymer chain is modeled using REBO [19] potential as explained in preceding section. Corresponding coefficients of C—C bonds are assumed as explained in Table 1, while the coefficient of C—H bonds are presented in Table 2.

Due to the huge amount of atoms involved in the polymer chain, for the bond bending, linear potential is used reducing required run-time for modeling:

$$U(\theta) = \frac{1}{2} K(\theta - \theta_0)^2 \tag{8}$$