Effects of stone–wales defects of carbon nanotubes on the elastic properties of the carbon nanotube-polyethylene nanocomposite and its interface

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Abstract
Carbon nanotube (CNT) filling in a polymer is an advanced approach to improve and manage the mechanical behaviors of polymer-matrix nanocomposites. However, some structural defects exist in CNTs, e.g., Stone–Wales (SW) defects on single-walled carbon nanotubes (SWCNT), which reduces the strength and changes the mechanical properties of CNT-reinforced nanocomposites. The influences of CNTs’ SW defects on the Young modulus of the CNT-polyethylene (PE) composite and its interface were investigated. All studies were performed through molecular dynamics (MD) simulations with the consistent force field (PCFF) on the platform of a large-scale atomic/molecular massively parallel simulator (LAMMPS). In the MD model of the CNT-PE nanocomposite, CNTs contained SW defects. The elastic modulus of the nanocomposite was obtained from its stress-strain relation, and that of the CNT-PE interface varied with strain according to the interfacial interaction energy. The correctness and rationality of the work were verified by comparing the results from references, experiments, and the rule of mixtures (ROM). The results showed that SW defects of CNTs reduced the mechanical strength no matter for the interface and integral nanocomposite. Specifically, with increased SW defect concentration (defined as the ratio of atoms in the SW defect region to total atoms of a CNT), the interfacial strength significantly weakened, and the elastic modulus of the integral nanocomposite reduced on the macro level. These results are beneficial to understanding the mechanical properties of CNT-PE composites and the design of related products.

1. Introduction
Reinforcing nanofillers in polymers can improve and manage the mechanical behaviors of polymeric nanocomposite materials [1]. Among the proposed nanofillers, CNTs with superior strength are preferred additives, which can enhance the mechanical properties of nanocomposites [2]. For instance, adding CNTs with 12% of the volume fraction (with a young’s modulus of about 1 TPa) to a PE matrix significantly increased the young’s modulus of the composite from several to 94.6 GPa [3]. Therefore, exploring how nanofillers improve the mechanical strength of these nanofiller-reinforced composites is vital for predicting their macro mechanical properties and performance-oriented material design [1].

In particular, the macroscopic mechanical properties of CNT-PE nanocomposites depend on the microstructure, closely related to the interfacial bonding strength in the interface region between the embedded CNT and its surrounding polymer [4]. Besides experimental measurements, atomistic-based modeling and simulations are preferred and more applied to investigate the correlation between the mechanical properties of the nanocomposites and their microstructures. The microstructure of composite materials can be controlled more effectively through these methods, which is more conducive to quantitative analysis and prediction of the influences of the microstructure on macroscopic mechanical properties [5].
Among atomistic-based techniques such as ab initio, tight bonding molecular-dynamic (TBMD), density functional theory (DFT), and molecular dynamic (MD), MD can provide acceptable accuracy with lesser running time [6]. For this reason, MD simulations are used to predict the macro-mechanical properties of CNT nanocomposites. For CNT-reinforced nanocomposites, previous studies indicate that the efficiency of CNTs as reinforcement is attributed to the load-transfer mechanism from the matrix to CNTs at the nanoscale. Besides, the interfacial bonding strength is a crucial issue for load transfer and reinforcement effects [7]. A CNT may have different geometries [8], chirality [9], and orientations [10]. These CNT’s features affect the interfacial bonding energy (corresponding to the interfacial bonding strength) and the mechanical properties of integral nanocomposites on the macro level. With the increased volume fraction of CNTs, the mechanical properties of nanocomposites enhance [8].

Arash et al [11] presented a method to predict young’s modulus in the interfacial region of CNT-reinforced PMMA nanocomposites and a three-phase model to predict the mechanical properties of nanocomposites. Polymer materials and polymeric matrix composites are sensitive to the loading rate and temperature. For exploring the influences of CNT-PE nanocomposites, Liu et al [12] and Singh et al [6] used MD simulations, finding that the loading rate and temperature significantly affect nanocomposite elastic properties and its interface.

Most of the above investigations have been performed on the assumption that single-walled CNTs are perfect without any defects. However, structural defects in single-walled CNTs are inevitable during their preparation [13]. Among these structural defects, SW defects such as the 5–7–7–5 SW defects commonly exist and are stable [13]. SW defects are composed of two pentagon-heptagon pairs and can be formed by rotating a sp² bond by 90° (see figure 1). As the result, these defects weaken the interfacial bonding strength to a great extent.
and affect the mechanical properties of the CNT-reinforced nanocomposites [14–16]. Therefore, the work focused on the effects of SW defects of CNTs on the interfacial bonding strength and mechanical properties of the integral nanocomposite.

2. Atomic modeling and simulation steps

2.1. Atomic modeling

The work used amorphous PE as the matrix and CNTs with chirality vector (9, 0) as reinforcement. For simplifying and representing the polymer matrix, a single chain of PE with 200 repeating units of -CH$_2$- were chosen as building blocks to simulate the actual PE. A periodic atomistic model of CNT-PE was constructed to avoid the end-effect of CNTs. All models were created using large-scale commercial software Materials Studio 8.0, and the modeling process was similar. In the whole simulation process, the polymer uniform force field (PCFF) was used and introduced to the force field.

Next, the defective CNT was embedded into a periodic cell (41.2 $\times$ 41.2 $\times$ 36 Å) with its length along the Z-axis. Then, the PE chain was filled into the crystal cell at a density of 0.85 g·cm$^{-3}$ to obtain the CNT-PE model (see figure 2). Furthermore, the polymer’s total potential energy was reduced to a minimum using the steepest descent method. Since the process of establishing the model is similar, only the process of building a model with a defect concentration of 1.4% is described here.

2.2. Force field

PCFF was used to describe the covalent interactions of atoms of CNT and PE and the non-covalent interactions at the composite interface. Figure 3 shows the bonded and non-bonded interactions of PCFF. In PCFF, the following formula is used to represent the total potential energy ($E_{nc}$) of composites.

$$E_{nc} = E_{bond} + E_{angle} + E_{dihedral} + E_{improper} + E_{non-bond}$$  \hspace{1cm} (1)

where $E_{bond}$, $E_{angle}$, $E_{dihedral}$ and $E_{improper}$ constitute the bonded interaction energy, while the non-bonded interaction energy ($E_{non-bonded}$) mainly considers van der Waals (vdW). Bond-stretching energy ($E_{bond}$) refers to energy changes caused by the stretching of the bonds along the bond axis. Bond-angle bending energy ($E_{angle}$) is the energy changes caused by the change in bond angles. Dihedral angular-distortion energy ($E_{dihedral}$) is the energy changes caused by the deformation of the molecular skeleton, which comes from the rotation of a single bond. Cross energy term ($E_{improper}$) refers to energy changes caused by the coupling of all the above actions. In this work, only the vdW interaction energy is considered for the non-bonded interaction energy, defined by the Lennard-Jones (LJ) 9–6 inter-atomic potential. Besides, the potential cutoff radius is set to 10 Å (see table 1 for other interatomic potential parameters). More detailed information and description of the second-generation PCFF can be found in [17].

2.3. Simulation procedure

The model was built to perform MD-simulation calculations on LAMMPS. First of all, the conjugate gradient method was used to reduce the total potential energy of the polymer to a minimum. Under the NVT ensemble, it was annealed to 500 K in 150 ps using a Nose-Hoover thermostat and then quenched to 150 K in 100 ps. The whole system was balanced for 200 ps under the NVE ensemble to make the volume and potential energy of the models relaxed and stable. At this point, the temperature of the system was 150 K, and the pressure in all
Figure 4. Molecular dynamics simulations apparatus for the CNT-reinforced PE nanocomposite.

Figure 5. Schematic diagram of transverse stretching device for composite materials.

Table 1. Lennard-Jones (LJ) 9–6 relative parameters.

| LJ 9–6 interaction | $\varepsilon$ (cal·mol$^{-1}$) | $\sigma$ (Å) |
|--------------------|-------------------------------|--------------|
| H–H                | 20                            | 2.995        |
| (C–C)$_{sp3}$      | 54                            | 4.010        |
| (C–C)$_{sp2}$      | 64                            | 4.010        |

Note: H–H is the interaction between carbon atoms; C–C is that between hydrogen atoms; subscripts sp2 and sp3 are the types of hybridization.
directions was 1 atm. After relaxation, the equilibrium density of the model was about 0.92 g cm\(^{-3}\), consistent with the density value of 0.95 g cm\(^{-3}\) in [18].

Then, molecular dynamics simulations can be performed under the NVT ensemble using the apparatus (see figure 4). During the simulation, the bottom atoms were fixed; the top atoms were stretched at a constant rate of \(3 \times 10^{-4} \text{Å ps}^{-1}\); the group of atoms in the middle were free to move in all directions. Similar stretching simulations were carried out on other models. Equation (2) was used to calculate the stress to obtain the stress-strain relationship throughout the simulation process, thus obtaining the elastic properties of the simulated material [19]:

\[
\sigma_{ij} = \frac{\sum_{K}^{N} m_{K} v_{K,ij} v_{K,j} + \sum_{K}^{N} f_{K,j} v_{K,i}}{V}
\]

where \(V\) is the volume of models; \(N\) the total number of atoms in the cell; \(v_{K,i}\) the \(i\) th component of velocity of the \(K\) th atom; \(v_{K,j}\) the \(j\) th component of the position vector of the \(K\) th atom; \(f_{K,j}\) the \(j\) th force component applied to the \(K\) th atom. Strain \(\varepsilon\) is obtained by

\[
\varepsilon = \frac{(\text{No. of steps}) \times \text{Timestep} \times \text{Velocity}}{\text{Length of CNT}}
\]

At the same time, transverse tensile simulation was conducted for each model according to the device in figure 5, and the parameters of the simulation process were the same as those of longitudinal tensile. In this way, we can obtain the transverse stress-strain curve of the composite material.

3. Results and discussion

MD simulations were used to predict the mechanical properties of the nanocomposite and its interfacial region in PCFF. In this chapter, we verified the correctness of the MD model and calculated the elastic moduli of CNT and pure PE. Furthermore, after calculating the macroscopic elastic modulus of the composite material, the elastic modulus of the interfacial region was obtained by the relationship between the interface energy and strain.

3.1. Validation of MD model
The work established the model with armchair-shaped CNTs (with chirality vector \((6, 6)\) as the reinforcement and PE as the matrix to verify the correctness of the established model and the simulation method used. The stress-strain curve was obtained by the axial-tension simulation. Under the same conditions, MD simulated results showed that Young’s modulus of CNT–PE nanocomposites was 106 GPa, consistent with the value of 103 GPa published by Mahboob et al [16]. This comparison verified that the MD modeling and simulation in the work were valid for further investigations.
3.2. Elastic properties of the pure PE matrix and CNTs

The value of the elastic modulus of the PE matrix was compared with that of the experiment under the same conditions to verify the reliability of the model. When the axial loading rate was $3 \times 10^6$ Å·ps$^{-1}$, Young’s modulus of pure PE was 1.25 GPa at a temperature of 300 K, which was in good agreement with 1.22 GPa reported by Alostaz et al.[20]. The following steps were performed to calculate the elastic modulus of pure PE. After balancing and relaxing the model of pure PE according to the steps discussed in the simulation, the axial strain was applied to obtain the elastic modulus of the model according to the stress-strain curve. The value of the elastic modulus of the PE matrix was 1.96 GPa.

The elastic properties of the selected SWCNT, whose chirality vector was $(9, 0)$, were also calculated using molecular dynamics simulations under a temperature of 300 K. The value of elastic modulus of the selected SWCNT was about 1,056.95 Gpa[6]. Table 2 shows the elastic modulus of CNTs containing SW defects, which reduces Young’s modulus of CNTs. The higher the concentration of SW defects, the more obvious the strength declines.

3.3. Elastic modulus of the interfacial region

In figure 6, the interface region is a hollow cylinder surrounded by the CNT and PE matrix. The properties of the interface region are introduced from three aspects, namely, the interface interaction energy, the thickness of the interface region, and the elastic modulus. The interfacial interaction energy between the CNT and PE matrix is controlled by the non-bonded interaction energy (i.e., only $E_{\text{vdW}}$ interaction energy). The interfacial interaction energy is calculated by

$$E_{\text{int}}(\varepsilon) = E_{\text{nc}} - E_{\text{pol}} - E_{\text{CNT}}$$

where $\varepsilon$ is the applied strain. As the simulation process goes on, the interface interaction energy under each strain can be obtained, so we can draw the curve of the strain and interface-interaction energy (see figure 7). Further, the regression analysis is used to estimate the correlation error of fitting curves for data in figure 7. For different curves, the determination coefficients ($R^2$) are obtained as follows: $R^2 > 0.98$ for 0 and 1.4%, $R^2 > 0.97$ for 2.8%, and $R^2 > 0.96$ for 4.2 and 5.6%. The initial interface-interaction energy decreases as the defect concentration on CNTs increases.

![Figure 7. Relationship between interfacial-interaction energies ($E_{\text{int}}$) and strains in different cases of SW defect concentrations.](image)

| SW defect concentration (%) | Young’s modulus (GPa) |
|----------------------------|----------------------|
| 0                          | 1.06                 |
| 1.4                        | 0.95                 |
| 2.8                        | 0.84                 |
| 4.2                        | 0.81                 |
| 5.6                        | 0.76                 |

Table 2. Calculated Young’s modulus of $(9, 0)$ SWCNTs obtained by MD simulations.
Then the elastic modulus of the interface is calculated by

\[
E_{\text{int}} = \frac{\partial^2 E_{\text{int}}(\varepsilon)}{\partial \varepsilon^2}
\]

where \( E_{\text{int}} \) is the interaction energy of the interfacial region; \( V_{\text{int}} \) the volume of the interfacial region (see equation (6)).
where $L$ is the length of CNTs placed parallel to the $z$-axis; $r_{\text{CNT}}$ the radius of CNTs; $t_{\text{CNT}}$ the thickness of the interface region. In general, visualization software VMD is used to obtain the radial distribution function curve (RDF) and interface region’s thickness. Figure 8 shows the RDF value of the PE particle does not change, remaining at 0 until the distance from CNTs is 2.3 Å. That is to say, the possibility of the atoms of PE occurring in the region less than 2.3 Å away from CNT is 0. Therefore, the thickness of the interface region is considered as 2.3 Å.

According to equations (5) and (6), the elastic moduli of the interfacial region are obtained in five different cases of SW defect concentrations (see table 3 and figure 9). With the increased SW defect concentration on CNTs, the elastic modulus of the interfacial region decreases linearly. More SW defects on CNTs mean the lower interfacial bonding strength and smaller elastic modulus in this interfacial region.

### 3.4. Elastic modulus of the nanocomposites

Specifically, zigzag-SWCNT with chirality vector $(9, 0)$ was chosen as the reinforcing material in the MD model of the CNT-PE nanocomposite. SW defects were artificially designed for CNTs, and pure PE was used as the matrix. As to CNT-reinforced PE nanocomposites, the curves of the stress varying with strain in the axial direction are shown in Figure 10 and Figure 11.
direction were obtained in five different cases of SW defect concentrations (see figure 10). For the same strain, the more SW defects on CNTs, the lower the stress is. Differences between stresses for different SW defect concentrations gradually increase with the strain. Similarly, we can plot the stress-strain relationship of the composite in the transverse direction (see figure 11).

Actually, for any one of the stress-strain curves, its slope in the linear elastic region (almost 0%–3% strain range) is just Young’s modulus of the nanocomposite. Thus, for five different cases of SW defect concentrations, corresponding longitudinal Young’s moduli were obtained by estimating their slopes and their stress-strain curves. These values are listed in the third column in table 3. The elastic modulus of nanocomposites gradually decreases with increased SW defect concentrations on CNTs. As can be seen from the figure 11, the transverse Young’s modulus of composites decreases slowly with the increase of SW defect concentration, similar to the change of longitudinal Young’s modulus. However, the effect of SW defect concentration on the longitudinal elastic modulus of composites is much greater than that on the transverse elastic modulus.

### 3.5. Comparative verification

MD-simulation results are compared with those by the continuum-based ROM. The ROM is based on the continuum-mechanics theory, assuming the perfect combination of three phases of nanocomposite materials (i.e., SWCNT, the PE matrix, and the interface between the two parts). According to the strain-coordination equation and stress-balance equation, Young’s modulus of nanocomposites can be expressed as

\[
Y_{nc} = V_{pe} Y_{pe} + V_{int} Y_{int} + V_{CNT} Y_{CNT}
\]

where \(V_{pe}, V_{int}, \) and \(V_{CNT}\) represent the volume fractions of PE, interface, and CNTs, respectively; \(Y_{pe}, Y_{int}, \) and \(Y_{CNT}\) represent Young’s moduli of PE, interface, and CNTs, respectively, and should meet

\[
V_{pol} + V_{int} + V_{CNT} = 1
\]

According to the micromechanical hypothesis, \(V_{CNT}\) can be calculated by regarding CNTs as a solid cylinder. As Rafiee and Madhavi reported, equivalent radius \(r_{CNT}\) and volume fraction of hollow CNTs are represented using the following formulas [21].

\[
r_{CNT} = \sqrt{2r_{CNT}t_{CNT}}
\]

\[
V_{CNT} = \frac{\pi r_{CNT}^2}{A_{nc}}
\]

where \(t_{CNT}\) is the wall thickness of the CNT; \(r_{CNT}\) the radius of the CNT; \(A_{nc}\) the cross-sectional area of models (41.2 × 41.2 Å).

The elastic modulus of the integral nanocomposites is obtained using this approach on the ROM. Table 4 shows the corresponding MD simulated results. Young’s modulus of the nanocomposites by the ROM approach is approximate to that by our MD simulation (MD: 33.08 GPa; ROM: 34.52 GPa; the relative error around 4%). The value calculated by the ROM is slightly larger than that by the simulation due to the assumption of a perfect bond between the three phases of CNTs, PE, and their interfaces in the models. As a consequence, the atomic modeling and simulation program performed in the work is verified by comparing Young’s modulus obtained using the molecular-dynamics simulation with that obtained by the ROM.

### 4. Conclusions

The work used CNTs with several SW defects as reinforcement and PE as the matrix to establish an atomic model of nanocomposites, thus studying the effects of SW defects on the overall elastic properties and
interface-region elastic properties of nanocomposites. After verifying by comparing the simulated results with those calculated by the ROM and reported by others, the work obtained the thickness range of the interface region (estimated through the radial distribution function -RDF), the interfacial interaction energy, and Young’s moduli of the interface region and integral nanocomposites.

(1) The elastic modulus of integral nanocomposites strongly depended on the selected CNT additives. The greater the strength of CNT, the better the enhancement effect.

(2) Inherent defects on CNTs reduced their strength and the cohesive strength of the interfacial regions of nanocomposites composed of them. The interface region was a key component for transferring loads, and reducing the strength of the interfacial region decreased the overall strength of the nanocomposite.

(3) SW defect can reduce the transverse and longitudinal elastic modulus of composites, and its influence on the longitudinal elastic modulus is much greater than that of the transverse elastic modulus.

We will consider other important factors, such as CNTs’ chirality, orientation, and temperature to have a more complete and deeper understanding of the effects of inherent defects on CNTs on the mechanical properties of CNT-reinforced nanocomposites.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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