Understanding the effect of functionalization in CNT-epoxy nanocomposite from molecular level

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Abstract

The excellent physical, mechanical, thermal and electrical properties of carbon nanotubes (CNTs) make them the promising reinforcements for polymer materials. The resulting nanocomposites have been applied in various applications, including but not limited to aerospace components and nanoelectronics. The mechanical performance of CNT reinforced nanocomposites is significantly affected by the interfacial interactions between CNT and polymer matrices. Enhancing the CNT-polymer interface from molecular level, such as chemical functionalization on CNTs, opens new perspectives for improving the mechanical properties of nanocomposites. Although there is a risk that functionalization may destroy the perfect surface of CNTs during fabrication, such chemical treatment can provide desired CNT dispersion state and orientation, resulting in significant improvement in mechanical properties of polymer nanocomposites. In this work, epoxy nanocomposite systems with pristine and functionalized CNTs are modeled respectively. Molecular dynamics simulations are applied to investigate the interfacial characteristics and the mechanical responses of these CNT-polymer nanocomposites. The results reveal that the functionalization can enhance the interfacial shear stress and the Young’s modulus of CNT-epoxy nanocomposites. The functional groups not only provide stronger interfacial adhesion with the epoxy matrix, but also act as the sites of mechanical interlocking during deformation. The understanding of the reinforcing mechanism from atomistic level provide physical new insights to material design for advanced nanocomposites.

1. Introduction

Carbon nanotubes (CNTs) present extraordinary physical, mechanical, thermal and electrical properties which act as the potential reinforcements to offer remarkable opportunities for the development of new materials and devices [1–3]. Polymer nanocomposites with CNT additives have attracted great attention in various engineering applications. In particular, epoxy resin, one of the most common thermosetting polymers, has been strengthened with CNTs and increasingly used as advanced structural materials in aerospace and automobile industry. The improved mechanical properties of CNT-reinforced epoxy nanocomposites over that of traditional epoxy materials have been reported experimentally and theoretically [4–7]. The tensile strength and flexural strength of epoxy composites filled with 0.1 wt% and 0.2 wt% CNTs were increased by 35% and 58% respectively compared to neat epoxy [4]. The mechanical properties present an effective enhancement with increasing CNT content, and the increase of 330% in Young’s modulus of epoxy composites can be achieved with 60 wt% CNTs [5]. In addition, the CNTs with low weight fractions limited the reorientation of epoxy chains during creep deformation [6], and the creep rate can even be reduced at elevated temperatures [7]. However, current degree of improvement still falls short of expectations as the increase in mechanical performance is usually limited by a threshold and the outstanding properties of CNTs are not fully utilized. It has been pointed out that the load transfer efficiency from epoxy matrix to CNTs plays a significant role in the enhancement of performance [8,9]. The load transfer between CNT and epoxy matrix is determined by the interfacial interactions, which include the weak van der Waals interaction between CNT and polymer matrix, the ionic or covalent bonding after chemical treatment, and the mechanical interlocking caused by unsmooth surface structure. The interfacial adhesion without any treatment mainly comes from the non-bonded interactions, which can cause inefficient load transfer. In addition, the poor dispersion state and the random orientation of CNTs in fabrication process can also result in less effective reinforcement, or even negative reinforcement.

Functionalization of CNTs is one of the potential solutions to
overcome the challenges arising from the fabrication and the interfacial properties. The functionalization modifies the interfacial interactions between CNT and epoxy with chemical treatments, which in turn provide improved material properties for practical applications [10–13]. The covalent functionalization, in particular, is regarded as a promising way to improve the load transfer efficiency by implementing bonded interactions between the filler and the polymer matrix [14–16]. Covalent functionalization of CNTs in nanocomposites can be achieved by either direct addition reactions of chemical reagents to the sidewall of CNTs or attachment of appropriate surface functional groups. For the epoxy-based nanocomposites, the covalent attachment on the CNTs can be either epoxy or amine functional groups [17]. The amine functional groups are commonly used as they have a high reactivity and can react with the epoxy matrix to form more than one covalent bond during cross-linking process. The chemical treatment helps in obtaining good dispersion state of CNTs in the epoxy matrix as surface functionalization helps prevent CNTs from agglomerating and forming bundles [18]. The functionalized CNTs with amine functional groups have been found to improve the mechanical properties of epoxy nanocomposites compared to the systems with unmodified CNTs [19,20]. The desired orientation of CNTs on polymer materials. The direct measurements have been realized using the nano-mechanical pull-out tests. A serious of nanotube pull-out experiments have been reported in the previous studies [21–25]. The interfacial shear strength in the CNT-epoxy nanocomposites has been measured using different techniques, such as transmission electron microscope (TEM), atomic force microscopes (AFM) and microelectromechanical systems (MEMS) [25]. Despite all these valuable advances, several limitations remain yet to be solved from experimental approach, such as how functionalized groups affect the interfacial properties in load transfer and the movement of polymer chains during deformation. Although the functionalization accounts for the improvement in nanocomposites, there are few studies that analyze the enhanced mechanical properties addressing the effect of functionalization on the interfacial properties of CNT-epoxy nanocomposites. Such knowledge is significant for the further design of nanocomposites with superior properties, which crucially needs more detailed characterization from atomistic level.

The nanoscopic modeling of the interfacial phenomena has been enabled by molecular dynamics (MD) simulations, which have been widely applied to investigate interfacial behaviors in different material systems [26–30]. The pull-out tests by MD simulations have been carried out in the previous studies to investigate the interfacial characteristics in polymer composites, which yield a good agreement with experimental observations [31]. The interfacial shear strength has been estimated, and the values are correlated to the length, the radius, the defect and the interactions of CNTs [31]. The functionalization of CNT on the thermal and mechanical properties has been investigated, and the results show that the compressibility of the matrix-filler interphase is reduced, which changes the glass transition temperature and the Young’s modulus of epoxy nanocomposites [32]. The progress on the understanding of material properties and interfacial behavior from nanoscale have shown that MD simulations can effectively capture interfacial interactions between CNT and epoxy matrix.

This work aims to investigate the effect of the functionalization of CNTs on the interfacial and mechanical properties in the epoxy nanocomposites, and to understand how the functionalization helps in the modification of epoxy-CNT interface from atomistic scale. The epoxy nanocomposites reinforced by the pristine CNT and the amine-functionalized CNT are constructed for comparison in the mechanical performance. To characterize the interfacial properties and the load transfer between CNT and epoxy matrix, the pull-out test is performed using MD simulations. In addition, the reinforcement in mechanical responses after functionalization is analyzed through the tensile deformation. The modification of the interface between CNT and epoxy matrix through functionalization is investigated, and the interfacial shear strength is found to be effectively improved. How the functionalization affects the interfacial behavior inside the nanocomposites is characterized through analyzing detailed atomic movement. The microstructural configurations at different stages are captured to unravel the interlocking effect of the functionalization and interpret how the interactions between functional groups and epoxy chains lead to the enhanced mechanical properties of nanocomposites. The interfacial interactions are also provided for the in-depth understanding of the reinforcing mechanism. The information from the change of atomic movement and interfacial properties suggests that the interlocking effect can be modified by varying the functionalized structures, which further enlightens the systematic design of advanced CNT-based nanocomposites.

2. Simulation details

2.1. Atomistic models

The two epoxy systems reinforced with pristine CNT and functionalized CNT are investigated in this work. MD simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [33]. The polymer consistent forcefield (PCFF) [34] is employed to describe the atomistic interactions within the nanocomposite systems. The partial charges of atoms are determined by the bond increment method. The applicability of PCFF for CNT-reinforced nanocomposite systems has been validated in the previous studies, which provided reliable results compared to the theoretical and experimental data [35–37]. The van der Waals interaction and the Coulombic interactions for the non-bonded part are calculated with a cutoff distance of 10 Å, which is normally used for the CNT-epoxy nanocomposites. The velocity-Verlet integrator is used in the integration of Newton’s equations of motion with a time step of 1 fs.

The widely used two-component epoxy system consisting of bisphenol A diglycidyl ether (DGEBA) monomer and triethylenetetramine (TETA) hardener is selected for the polymer matrix. The corresponding chemical structure and atomistic model for a single segment is shown in Fig. 1(a) and (b). For the nanofiller, the armchair (5,5) single-wall CNT (SWCNT) with a diameter of 6.8 Å and a length of 49.2 Å is chosen. The CNT diameter and chirality have been found to have limited effect on the Young’s modulus [38]. Although the CNT length and corresponding aspect ratio (i.e. 7.2) are smaller than the size in experiment, this model can reproduce sufficient load transfer at the interface while preventing quick drop of stress near the end of CNT. It is found that the CNT surface within the simulation length scale affects the local dynamics of polymer chain up to a distance of around 2 nm from the surface, but the perturbation in global polymer chain can extend to further distances [39]. The interactions at the nanoscale have impact on the macroscale, and therefore affect the properties of nanocomposites. The local density profile and polymer chain dynamics at the interfacial area with the selected CNT aspect ratio can also be characterized to interpret the interfacial behavior [39]. In addition, this model can act as the basic unit for nanocomposite structure at the nanoscale, which can be upscaled to the macroscopic level for the multiscale analysis. It should be noted that the straight CNT with good alignment along loading direction is selected to achieve the maximum strengthening effect on mechanical properties by getting rid of the complex interplay of different parameters such as the curvature. In this way, how the variable, i.e. the functionalization, affects mechanical preformation and interfacial behavior in nanocomposites is investigated in a clear manner. The amido-amine groups are selected as the functional groups for CNT, which have been applied in existing experiments and modeling [32, 40–42]. In the functionalization process, the functional groups tend to be formed at the end and defect sites of CNT as these sites have higher chemical reactivity [32,43,44]. Therefore, the amine functionalized...
CNT is prepared by adding five amido-amine groups onto the end of the pristine CNT according to the CNT chirality, as shown in Fig. 1(c). In the modeling process, the nanocomposite structure is initiated by inserting the SWCNT fragment in the simulation cell, and by randomly generating the monomers and the hardeners based on the ratio of 3:1 to surround it. The models contain 16150 and 16230 atoms in total for CNT-epoxy nanocomposites and functionalized CNT-epoxy nanocomposites respectively, including 15750 atoms of epoxy, 400 atoms of CNT and 480 atoms of functionalized CNT. The uncross-linked structures are equilibrated for 50 ps in the isothermal and isochoric ensemble at 300 K, followed by another 50 ps equilibration in the isothermal and isobaric ensemble at 300 K and 1 atm. Then the cross-linking reaction is performed by a crosslinking algorithm [45]. The procedure mainly involves the following steps: (1) the reactive atoms on the monomers and the hardeners are recognized; (2) the epoxide groups comprising the recognized reactive atoms on the monomers are opened, and connected with the reactive atoms on the hardeners when the reaction radius is reached; (3) the unreacted atoms are saturated with hydrogen atoms; (4) the cross-linked structure is relaxed for the next reaction. The reaction radius is set to be 3 to 10 Å with an increment of 0.5 Å. The cross-linking process of the nanocomposites is completed when all the potential reactive atoms within the reaction radii are reacted.

2.2. Simulation methods

The cross-linked nanocomposite structures are equilibrated under the isothermal condition at 300 K for 1 ns after the initial energy minimization. The root-mean-square distance (RMSD) is examined to confirm the fully equilibrium state. Prior to the loading, the edge of the epoxy matrix is constrained to avoid the simultaneous drift together with the CNT along the loading direction. Another 100 ps equilibrium at 300 K is employed to further relax the constrained system. The pull-out simulation is carried out to determine the ISS in the nanocomposite systems using steered molecular dynamics (SMD) approach. SMD simulation is designed to provide microscopic details of mechanical response and insights of molecular mechanisms based on the principles of AFM technique. Similar to the pull-out experiments using AFM tip [21], SMD simulation is carried out by applying an external force to the end of CNT in constant velocity mode. Each defined atom within the CNT is subjected to a force of magnitude

\[ F = k(r - R_0) \]

where \( F \) is the spring constant, \( r \) is the pulling rate, \( R_0 \) is the initial equilibrium position of the center of mass (COM) of the loading region and \( R(t) \) is the position of the COM of the loading region at time \( t \), \( m_1 \) is the mass of the atom and \( m \) is the total mass of the CNT. During the pull-out process, the CNT is pulled out along the axial direction (z axis) with a constant velocity of \( 1 \times 10^{-4} \) Å/fs through a steered force generated by tethering a spring to one end of the CNT. Limited by the time scale in MD simulations, the selected pulling velocity is several orders of magnitude higher than that used in the AFM experiments. However, it can capture the interfacial behavior between the embedded filler and surrounding matrix without the influence of molecular thermal vibration [46,47]. The work done during the pulling process is averaged over multiple independent configurations based on Jarzynski’s equality along the pulling path, which yields an estimate of the potential of mean force (PMF) as the pull-out energy. The average ISS can be estimated based on the pull-out energy \( E_{\text{pull-out}} \), as indicated in Eq. (1):

\[ r = \frac{2E_{\text{pull-out}}}{\pi DL^2} \]

where \( D \) and \( L \) are the diameter and the embedded length of the CNT respectively.

In the tensile deformation, the tensile load is applied in a step-wise manner along the CNT direction, as CNTs are strong in the axial direction and the alignment towards the loading should lead to improved mechanical properties. The system is deformed at a strain rate of \( 1 \times 10^{-5} \) s\(^{-1}\) at NVT ensemble with the temperature of 300 K. This tensile strain rate is typically used in tensile deformation of epoxy systems, which can predict the Young’s modulus that is close to the experimental measurement [45,48]. The whole simulation processes including the pull-out and tensile tests are repeated three times by using different initial velocities and averaging the calculation results to minimize the random error.

3. Results and discussion

3.1. Pull-out simulations

The pull-out simulations for pristine CNT-epoxy and functionalized CNT-epoxy nanocomposites are performed to investigate the interfacial properties and the load transfer ability between CNT and epoxy matrix. The snapshots of CNT pulling out from epoxy matrix in the two material systems are captured in Fig. 2. The interactions between the C atoms on CNT wall and the polymer matrix are non-bonded interactions. As the charge distribution on CNTs is even, the contribution of electrostatic interactions between CNT and epoxy matrix on the interface is insignificant [49]. The non-bonded interactions mainly come from van der Waals (vdW) interactions between CNT and epoxy matrix. For the interfacial binding of epoxy chains on the CNT sidewall, the vDW interactions is primarily attributed to the π-π stacking between C atoms of

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**Fig. 1.** Chemical and atomistic structures of (a) DGEBA monomer, (b) TETA cross-linker and (c) amine functionalized CNT. The carbon, oxygen, nitrogen and hydrogen atoms are shown in gray, red, blue and white color, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
CNT and the aromatic ring of epoxy chain, which has been observed in the previous studies [9,50]. During the pull-out process, the interfacial interactions between CNT atoms and epoxy chains at the original position are firstly cut off, and then reconstructed at the new position, as shown in Fig. 2. There is no connection between CNT and the epoxy matrix after the complete pull-out of the pristine CNT, while the functional groups at the end of CNT still interact with the epoxy chains as shown in Fig. 2(c) and (f). The results of PMF from SMD simulations are recorded during the pull-out process in Fig. 3(a). The results show that the pull-out energies increase almost linearly with the displacement, and reach a stable value after the reinforcement is fully pulled out from the epoxy matrix, which are in a good agreement with the previous results [46]. The pull-out energy in the functionalized CNT case is higher than that in the pristine CNT case. The interaction energies between CNT and epoxy are calculated as shown in Fig. 3(b). The negative value of interaction energy indicated that there is an attractive interaction between CNT and epoxy matrix. From the simulation results, the functionalization improves the interaction between CNT and epoxy matrix.

The ISS can be estimated from the pull-out energies for the two cases using Eq. (1). The ISS of pristine CNT-epoxy interface is calculated to be

![Fig. 2. Snapshots of the two material systems during the pull-out process. The corresponding interatomic changes are magnified in the subfigures, in which gray and black represent the matrix and the CNT respectively. Red and green represent the functional groups and the selected epoxy chains that interact with CNT through the \( \pi-\pi \) stacking respectively. In (a)–(c) pristine CNT-epoxy nanocomposite, epoxy chains interact with CNT through non-bonded interactions, and a complete detachment between CNT and epoxy matrix is observed after pulling out of CNT. In (d)–(f) functionalized CNT-epoxy nanocomposite, epoxy chains interact with both CNT and functional groups, and the interaction still maintains between epoxy chains and functional groups after pulling out of CNT. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)](image1)

![Fig. 3. (a) Pull-out energies during the pull-out of CNTs; (b) Interaction energies of CNT and epoxy matrix during the pull-out of CNTs.](image2)
77.9 MPa, and the ISS of functionalized CNT-epoxy interface is calculated to be 130.9 MPa. The simulation results are within the range of 35–376 MPa measured from the experiments [51]. The improvement of 68% from the functionalization indicates better interfacial adhesion between functionalized CNT and epoxy matrix.

To further explore the load transfer mechanism in the nanocomposites, the relative atomic displacements are estimated between the adjacent atomic configurations. The interactions between CNT and epoxy matrix cause the local deformation of nearby epoxy chains during the pull-out process. In the beginning for the pristine CNT case, only the epoxy chains at the adjacent region around the interface show large displacements as shown in Fig. 4(a). For the functionalized CNT case, the epoxy chains surrounded the tail of CNT are affected by the movement of the functional groups as plotted in Fig. 4(d). The pull-out of CNT in the nanocomposites releases the preoccupied space inside the epoxy matrix, which allows the relaxation of epoxy chains at the free end of CNT. The epoxy chains start to move towards the vacancy surrounding the tail of CNT, and such movement is captured in both nanocomposite systems in Fig. 4(b) and (e). The atoms of epoxy matrix are more active in the functionalized CNT case, suggesting more epoxy chains are affected by the functional groups. Before the complete pull-out, the regions with large displacements are mostly located at the end of CNT, and the amount of these atoms is greater in the functionalized CNT case than that in the pristine CNT case as compared in Fig. 4(c) and (f). This is further confirmed in Fig. 4(g) which shows the fraction of atoms with relevant atomic displacements over 2 Å. The functionalized CNT interacts with more epoxy chains, leading to more severe local deformation during the pull-out process and higher ISS in CNT-epoxy nanocomposite. The results suggest that the introduction of the functional groups can cause better mechanical interlocking in nanocomposite, which effectively strengthens the interface between CNT and epoxy matrix.

3.2. Tensile deformation

The better interfacial interaction and load transfer ability are expected to enhance the mechanical properties in nanocomposites. The tensile deformation is carried out to investigate such improvement. The stress-strain curves for pristine CNT-epoxy nanocomposites and functionalized CNT-epoxy nanocomposite under the tensile deformation are shown in Fig. 5. The stress-strain curves in the two cases have similar trends. The stress increases nearly linearly with the increasing strain in an elastic regime at the beginning stage of deformation. Further deformation of the nanocomposite causes an increase of stress in a nonlinear relationship with the increasing strain, suggesting the onset of hardening stage. Such trend is close to the experimental measurements for epoxy-based composites [52–54]. The Young’s modulus of these two systems are calculated as 4.31 GPa and 5.22 GPa by linear fitting to the elastic region, respectively. The previous investigation shows that the Young’s modulus is insensitive to the strain rate in epoxy matrix, the value of which is the applied strain rate in this work [48]. The simulation results are in a good agreement with experimental measurement ranging from 2.7 GPa to 5 GPa [55,56]. The Young’s modulus in the functionalized CNT case is 21% higher than that in the pristine CNT case, showing the reinforcing effect on the tensile properties of nanocomposites. To provide accessible information for experiments, the rule of mixtures can be applied as the effective medium model to analyze the material properties from multiscale perspective. The rule of mixtures has been used to predict modulus and strength of polymer composites reinforced by continuous and unidirectional fibers [57,58]. It can be extended to estimate the elastic modulus of CNT-epoxy nanocomposites. The longitudinal elastic modulus $Y$ of polymer composites under constant-strain condition is as shown in Eq. (2),

$$Y = Y_f V_f + Y_m V_m$$  \hspace{1cm} (2)

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**Fig. 4.** The cross-sectional views of the atomic configurations in (a)–(c) pristine CNT-epoxy and (d)–(f) functionalized CNT-epoxy nanocomposites at different sliding distances. The atoms are colored according to the relevant atomic displacements calculated according to the adjacent atomic configurations. Atoms colored as yellow are with relevant atomic displacements over 2 Å. The orange circles indicate the regions contain most atoms colored in yellow around the CNT, especially at the end. (g) The fractions of number of atoms with relevant atomic displacements over 2 Å in the nanocomposites during pull-out process. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
For the short filler, the longitudinal elastic modulus can be modified as [58].

\[
Y = Y_f \left(1 + \frac{\eta_f V_f}{V_m} \right) \eta_f = \frac{Y_f / Y_m - 1}{Y_f / Y_m + \eta_f} \quad \zeta = 2L / D
\]  

(3)

where \(Y_f\) and \(Y_m\) are effective longitudinal elastic modulus of short fiber and polymer matrix respectively, and \(V_f\) is volume fraction of short fiber. \(\eta_f, L\) and \(D\) are length efficiency factor, length and diameter of short fiber respectively.

The volume fractions satisfy \(V_f + V_m = 1\). The volume taken up by the CNT is given by:

\[
f_{NT} = \pi L \left(\frac{D}{2} + h_{vdW}\right)^3
\]

(4)

where \(h_{vdW}\) is the equilibrium van der Waals separation distance between CNT and epoxy matrix obtained from MD simulations. Based on the above equations and the values from simulations, the analytical result for the longitudinal elastic modulus is calculated 4.71 GPa. By combining the atomistic model and the effective medium model, the mechanical properties of bulk materials with different structural and geometrical parameters, such as CNT dimension and volume fraction, can be predicted for material design. The multiscale modeling from the building block at the nanoscale to the complicated situation at the macroscale is shown in Fig. 6.

The corresponding energy variations in the two nanocomposite systems during tensile deformation are recorded as illustrated in Fig. 7. Compared to the pristine CNT case, these energy variations are much higher in the functionalized CNT case. In both cases, the change in the potential energy is mainly correlated with the change in the non-bonded energy, while the energies associated with the bond length, bond angle and improper torsions remain almost unchanged in the deformation process. The increase of the non-bonded interaction is attributed to the epoxy chain slippage in the deformation. Unlike the pristine CNT case, the dihedral energy immediately decreases with the increasing strain due to the rotation of conformation to a lower state in the functionalized CNT case, suggesting that the main deformation involves the dihedral rotations and non-bonded interactions in the whole simulation region.

The microstructural evolution in the tensile deformation are captured to further analyze the strengthening mechanism of functionalization. The distributions of the atoms with different relevant atomic displacement are shown in Fig. 8. At the elastic region with small strain, the local deformation with relevant atomic displacement over 2 Å is distributed almost evenly inside the epoxy matrix as depicted in Fig. 8(a) and (d). The number of epoxy atoms that move around the CNT surface in the pristine CNT case is greater than that in the functionalized CNT case, indicating the mobility of epoxy chain is inhibited with the functional groups. With increasing strain, the mobility of epoxy chain is increased as shown in Fig. 8(b) and (e). This upward trend can be confirmed by the change in the fractions of number of atoms with relevant atomic displacements over 2 Å as shown in Fig. 8(g). The regions of local deformation inside epoxy matrix are expanding in the pristine CNT cases. However, the deformation is located not only at the ambient epoxy matrix, but also at the end of functionalized CNT. This is because the functional groups interact with the neighboring epoxy chains, and restrict the movement of these atoms towards the tensile direction. In addition, the minor voids are generated inside the epoxy matrix as well as at the ends of pristine CNT. The creation and growth of the voids are key elements in the fracture of material systems under tensile deformation. These voids change the stress distribution in the system, which continuously grow into cavities and lead to fracture of materials in the following deformation process. As the non-reactive forcefield is selected in this study, which cannot simulate the covalent bond breaking situation, the generation of minor voids is related to the interfacial separation between CNT atoms and epoxy matrix and the sliding movement among epoxy chains. These minor voids keep expanding with the increase of the strain, indicating the crack propagation and the initiation of fracture as shown in Fig. 8(h). The functionalized CNT shows a better interaction with epoxy matrix, and less minor voids appears in the region surrounding the CNT. During tensile deformation, the functionalized CNT has the mechanical interlocking effect on the epoxy chain, which controls the mobility of epoxy chains and the stress trend, as shown in Fig. 9. The functional groups provide strengthened interfacial properties between CNT and epoxy matrix, which lead to improved mechanical performance in the CNT-epoxy nanocomposites. In addition to improvement in tensile properties, the interfacial modification through functionalization on CNT-based nanocomposite suggests the promising influence to the long-term performance in structural applications. The improved matrix-filler interfacial interactions with less aggregation of CNTs slow down the relaxation process of epoxy matrix under the constant stress condition, leading to enhanced creep resistance [9,59]. The creep behavior of functionalized CNT-epoxy nanocomposites will be considered in future study.

The simulation results reveal the role of functional groups in interfacial modification, and provide the insights into the molecular mechanisms that govern the interfacial properties and mechanical performance with the addition of functional groups on CNT. Such information of interfacial interactions from atomistic level is crucial for further improvement of CNT-based nanocomposites. The current work only considers the amine functional group that is suitable for epoxy system. For different polymer material systems, further manipulations using MD simulations on varying the specific parameters of functional groups, such as number and type on CNT, along with experimental techniques, will provide effective guidelines for designing CNT-based nanocomposites for various engineering applications.

4. Conclusions

In this work, the effect of interfacial modification using functionalized CNT on the strengthening of epoxy nanocomposites is investigated using MD simulations. The interfacial properties and load transfer ability are studied through pull-out tests. The simulation results show that the ISS of functionalized CNT-epoxy interface is 68% higher than that of pristine-epoxy interface. The functionalized CNT has stronger interfacial interactions with epoxy matrix, and the introduction of the function group causes more severe local deformation during the pull-out process of epoxy matrix under the constant stress condition, leading to enhanced creep resistance [9,59]. The creep behavior of functionalized CNT-epoxy nanocomposites will be considered in future study.

The simulation results reveal the role of functional groups in interfacial modification, and provide the insights into the molecular mechanisms that govern the interfacial properties and mechanical performance with the addition of functional groups on CNT. Such information of interfacial interactions from atomistic level is crucial for further improvement of CNT-based nanocomposites. The current work only considers the amine functional group that is suitable for epoxy system. For different polymer material systems, further manipulations using MD simulations on varying the specific parameters of functional groups, such as number and type on CNT, along with experimental techniques, will provide effective guidelines for designing CNT-based nanocomposites for various engineering applications.
Fig. 7. The evolution of energy changes during tensile deformation in (a) pristine CNT-epoxy and (b) functionalized CNT-epoxy nanocomposites. The change of potential energy increases with the increasing change of non-bonded energy in the functionalized CNT case, which indicates the functional groups can effectively enhance the interfacial interactions.

Fig. 8. The cross-sectional views of the atomic configurations in (a)–(c) pristine CNT-epoxy and (d)–(f) functionalized CNT-epoxy nanocomposites during tensile deformation. Atoms colored as yellow are with relevant atomic displacements over 2 Å. (g) The fractions of atoms with relevant atomic displacements over 2 Å in the nanocomposites during tensile deformation process. (h) The void generated in the pristine CNT-epoxy nanocomposites during tensile deformation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
process, which significantly improves the load transfer between CNT and epoxy matrix. The tensile test is carried out to investigate the mechanical properties of the two nanocomposite systems. The Young’s modulus of functionalized CNT-epoxy nanocomposite is 31% higher than that of pristine CNT-epoxy nanocomposite. The reinforcement mechanism with functionalization on CNT is revealed. The functional groups offer additional mechanical interlocking during tensile deformation, which effectively enhances the mechanical properties. Interfacial modification through functionalization improves the interfacial interactions between CNT and epoxy, and therefore the mechanical performance in epoxy nanocomposites. The understanding of functionalization obtained from molecular level provides insights to material design for advanced epoxy nanocomposites for practical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Wei Jian: Conceptualization, Methodology, Software, Formal analysis, Writing - original draft. Denvid Lau: Funding acquisition, Project administration, Conceptualization, Supervision, Writing - review & editing.

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