Effect of CNT Morphology on the Interfacial Properties of Nanocomposites

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ABSTRACT

Most existing studies assume CNTs to be straight and uniformly dispersed within the polymer matrix. In this work, we investigate the effect of waviness and agglomeration on the interfacial properties of CNT-reinforced epoxy composites. MD simulations of numerical pull-out tests were carried out of CNTs, with different curvatures and bundle diameters, fully embedded in an epoxy resin to evaluate the corresponding interfacial shear strength. The results of our MD simulations revealed the following. The pull-out force of the curved CNTs is significantly higher than its straight counterpart and increases further with the increase in the waviness of the CNTs. It also reveals that agglomeration of CNTs leads to a reduction in the ISS and poor load transferability, and that this reduction is governed by the size of the agglomerate. The simulation results were also used to develop a generalized relation for the ISS that takes into consideration the effect of waviness and agglomeration of CNTs of CNT-polymer composites.

Keywords: molecular dynamics, nanocomposites, carbon nanotube, agglomeration, waviness

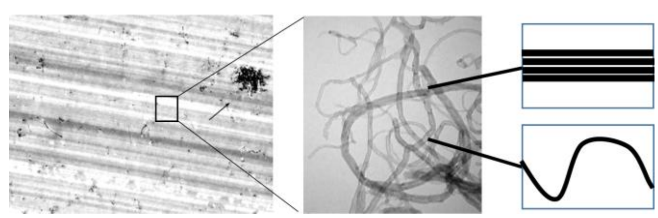
1 INTRODUCTION

Owing to their remarkable mechanical and physical properties, it is believed that few weight percentages of CNTs can significantly improve the mechanical, electrical, and thermal properties of CNT-based composites [1]. However, the full potential of CNTs as a reinforcement material is limited by the tendency of CNTs to agglomerate and deform locally into wavy shapes [2]. The presence of agglomerates limits the stress transfer between the nanotubes inside the bundle and from the matrix to the CNTs, leading to a nanocomposite with inferior properties [3]. Due to their high aspect ratio and low bending stiffness, CNTs tend to bend or unfold when dispersed in polymer matrices [1,4], which means that the strength of the CNT will depend significantly on its curvature and shape [1].

Moreover, the mechanical performance of CNT-reinforced composites is significantly influenced by the interfacial properties between the dispersed CNTs and the surrounding matrix [1,2]. Higher interfacial shear stress (ISS) means better stress transfer from the polymer to the reinforcing CNTs [1,4]. Understanding the effect of waviness and agglomeration on the interfacial properties is essential in identifying how reinforcing mechanisms work. However, measuring this effect experimentally via direct Pull-out tests is challenging, especially when dealing with single wall carbon nanotubes (SWCNTs). To overcome this problem, we conducted MD simulations of the pullout tests of CNTs with different curvatures and bundle sizes to investigate the effect of CNT morphology of the interfacial properties. The pull-out force is calculated from the change in the potential energy of the system during the pull-out process and used to calculate the ISS. The results of our research could be used to shed some light on the enormous scatter in the interfacial shear strength (ISS) values provided in the literature.

2 MOLECULAR DYNAMICS MODEL

In order to properly design nanocomposites and optimize their properties, the effect of all variables, including nanotube waviness and agglomeration, on their performance must be considered. Controlling such parameters experimentally can be quite difficult and intricate. Figure 1 shows the steps involved in the hierarchical multiscale model. The dispersion state and the morphology of the CNTs inside the polymer matrix is quantified using images obtained by a scanning electron microscope (SEM) and an atomic force microscope (AFM) (See Fig. 1). Amongst the most common approaches for measuring the ISS of CNT-polymer nanocomposites is the pull-out test. Figure 2 shows a schematic representation of the pull-out model and the applied boundary conditions. The proposed model considers only weak bonding (van der Waal and electrostatic forces) between the embedded nanotubes and the surrounding matrix.



(a) (b) (c)

Figure 1: Experimental results showing wavy nature of CNTs: (a) SEM image of CNT-epoxy composites with different scales and (b) A schematic representation of agglomerated and wavy CNTS (From Ref. [4]).

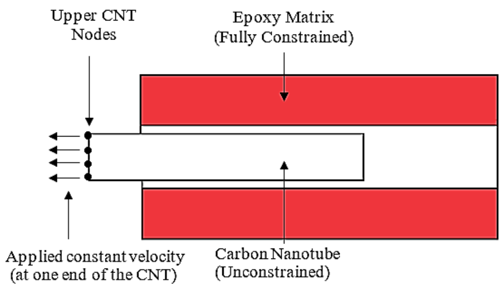


Figure 2: Schematic diagram showing the pull-out of partially embedded CNT from Epoxy matrix and the applied boundary conditions

To model the surrounding matrix, we used a specific two-component epoxy material based on a diglycidyl ether of bisphenol A (DGEBA) epoxy resin and triethylene tetramine (TETA) curing agent, which is typically used in the aerospace industry. During the curing process, the hydrogen atoms in the amine groups of the hardener (TETA) react with the epoxide groups of the resin (DGEBA) forming covalent bonds. The resin/curing agent weight ratio in the epoxy polymer was set to 2:1 in order to achieve the best elastic properties [4]. Five RVEs were constructed to represent an epoxy matrix reinforced with: (i) a single CNT, (ii) a bundle of three CNTs, (iii) a bundle of seven CNTs, (iv) a bundle of nineteen CNTS, and (v) a bundle of thirty-seven CNTS, as shown in Fig. 3. All nanotubes are (5,5) armchair SWCNT of length 80 Å and aspect ratio ~118.

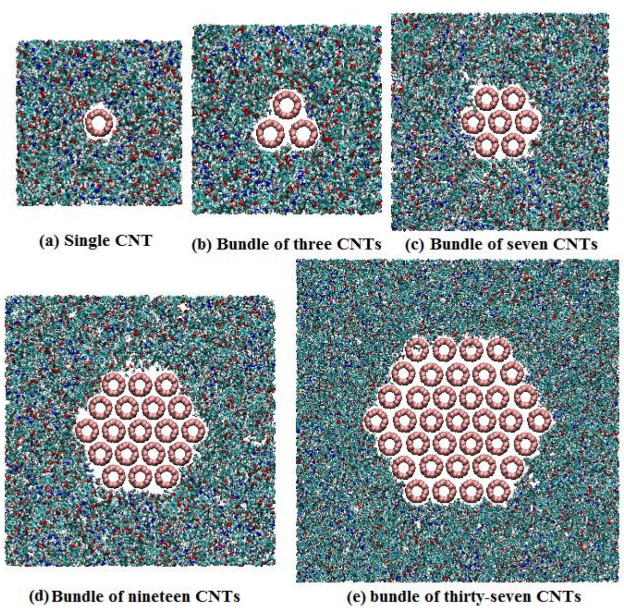
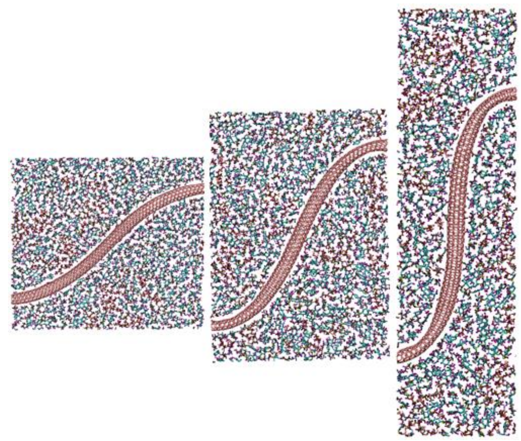


Figure 3: MD models used in the agglomeration study.

To study the effect of CNT waviness, MD simulations will be conducted for RVEs reinforced with wavy nanotubes of different curvatures, as shown in Fig. 4a to c. In the proposed model, nanotubes are considered to have a sinusoidal shape:

$$y = a\cos\left(\frac{\pi z}{2\lambda}\right) with \ z \in [0, \lambda] \quad (1)$$

where a and λ are the amplitude and the quarter wavelength of the wavy nanotube, respectively. The parameter $\alpha = a/\lambda$ is used as a shape parameter that defines the degree of curvature of the nanotube. Three curved single wall carbon nanotubes were generated and equilibrated before using them as reinforcement fibers in the RVE of the nanocomposites. All nanotubes were selected to be (5,5) armchair SWCNT of length 270 Å and aspect ratio ~400. The simulation region in each case was constructed by randomly placing the cross-linked epoxy structures around the embedded nanotube, as shown in Fig. 4. The size of the RVE in each case was adjusted in such a way that the CNT volume fraction in it remains constant at 1.2%.



(a) (b) (c)

Figure 4: MD unit cells reinforced with curved CNTs with different curvatures.

We conducted MD simulations of the pull-out test of CNTs from epoxy matrix to determine the binding energy between them. The binding energy is equal to the change in the total potential energy of the system after the embedded nanotube is entirely pulled out. The work done by the pull-out force at any point is equal to the change in the potential energy of the system at this point [4]. Therefore, the pull-out force at any moment can be calculated from the derivation of the interfacial energy with respect to the axial distance at this moment. In the current analysis, the magnitude of the pull-out force throughout the MD simulation was approximated as the incremental change in the potential energy of the system every Angstrom:

$$F_{pull-out} = \frac{\Delta PE}{\Delta x} \quad (2)$$

Where ΔPE is the potential energy increment at each displacement increment Δx=0.1 nm. Assuming uniform shear stress distribution along the interface area of the CNT, the average ISS can be calculated simply by balancing the forces:

$$ISS = \frac{F_{pull-out}}{\pi(D_{CNT}+h_{vdw})L_{CNT}} \quad (3)$$

where, F_{max} is the maximum pull-out force recorded at the beginning of CNT deboning, D_{CNT} is the CNT diameter, L_{CNT} is the embedded fiber length, h_{vdw} is the interfacial separation distance between the CNT and the epoxy, and $\pi(D_{CNT}+h_{vdw})\,L_{CNT}$ is the effective CNT interface area. During the pullout simulation, all atoms at one one-end of the fully embedded CNT/CNT bundle is pulled-out from the matrix at a constant velocity of 1×10^{-4}Å/fs while the remaining atoms of the nanotube are equilibrated in the NVT ensemble at 300 K to calculate the potential energy of the system. Our MD simulations are conducted with LAMMPS code [5] using the consistent valence force field (CVFF) [6]. This force field is implanted in LAMMPS and has been successfully used by other researchers to predict the elastic and interfacial properties of CNT-epoxy composites [1].

3 RESULTS AND DISCUSSION

We conducted a series of MD simulations to determine the effect of CNT waviness and agglomeration on ISS of CNT-reinforced polymer composites. In general, the value of the shear stress at the CNT-polymer interface determine the efficiency of stress transfer from the matrix to the embedded nanotubes [7]. These CNTs reinforce the matrix by sharing the applied load until either the failure of the interface or the fracture of the CNTs. The maximum shear stress that the interface can resist before the deboning starts is called the interfacial shear stress (ISS). Five MD simulations of the pull-out test of CNT bundles of different diameters were conducted to determine quantitatively the effect of agglomerate size on the interaction/binding energy, pull-out force, and ISS of CNT-epoxy composites. The pull-out process was completed until the fully embedded nanotube bundles were completely pulled out from the epoxy. Figure 5 shows snapshots of the pull-out simulation for the five nanocomposite systems considered. The pull-out forces shown in Figure 6 were calculated from the slope of the binding energy curves.

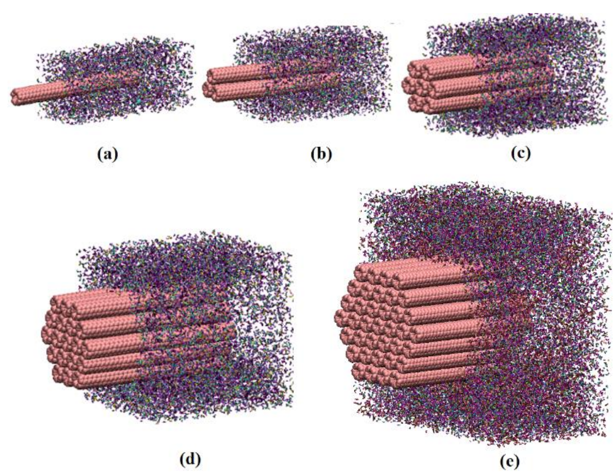


Figure 5: Snapshots of the nanocomposite system at the middle of the pull-out of: (a) a single CNT, (b) a bundle of three CNTs, (c) a bundle of seven CNTs, (d) a bundle of nineteen CNT and (e) a bundle of thirty-seven CNT.

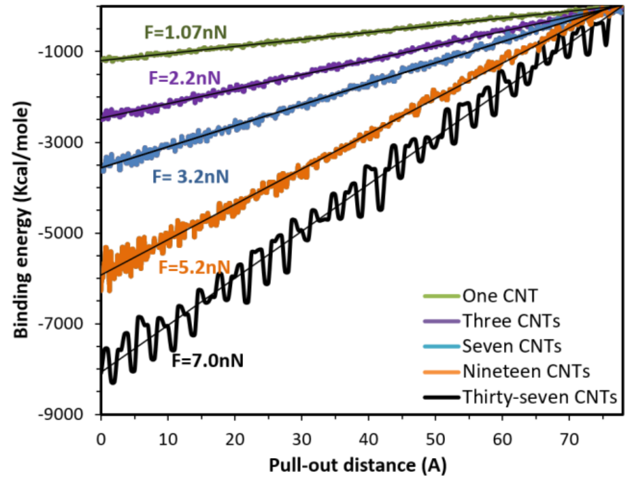


Figure 6: Binding energy plots during the pull-out of CNT bundles of different sizes and a well-dispersed individual CNT from epoxy matrix as a function of pull-out displacement.

An approximate function relating the number of CNTs, NCNT, in the bundle and the ISS is obtained by curve fitting the simulation results:

$$ISS = 45.92 * N_{CNT}{}^{-0.116} \tag{4}$$

The relationship between the ISS and the number of CNTs in the bundle is non-linear in which the ISS exhibits a rapid initial decrease with the increase of the agglomerate size. This decrease is caused by the substantial reduction in the effective surface area of the bundle compared with the total surface area of a single well-dispersed CNT. These CNT agglomerates act as failure initiation sites due to their poor interfacial adhesion with the surrounding matrix.

Three MD simulations of the pull-out test of CNTs with different curvatures were conducted to determine quantitatively the effect of waviness ratio on the interaction/binding energy, pull-out force, and ISS of CNT-epoxy composites. The pull-out process was completed when the fully embedded nanotube was fully pulled out from the epoxy. Figure 7 shows snapshots of the pull-out simulation of a curved CNT having a waviness ratio α=0.14, where one end of the nanotube was pulled out with a constant velocity. Figure 9 shows the variation of the pull-out force during the simulation. For straight CNTs, the applied pull-out force was only responsible for overcoming the non-bonded interactions between CNT's atoms, and the surrounding polymer molecules. However, for curved nanotubes, an additional work is required, especially at the beginning to overcome the resistance of the curved nanotube against shape change and the accompanying change in the potential energy of the deformed CNT. The obtained pull-out forces were used in Eq. (3) to calculate the average ISS. An approximate function relating the waviness ratio of CNTS and the ISS is obtained by curve fitting the simulation results:

$$ISS = 13211\,\alpha 3 - 6713\,\alpha 2 + 1295\,\alpha + 41.2 \tag{5}$$

Equation 5 indicates a third-order polynomial relationship between the ISS and the waviness ratio, α, of the CNT, signifying the significant impact of the morphology of the dispersed nanotubes on the interfacial properties of the nanocomposite. These predictions agree with the experimental results of Zhang et al. [8]. The results obtained for the separate effect of CNT waviness and agglomeration on the interfacial properties are used here to determine their combined effect on the ISS. All agglomerates are considered to be of hexagonal shapes. An approximate function relating the waviness ratio, α, and the number of CNTs in the nanotube bundle, N_{CNT}, with the ISS is obtained

$$ISS = N_{CNT}^{-0.116}\,(320.6\,\alpha^3 - 162.9\alpha^2 + 31.4\,\alpha + 1)\,ISS^* \quad (10)$$

where ISS^* is the interfacial shear stress between straight and well-dispersed CNT and epoxy matrix. Figures 9 shows the variation of the ISS with the waviness ratio and the number of the CNTs in the bundle. This Figure can be used to obtain the ISS for CNTs with a wide range of curvatures and agglomerate sizes.

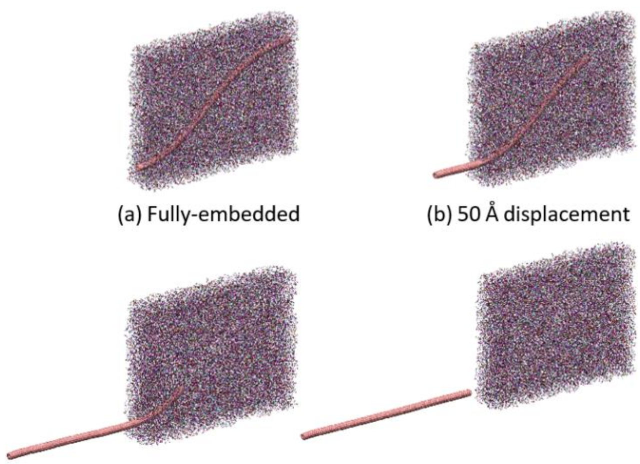


Figure 7: Snapshots of the CNT/epoxy composite during the pull-out of a wavy CNT (α=0.14).

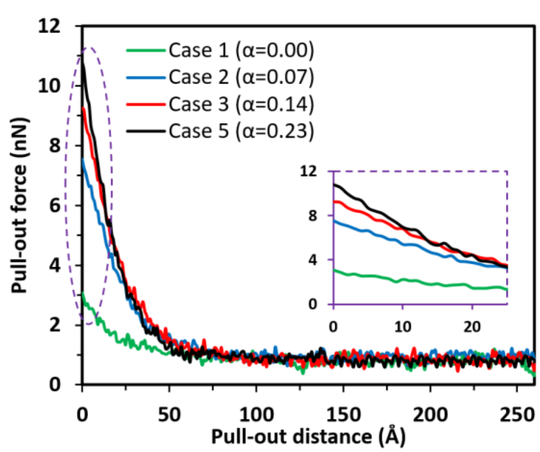


Figure 8: Binding energy plots during the pull-out of CNTs with different curvatures from epoxy matrix as a function of pull-out displacement.

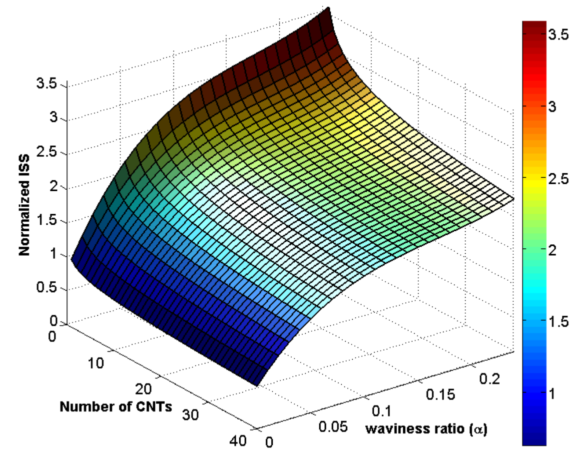


Figure 9: Variation of the interfacial shear stress with the number of CNT layers and waviness ratio of the CNTs inside the pulled-out bundles.

4 CONCLUSION

We conducted molecular dynamics simulations to determine the effect of nanotube waviness and agglomeration on the ISS of CNT-reinforced thermoset composites. Our work reveals the following: (i) the ISS increases with the increase in the waviness ratio of the CNT, (ii) the force required to initiate the pull-out of a curved CNT was found to be significantly larger than that needed for a straight CNT, and this was determined to be due to the work required to straighten the curved structure, (iii the influence of waviness on the interface strength starts to diminish when the CNTs agglomerate into bundles, and (iv) the ISS decreases significantly with the increase in the size of the CNT bundle. The results reveal that waviness and agglomeration, which are typical in nanocomposites, play a significant role in determining the interfacial shear strength of CNT-reinforced thermoset epoxies.

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