

Density functional theory study of epoxy polymer chains adsorbing onto single-walled carbon nanotubes: electronic and mechanical properties

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Abstract We performed first principles calculations based on density functional theory (DFT) to investigate the effect of epoxy monomer content on the electronic and mechanical properties of single-walled carbon nanotubes (SWCNTs). Our calculation results reveal that interfacial interaction increases with increasing numbers of epoxy monomers on the surface of SWCNTs. Furthermore, density of states (DOS) results showed no orbital hybridization between the epoxy monomers and nanotubes. Mulliken charge analysis shows that the epoxy polymer carries a positive charge that is directly proportional to the number of monomers. The Young's modulus of the nanotubes was also studied as a function of monomer content. It was found that, with increasing number of monomers on the nanotubes, the Young's modulus first decreases and then approaches a constant value. The results of a SWCNT pullout simulation suggest that the interfacial shear stress of the epoxy/SWCNT complex is approximately 68 MPa. These results agreed well with experimental results, thus proving that the simulation methods used in this study are viable.

Keywords Epoxy/SWCNT complex · Density functional theory · Electronic properties · Mechanical properties

Introduction

In the area of nanotechnology, polymer nanocomposites based on nanofillers have attracted significant attention as

lightweight high-strength fiber-reinforced materials [1–3]. Among these polymeric nanocomposites, epoxy reinforced with carbon nanotubes (CNTs) is being investigated for a wide range of industrial, military, aeronautic, and aerospace applications [4–6].

It is well established from research on CNT-reinforced polymer composites over the past few years that the efficiency of load transfer from the polymer matrix to the nanotubes depends critically on the interfacial bonding between the nanotubes and the polymer matrix (CNT/polymer) [7, 8]. Thus, to take advantage of the very high Young's modulus and strength of CNTs, efficient load transfer from the polymer matrix to the nanotubes is required. However, due to the difficulties associated with the experimental techniques used to study the CNT/polymer interface, molecular modeling may serve to explain the importance of various factors governing the interfacial characteristics of CNT-reinforced polymer composites [9]. Molecular dynamics (MD), molecular mechanics (MM), Monte Carlo (MC) simulations and quantum mechanics (QM) calculations are the most common molecular modeling techniques [10].

Density functional theory (DFT) is a quantum mechanical modeling method used in physics and chemistry for the study of structural, electronic, dynamical and mechanical properties in materials science. The reason for this lies both in the ability of the DFT method to treat models of relatively large sizes (several hundred atoms) compared to other first-principles methods, and in the degree of accuracy that can be achieved for various systems in a systematic fashion [11–13].

To date, MD simulations have been used to calculate the interfacial binding and shear strength between CNTs and polymer matrices in CNT/polymer composites. Yang et al. [14] investigated the interaction between single-walled carbon nanotubes (SWCNTs) and polyethylene/polypropylene/polystyrene using MD simulations. Their results showed

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that the monomer structure plays a very sensitive role in determining the strength of interaction between SWCNTs and polymers. Gou et al. [9] reported the interfacial bonding of SWCNT-reinforced epoxy composites using computational methods. The interfacial bonding strength between the nanotube and the cured epoxy resin was calculated to reach values of up to 75 MPa. However, Liao and Li [15] investigated the effect of the polystyrene monomer content on the interfacial characteristic of a SWCNT-reinforced polystyrene composite system through MM simulations. They found that the binding energy between the filler and polystyrene increased from -0.41 eV for a single monomer to -0.22 eV for an 80-monomer chain. Furthermore, their results showed that the interfacial bonding strength of the polystyrene/SWCNT system is approximately 160 MPa, significantly higher than most carbon-nanofiber-reinforced polymer composite systems.

In the current work, for the first time, the fundamental goal was to evaluate the adsorption properties and mechan-

ical strength of epoxy/SWCNT complexes using DFT calculations by incorporating the effects of the monomer content and type of nanotubes.

Computational methods

All systems were optimized using the DFTB+ program package [16]. DFTB+ uses the self-consistent charge density functional tight-binding (SCC-DFTB) method based on the second-order expansion of the Kohn-Sham total energy in DFT with respect to charge density fluctuation within the tight-binding framework. This method has been applied to calculate binding energies and geometries, and the resulting mean average deviations from the experimental values are comparable to those of full DFT calculations with a double- ζ plus polarization basis set [17]. The geometrical optimizations were performed using the conjugate gradient algorithm. Furthermore, all of the total energy calculations

Fig. 1a–e Optimized configurations of epoxy/(6,0) single-walled carbon nanotube (SWCNT) complexes. **a** Monomer, **b** two-monomer, **c** three-monomer, **d** five-monomer, **e** eight-monomer

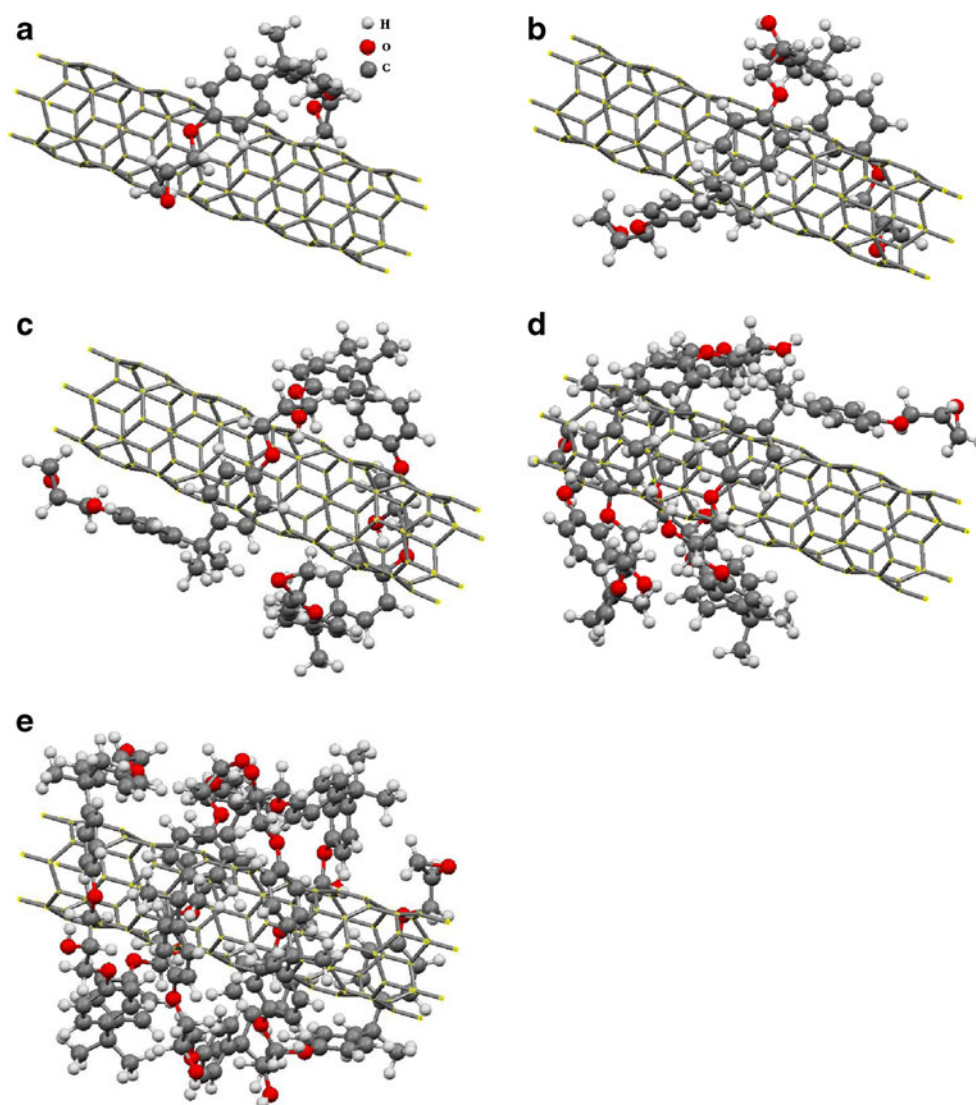
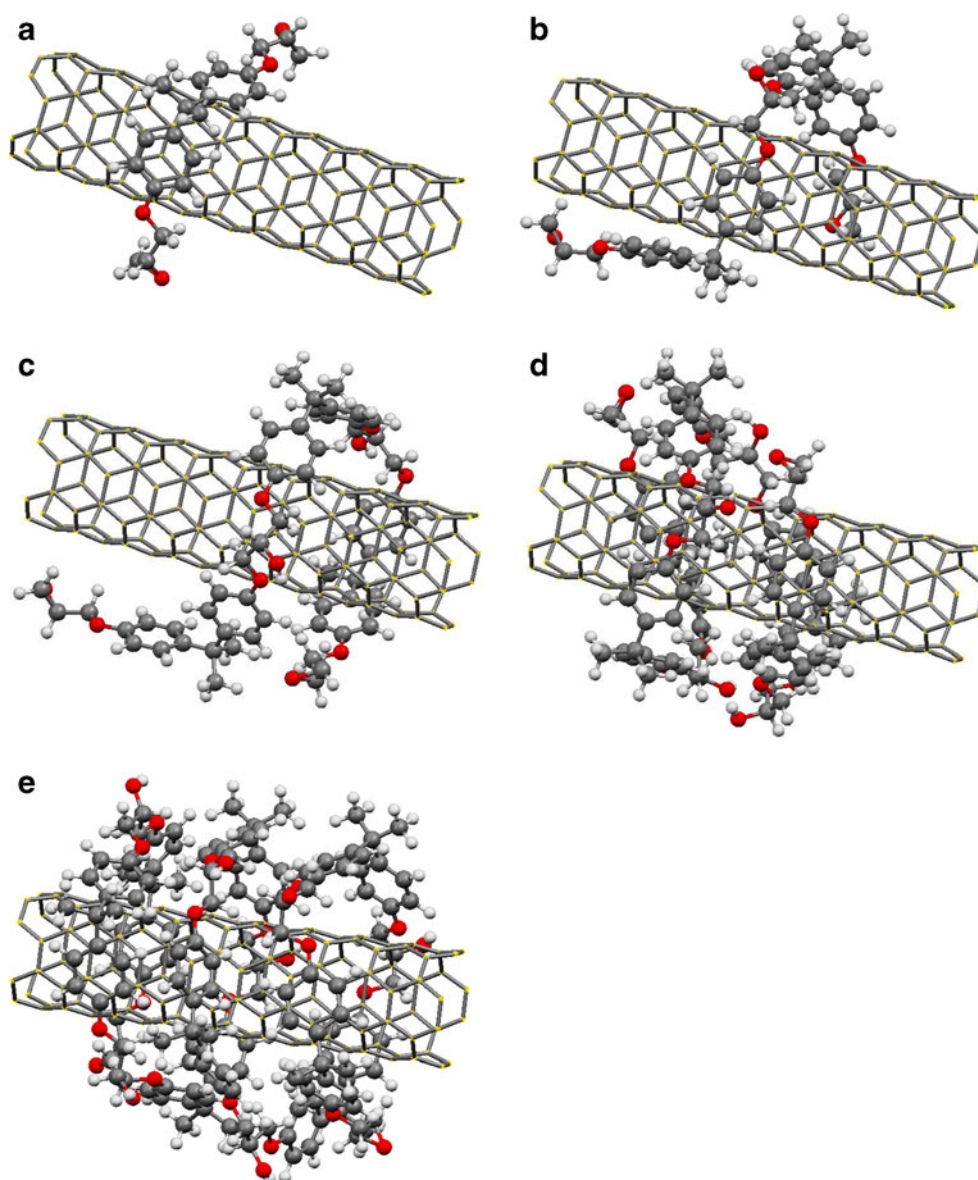


Fig. 2a–e Optimized configurations of epoxy/(4,4) SWCNT complexes.

a Monomer, **b** two-monomer, **c** three-monomer, **d** five-monomer, **e** eight-monomer



of the systems were performed within the framework of DFT, as implemented in the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code [18–21]. The exchange and correlation potential was treated using a generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [22]. All of the calculations were performed using a double- ζ plus polarization (DZP) basis set with an energy shift of 100 meV. Periodic boundary conditions and supercell approximations, with a lateral separation of 27 Å between the tube centers, were employed to ensure that the nanotubes and epoxy monomer did not interact with their periodic images. Along the tubes, k -points were used for the axes, with a $1 \times 1 \times 5$ Monkhorst-Pack grid for the Brillouin zone integration. The mesh cut-off, which is the energy that corresponds to the grid spacing, was chosen to be 120 Ry. The basis set superposition error (BSSE) was eliminated by adding ghost

atoms to the calculation of the isolated adsorbate. The ghost atoms employ basis functions but do not otherwise affect the calculation (i.e., no projectors or compensation charges), ensuring that the same degrees of freedom are available to the wave functions in all of the calculations. This procedure is called the counterpoise method, and the binding energy for the adsorption of the polymer onto the nanotube surface was obtained from the following expression:

$$E_b = E_{(CNT-epoxy)} - E_{(CNT_{ghost}-epoxy)} - E_{(CNT-epoxy_{ghost})} \quad (1)$$

where $E_{(CNT-epoxy)}$ is the total energy of the CNT interacting with the epoxy polymer. The ‘ghost’ CNT/epoxy terms correspond to the interactions introduced by the counterpoise method. Furthermore, we employed the ab initio van der Waals-density functional (vdW-DF) method [23, 24] to

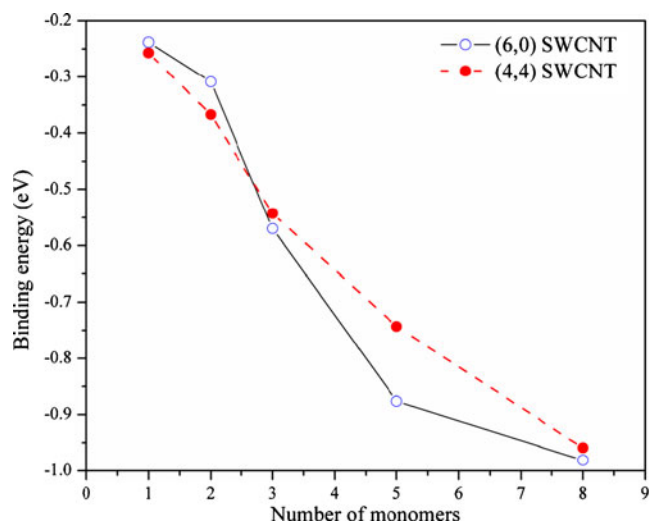


Fig. 3 Variation in binding energy with number of monomers adsorbed onto the surface of a (6,0) SWCNT

include long-range attractive contributions to van der Waals interactions, so-called “London dispersion forces” [25, 26].

Results and discussion

Electronic properties

First, we studied the interfacial bonding properties of Epon828 epoxy on a pristine (4,4) and (6,0) SWCNT (epoxy/SWCNT). Random coils of Epon 828 epoxy $[(-C_{21}O_4H_{24})_n]$ molecules with $n=1, 2, 3, 5,$ and 8 were constructed and optimized around the nanotube surface. We did not consider more than eight-monomer epoxy chains interacting on the nanotube surface due to steric hindrance. The optimized geometries of the adsorbed epoxy molecules on the surface of a (6, 0) and (4,4) SWCNT are shown in Figs. 1 and 2. According to our results, the binding energy decreases with the increasing number of monomers on the nanotube, and it appears to stabilize for longer epoxy chains. Figure 3 shows the calculated binding energy versus the number of epoxy monomers on the surface of nanotubes. The negative values of binding energies were assumed to be attractive interfacial interaction between the nanotube and epoxy resin. For example, the binding energy for the epoxy/(6, 0) SWCNT complex decreased from -0.24 eV for a

Table 1 Geometry parameters of (6,0) and (4,4) single-walled carbon nanotubes (SWCNT) before and after epoxy monomer adsorption

System	d_p (Å)	d_c (Å)	d_v (Å)
(6,0) SWCNT	1.412	1.436	–
Monomer/(6,0) SWCNT	1.422	1.446	–
Two-monomer/(6,0) SWCNT	1.426	1.449	–
Three-monomer/(6,0) SWCNT	1.425	1.452	–
Five-monomer/(6,0) SWCNT	1.425	1.454	–
Eight-monomer/(6,0) SWCNT	1.424	1.455	–
(4,4) SWCNT	–	1.409	1.394
Monomer/(4,4) SWCNT	–	1.423	1.424
Two-monomer/(4,4) SWCNT	–	1.425	1.425
Three-monomer/(4,4) SWCNT	–	1.426	1.427
Five-monomer/(4,4) SWCNT	–	1.426	1.428
Eight-monomer/(4,4) SWCNT	–	1.428	1.428

monomer to -0.98 eV for an eight-monomer chain. Thus, according to the above results, the interfacial interaction between epoxy and nanotubes enhances with the increasing number of epoxy monomers. Furthermore, we found that an epoxy molecule on a (6,0) SWCNT is more stable than that on a (4,4) SWCNT for more than two monomers on a chain. The binding distance, which is defined as the length between the H atom of an epoxy molecule and the central C atom of a nanotube, was calculated for (6,0) and (4,4) nanotube complexes. These values for the binding distance of epoxy/(6,0) and (4,4) SWCNT complexes are approximately in the range of 2.82 – 2.85 Å. In the optimized (6,0) and (4,4) SWCNTs and their combined systems, two types of C–C bonds can be found: one parallel (d_p) or vertical (d_v) with the tube axis, and the other one diagonal (d_c) to the tube axis (Fig. 4). The geometry parameters are also calculated and listed in Table 1. Our results show that the C–C bond lengths of the (6,0) and (4,4) SWCNTs increase with increasing the number of epoxy monomers on the surface of the nanotubes.

Furthermore, to investigate the change in electronic structure of the nanotubes caused by the adsorption of an epoxy molecule, the net charge transfer between a nanotube and an epoxy molecule was calculated using Mulliken analysis [27]. Charge analysis using the Mulliken method indicates that 0.06, 0.01, and 0.13 electrons charges are transferred from the carbon, oxygen, and hydrogen atoms to the carbon

Fig. 4 Definition of C–C bond lengths for the (6,0) and (4,4) SWCNT

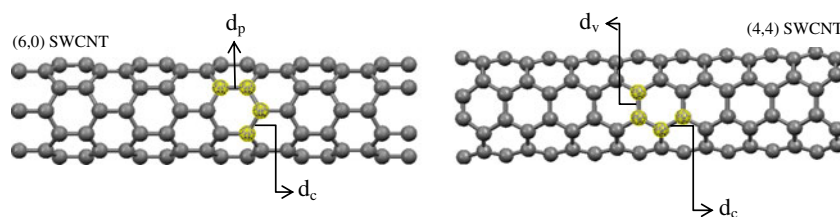


Table 2 Calculated charge on each atom and charge transfer between atom and (6,0) SWCNT for monomer/(6,0) SWCNT complex

Type of atom	Amount of atom	Charge on atom (electrons)		Charge transfer (electrons)
		Before adsorption	After adsorption	
C	21	86.761	86.699	+0.062
O	4	25.168	25.159	+0.009
H	24	20.071	19.941	+0.130

atoms within the sidewall of (6,0) SWCNT, respectively (Table 2). Therefore, we conclude that the hydrogen atoms play the most effective role in interaction between epoxy monomer and nanotubes. We found that, as the number of epoxy monomers increases on the surface of a nanotube, the negative charge on the SWCNT increases. As listed in Table 3, approximately 0.47 electrons is transferred from the eight-monomer epoxy to the (6,0) SWCNT, which is 2.3 times more than the 0.20 electrons transferred in the monomer epoxy/(6,0) SWCNT complex. Thus, electron transfer appears to play an important role in the stability of epoxy/SWCNT complexes.

The density of states (DOS) of these complexes was analyzed to better understand the type of bonding that occurs through electronic structure. The calculated DOS for the combined system of epoxy/SWCNT (6,0) was compared to the corresponding DOS for the individual entities (epoxy/SWCNT and epoxy), as shown in Fig. 5. From the spectra obtained, it was found that the DOS of the combined system of the epoxy/SWCNT (6,0) system matches rather exactly the superposition of the DOS of the individual parts. This finding reveals that the epoxy interacts weakly with SWCNTs, and that no significant hybridization exists between the respective orbitals of the two entities in the adsorption process.

In addition, comparison of the DOS of a monomer and (6,0) SWCNT with that of a monomer epoxy/(6,0) SWCNT complex (Fig. 5) revealed that a slight shift to the right occurs in the DOS of the epoxy/SWCNT complex. These results, along with the binding energy values, show that the dominating interaction between epoxy molecules and nanotubes is physisorption; the weak interaction was obtained quantitatively in terms of binding energies. Our results show that adsorption of an epoxy monomer onto the surface of a nanotube induces a shift in the Fermi energy

position due to charge transfer to the nanotube surface. Additionally, the Fermi energy position is shifted to a high energy level by increasing the number of monomers on the surface of the nanotube. According to Table 3, in going from a single epoxy monomer and to an eight-monomer epoxy adsorbed onto the surface of a (6, 0) SWCNT, the Fermi energy of the nanotube rises from -6.06 to -5.76 eV, whereas the Fermi level of the intrinsic nanotube is -6.21 eV.

Mechanical properties

We consider here the effect of the increasing number of epoxy monomers on the elastic constants of the (6, 0) SWCNT using DFT calculations implemented by the SIESTA code. Young's modulus is definitely the most interesting quantity for measuring the strength of the nanotubes and complexes under study. To obtain the Young's modulus along the axial direction, complexes were compressed or elongated gradually in small increments, and the strain energy E_s was obtained at each axial strain value ε . The step increase in this simulation was 0.007 Å. Figure 6 shows the variation in the strain energy of the complexes as a function of the applied strain in the harmonic region. The conventional definition of Young's modulus involves the second derivative of the strain energy with respect to strain. The Young's modulus is given by the following expression:

$$Y = \frac{1}{V_0} \left(\frac{\partial^2 E_s}{\partial \varepsilon^2} \right)_{\varepsilon=0} \quad (2)$$

where V_0 is the equilibrium volume of the system. The Young's modulus results for an intrinsic (6,0) SWCNT and epoxy/SWCNT complexes are depicted in Table 3. The calculated Young's moduli of the SWCNTs compare excellently to experimental findings. A large variation in the

Table 3 The net charge transfer, Fermi energy, and Young's modulus of the studied complexes

Complex	Charge transfer (e)	Fermi energy (eV)	Modulus (GPa)
(6,0) SWCNT	–	-6.21	1,075.2
Monomer/(6,0) SWCNT	0.201	-6.06	947.2
Two-monomer/(6,0) SWCNT	0.275	-6.04	885.1
Three-monomer/(6,0) SWCNT	0.328	-5.90	841.1
Five-monomer/(6,0) SWCNT	0.389	-5.77	824.6
Eight-monomer/(6,0) SWCNT	0.467	-5.76	813.7

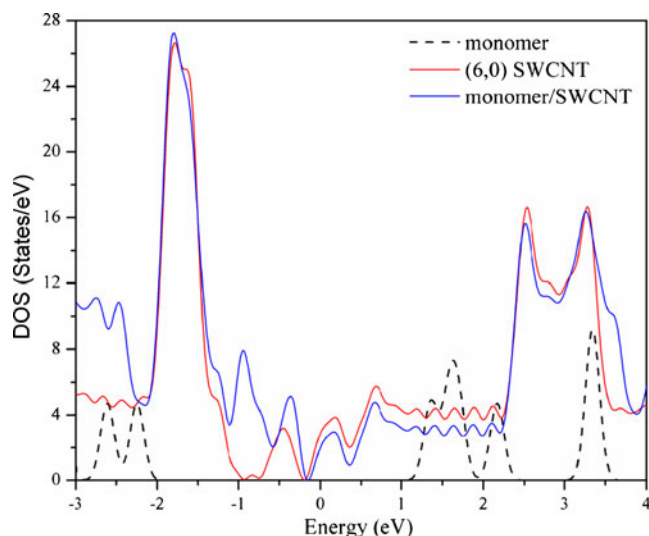


Fig. 5 Calculated density of states (DOS) for a monomer/(6,0) SWCNT complex. The Fermi level is localized in zero field

Young's moduli was reported as function of nanotube diameter, from 0.4 to 1.7 TPa with a mean of 1 TPa, using transmission electron microscopy and atomic force microscopy [28–30]. Atomistic studies have also been reported for calculation of the Young's modulus of carbon nanotubes by the DFT method. Milowska et al. [31] employed SIESTA code and revealed the Young's modulus of a SWCNT to be 1,020 GPa. Furthermore, Cai et al. [32] used the same method implemented by the Dmol³ modeling program for (10, 0) nanotubes and reported that the obtained modulus of the nanotubes is approximately 950 GPa.

We also studied the dependence of the Young's modulus on the number of epoxy monomers. The results for epoxy/SWCNT complexes are presented in Table 3 and Fig. 7. The figure shows that, with increasing number of monomers on the surface of a (6, 0) SWCNT, the Young's

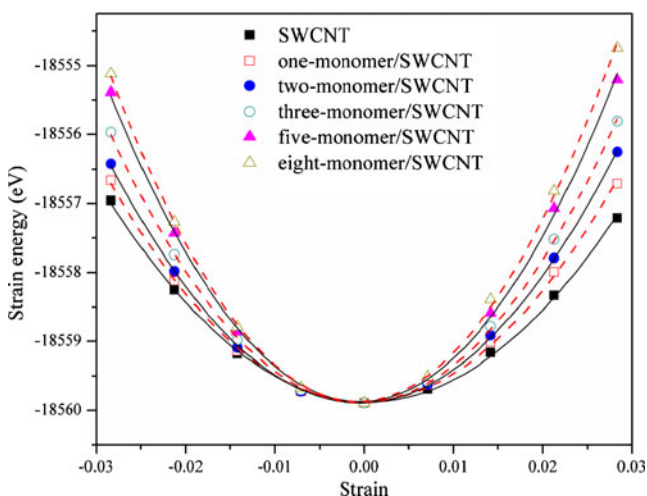


Fig. 6 Dependence of strain energy on the strain for epoxy/(6,0) SWCNT complexes

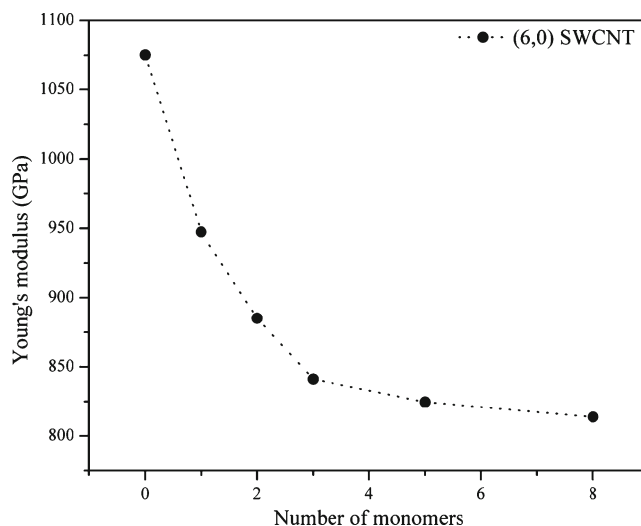


Fig. 7 Variation in Young's modulus with the number of monomers adsorbed onto the surface of (6,0) SWCNT

modulus decreases rapidly initially, then slowly, and finally approaches a constant value of 813.7 GPa. From the (6,0) SWCNT geometry after epoxy adsorption, we found that when epoxy monomers are adsorbed onto the nanotube surface, the C–C bond lengths increase, thus explaining why the epoxy/SWCNT complex is softer than pristine nanotube (Table 1). It should be noted that experimental studies on the effect of monomer content on the mechanical properties of nanotubes are challenging and have not yet been evaluated. Therefore, we have provided a valuable theoretical study for the realistic prediction of the mechanical properties of such complexes.

We next calculated the interfacial shear stress for an eight-monomer/(6,0) SWCNT complex. Interfacial shear stress is a critical parameter controlling the efficiency of stress transfer and hence some of the important mechanical properties of the complexes, such as elastic modulus, tensile strength, and fracture toughness. To characterize the interfacial shear strength of the complexes, pullout simulations of a SWCNT were performed. The SWCNT was pulled out of an epoxy resin along the tube axis direction Z . The pullout energy, E_{pullout} , is defined as the energy difference between the fully embedded nanotube and the complete pullout configuration. The pullout energy can be related to the interfacial shear stress, τ_i , by the following relation:

$$E_{\text{pullout}} = \int_{z=0}^{z=L} 2\pi r (L - Z) \tau_i dz \quad (3)$$

$$\tau_i = \frac{E_{\text{pullout}}}{\pi r L^2} \quad (4)$$

where r and L are the radius and length of the nanotube embedded in the polymer, respectively, and z is the

displacement of the nanotube along the longitudinal tube axis. During the initial stage of the pullout (fully embedded nanotube), the total energy of the complex was $-58,541.21$ eV. After complete pullout, the total energy increased to $-58,540.25$ eV. From the pullout simulation, the interfacial shear strength between the nanotube and resin was shown to be approximately 68 MPa. This simulation result obtained by the DFT method is in accordance with previous experimental and theoretical results, which proves that the simulation method in this paper is viable. Cooper et al. [33] measured the interfacial strength directly by drawing out individual SWCNT ropes and MWCNTs bridging across holes in an epoxy matrix using a scanning probe microscope tip. Based on these experiments, the interfacial shear strength between the MWCNTs and the epoxy matrix was calculated to be in the range of 35–376 MPa. Gou et al. [9] studied the interfacial shear stress of an epoxy/SWCNT complex by a combination of computational (molecular dynamics simulations) and experimental methods. The interfacial shear strength between the nanotube and the epoxy polymer was calculated to be up to 75 MPa, indicating that there could be an effective transfer of stress from the epoxy polymer to the nanotube.

Conclusions

In the present study, we first used the SCC-DFTB method for structural optimization, and first-principles simulations based on DFT method were then used for total energy calculations. We analyzed the effect of epoxy monomer quantity on the intermolecular binding, elastic modulus, and interfacial shear stress of epoxy/SWCNT complexes. It was found that the binding energy between an epoxy molecule and nanotube decreases as the number of monomers increases, which leads to more efficient charge transfer from the epoxy to the nanotube. For example, the binding energy increases from a low value of -0.24 eV for a monomer epoxy/(6, 0) SWCNT system to -0.98 eV for a complex with eight monomers adsorbed on to the surface of nanotube. Additionally, the amount of charge transferred increased by about 0.27 electrons. Moreover, the calculated DOS of the combined system is nearly a superposition of the DOS of the entities; moreover, the DOS near the Fermi level is not affected by the adsorption of adsorbates onto the surface of SWCNTs. These adsorption properties are typical of physisorption, and the interaction was obtained quantitatively in terms of binding energies. We found that the Young's modulus decreases rapidly as the number of monomers increases, and then slowly reduces to a constant value. Furthermore, the results of a (6, 0) SWCNT

pullout simulation suggest that the interfacial shear stress between an eight-monomer epoxy and nanotube is equal to 68 MPa.

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