



In-plane elastic moduli of covalently functionalized single-wall carbon nanotubes



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ABSTRACT

Effective utilization of single-wall carbon nanotubes (SWCNTs) as reinforcements in composites necessitates their strong interfacial bonding with the surrounding matrix. The covalent functionalization of SWCNTs is an effective method to enhance this bonding. However, covalent bonds introduced by a functional group may alter the pristine structure of the SWCNT and affect its mechanical properties. Thus it is important to delineate effects of covalent functionalization on elastic properties of a SWCNT. We study here effects of covalent functionalization on Young's modulus, Poisson's ratio and shear modulus of a SWCNT in the graphitic plane. We consider hydrogen (–H), hydroxyl (–OH), carboxyl (–COOH), and amine (–NH₂) as model functional groups in this work. We use molecular mechanics (MM) simulations with the MM3 potential and the software TINKER to analyze simple tension and torsional deformations of pristine and functionalized SWCNTs. As is commonly assumed, we hypothesize that the response of a SWCNT to these deformations is the same as that of an energetically and geometrically equivalent continuum cylinder of wall thickness 3.4 Å. From curves of the strain energy density of deformation versus the axial strain and the shear strain for each functionalization group, values of Young's modulus and the shear modulus, respectively, are deduced. From results of the tension tests on a pristine and a SWCNT fully functionalized with hydrogen (–H), Poisson's ratio is computed. It is found that for each functional group studied and 20% functionalization, Young's modulus and the shear modulus decrease by about 34% and 43%, respectively, and Poisson's ratio of the functionalized SWCNT is more than that of the pristine SWCNT. These results should help in determining mechanical properties of SWCNT reinforced nanocomposites by using a micromechanics approach.

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1. Introduction

Researchers have employed experimental and analytical techniques, density functional theory (DFT), molecular dynamics (MD) and molecular mechanics (MM) simulations to predict mechanical properties of carbon nanotubes (CNTs). Assuming that the wall thickness of a single-wall CNT (SWCNT) can be approximated as 0.34 nm, Treacy et al. [1], Wong et al. [2], and Krishnan et al. [3] experimentally determined that Young's modulus of a CNT is in terapascal (TPa) range. Xing et al. [4] employed MD simulations to predict Young's modulus of a SWCNT. Li and Chou [5] computed elastic properties of CNTs using combined structural mechanics and MM approach. Chang and Gao [6] investigated size dependent elastic properties of SWCNTs through MM simulations. Sears and Batra [7] determined the wall thickness, Young's modulus, and Poisson's ratio of CNTs using MM simulation with the MM3 potential and the software TINKER. They assumed that the

responses of a SWCNT in simple tension and pure torsional deformations are energetically equivalent to those of a thin cylinder made of an isotropic and homogeneous material and of length, mean radius and thickness equal to those of the SWCNT. They found the wall thickness and Young's modulus of a SWCNT to be 0.046 nm and 7.26 TPa, respectively. Shen and Li [8] used MM potential and energy equivalent principle to determine values of five elastic constants of a CNT assuming the CNT as a transversely isotropic material with the centroidal axis of the tube as the axis of transverse isotropy. Batra and Sears [9] proposed that the axis of transverse isotropy of a CNT is a radial line rather than the centroidal axis. By studying with MM simulations radial expansion of a SWCNT, they showed that Young's modulus in the radial direction is about 1/4th of that in the axial direction. Gupta and Batra [10,11] predicted the material moduli of a SWCNT and the wall thickness of the equivalent continuum cylinder by matching frequencies of bending, axial and torsional vibrations as well as that of radial breathing modes of a free-free SWCNT with those of the equivalent continuous cylinder. As pointed out, amongst others, by Gupta and Batra [10,11], different techniques give varying values for the wall thickness of a SWCNT. Wu et al. [12] developed an atomistic based

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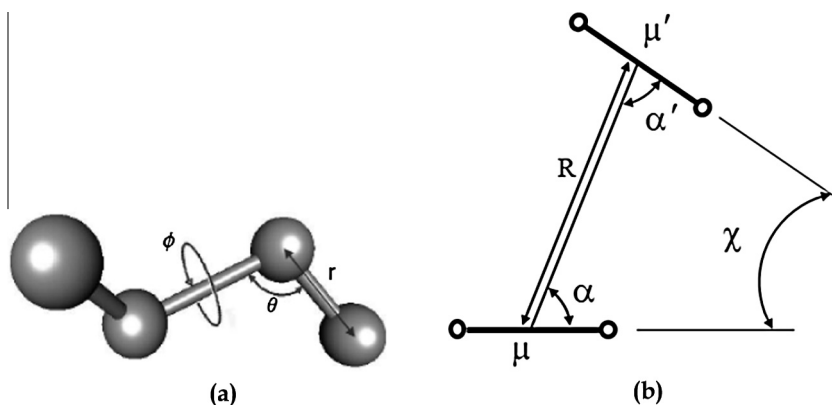


Fig. 1. Definitions of some variables in the MM3 potential. (a) Parameters r , θ and ϕ [7] and (b) parameters involved in dipole-dipole interaction [45].

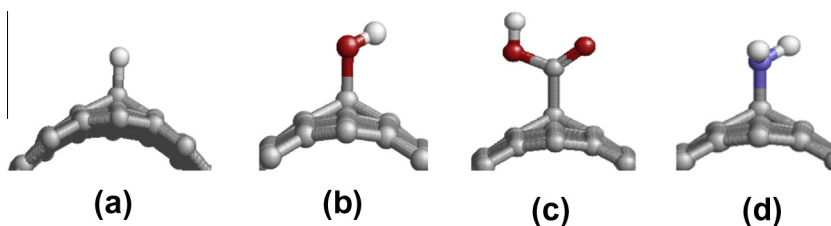


Fig. 2. Schematics of a carbon atom of the CNT attached with (a) hydrogen ($-H$), (b) hydroxyl ($-OH$), (c) carboxyl ($-COOH$), and (d) amine ($-NH_2$) groups.

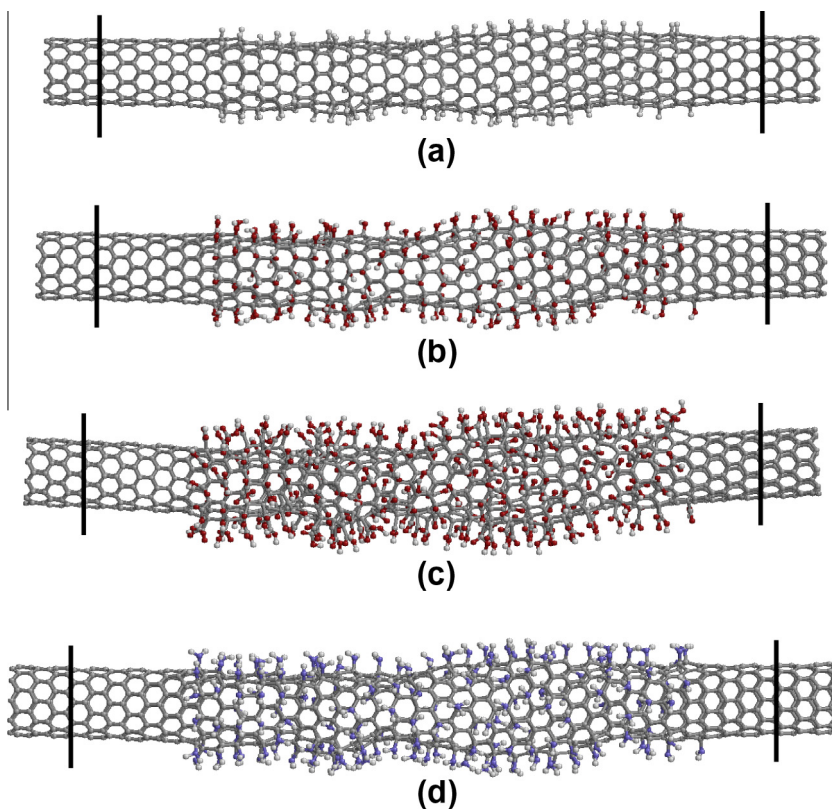


Fig. 3. Schematics of a (10, 0) SWCNT having 20% of randomly selected carbon atoms functionalized with (a) hydrogen ($-H$), (b) hydroxyl ($-OH$), (c) carboxyl ($-COOH$), and (d) amine ($-NH_2$) groups (Black vertical lines denote rings of carbon atoms where boundary conditions are specified).

finite deformation shell theory for a SWCNT and found its stiffness in tension, bending, and torsion.

The SWCNTs due to their cylindrical shape, large length to diameter ratio, and high specific properties are potential candi-

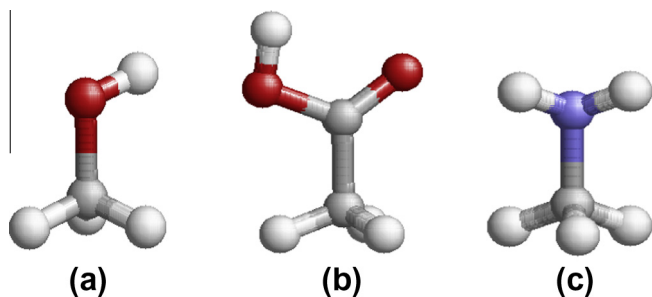


Fig. 4. Structures of (a) methanol, (b) acetic acid, and (c) amino methane generated using SMILES.

dates as reinforcements in composites. However, the effectiveness of SWCNTs as reinforcements depends on their uniform dispersion in and strong adhesion with the surrounding matrix. It has been very challenging to simultaneously meet these two requirements. The functionalization of SWCNTs appears to be an effective means of achieving good bonding between SWCNTs and the surrounding matrix. The surface properties of CNTs can be modified by either physical or chemical functionalization. The physical functionalization is achieved by attaching noncovalent groups such as polymer, peptides or surfactants to the nanotubes. It is advantageous since it does not alter the pristine structure of nanotubes and hence their mechanical properties. However, these functional groups are attached to nanotubes with weak van der Waals interactions resulting in low load transfer efficiency between the nanotube and the matrix. In comparison, the chemical functionalization involving the covalent attachment of functional groups to atoms of CNTs provides relatively strong interfacial bonding between CNTs and the surrounding matrix thereby enhancing the load transfer efficiency. Grujicic et al. [13] have shown that the covalent functionalization of triple-walled CNTs improves the load transfer efficiency especially when loads are applied in a direction orthogonal to the CNT axis. Experimental works [14–18] have demonstrated the effectiveness of covalent functionalization in increasing the interfacial bonding strength between CNTs and polymer chains.

Although chemical functionalization enhances the binding of SWCNTs with the surrounding matrix, it may damage their cylindrical shape due to the introduction of covalent bonds, and reduce the average value of their moduli. Much of the research work on the determination of elastic properties of SWCNTs has considered pristine SWCNTs. Since the covalently functionalized SWCNTs would be better candidates for reinforcements in a composite than the pristine SWCNTs, it is important to determine the effect of covalent functionalization on elastic moduli of a SWCNT. Zhang et al. [19] used atomistic simulations to analyze mechanical properties of hydrogenated SWCNTs and found a decrease in their Young's modulus, strength, and ductility with an increase in the percentage of C–H bonds. Kuang and He [20] computed Young's moduli of vinyl functionalized SWCNTs using MM simulations with the condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field and found that Young's modulus depends on the density of the sp^3 hybridized carbon atoms and chirality of the CNTs. They found up to 33% reduction

Table 1
Values of geometric parameters in the hydroxyl group.

	Methanol	CNT–OH
R–O–H angle (degrees)	108.13	109.18
R–O length (nm)	0.143	0.143
O–H length (nm)	0.095	0.095

R denotes sp^3 hybridized carbon atom.

Table 2
Values of geometric parameters in the carboxyl group.

	Acetic acid	CNT–COOH
C–O–H angle (degrees)	107.39	107.6
R–C–O angle (degrees)	112.04	111.89
R–C=O angle (degrees)	126.04	126.27
C–O length (nm)	0.135	0.135
C=O length (nm)	0.120	0.121
O–H length (nm)	0.097	0.097
R–C length (nm)	0.150	0.153

R denotes sp^3 hybridized carbon atom.

Table 3
Values of geometric parameters in the amine group.

	Amino methane	CNT–NH ₂
H–N–H bond angle (degrees)	106.35	106.09
R–N–H bond angle (degrees)	112.35	113.29
Dihedral angle between two R–N–H planes	119.78	121.38
N–H bond length (nm)	0.101	0.101
R–N bond length (nm)	0.146	0.146

R denotes sp^3 hybridized carbon atom.

in Young's modulus with 38% of carbon atoms functionalized. Namilae et al. [21] found that for uniaxial tensile deformations of vinyl functionalized SWCNTs the fracture strain decreased with an increase in the functionalization. Ling et al. [22] predicted Young's modulus of functionalized CNTs using MM and MD simulations with the COMPASS force field and observed that Young's modulus depends on the functionalizing material and the amount of functionalization. Recently, Milowska and Majewski [23] studied effect of different functional groups on elastic properties of functionalized CNTs using DFT calculations. Their results showed that an increase in the amount of covalently bound material to the wall of a CNT decreases Young's, shear and bulk moduli.

An important factor in selecting a covalent group to functionalize a SWCNT is the feasibility of chemical functionalization. Khare et al. [24] developed hydrogenated CNTs using electric discharge. The oxygen containing groups such as hydroxyl (–OH) and carboxyl (–COOH) can be bonded to the wall of a CNT by treating the CNT in an oxidizing environment such as a mixture of concentrated H_2SO_4 and HNO_3 or H_2SO_4 and H_2O_2 [25]. An advantage of these groups is that they can be easily substituted by other functional groups allowing additional modification of the CNTs [26–28]. Haddon et al. used the nanotube-bound carboxylic acid groups for attaching long alkyl chains to SWCNTs via amide linkages [29–31] and via carboxylate-ammonium salt ionic interactions [32]. Sun et al. showed that the esterification of the carboxylic acid groups could also be used to functionalize and solubilize nanotubes of any length [33–35]. Wilson et al. illustrated the use of anilines to functionalize nanotubes [36]. It is also possible to synthesize amino functionalized CNTs by NH_3 plasma treatment [37] or by substitution of –F in fluorinated CNTs with diamines [38]. Noting that there are many functionalizing agents, we limit ourselves to somewhat arbitrarily chosen four groups, namely, –H, –OH, –COOH, and – NH_2 , and study their effects on modifying elastic moduli of a SWCNT for varying percentage of functionalization. We use MM simulations and the freely available software TINKER [39] to accomplish this objective. It is found that the elastic moduli of a SWCNT decrease with an increase in the number of carbon atoms that are functionalized.

The rest of the paper is organized as follows. The MM3 potential and the virtual tests are described in Section 2. In Section 3, we first show that our approach of functionalizing carbon atoms gives results consistent with those obtained by other investigators. We

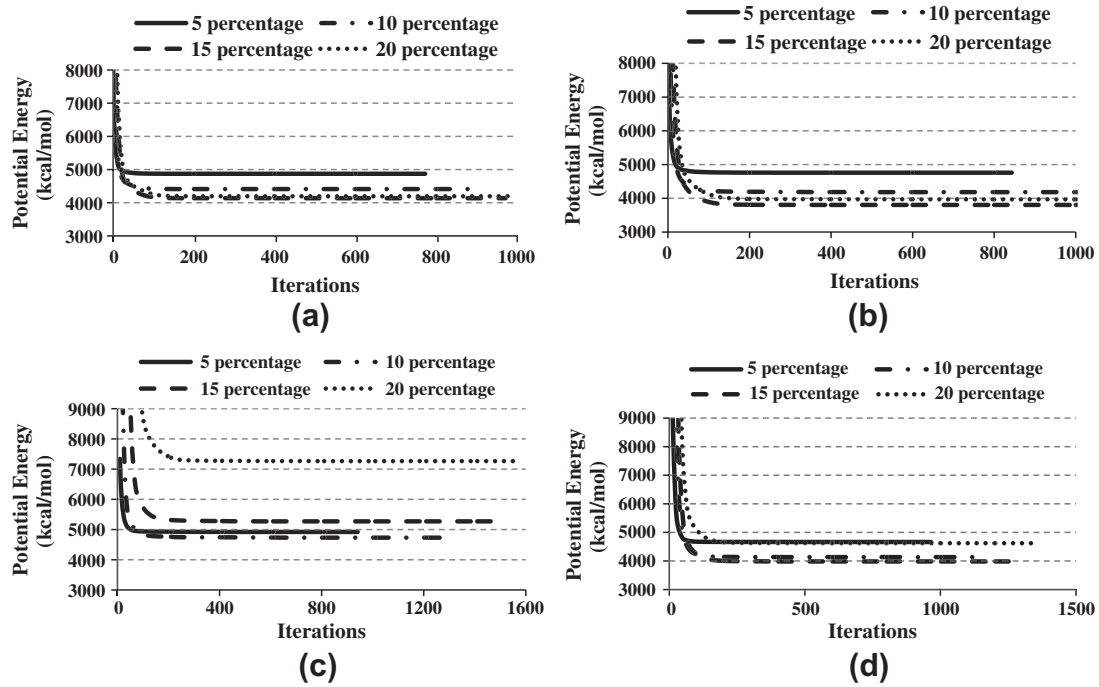


Fig. 5. For different percentages of functionalization, potential energy vs. the number of iterations during the minimization of the potential energies of the SWCNT functionalized with (a) –H, (b) –OH, (c) –COOH, and (d) –NH₂ groups.

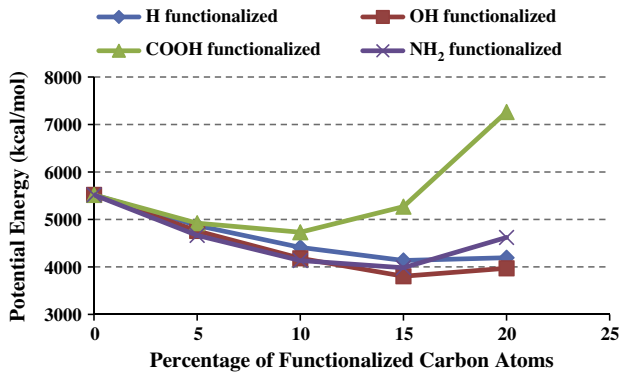


Fig. 6. Potential energies in the relaxed configuration of the SWCNT functionalized with (a) –H, (b) –OH, (c) –COOH, and (d) –NH₂ groups.

then deduce values of Young's and shear moduli as a function of the number of carbon atoms functionalized and the functionalizing agent. Conclusions of this work are summarized in Section 4.

2. Molecular mechanics simulations

2.1. Force-field

The MM3 potential [40] with higher order expansions and cross-terms has been used to model interatomic interactions. This potential is suitable for studying deformations of CNTs because of similarities between sp² bonds in the hexagonal structure of CNTs and the hexagonal structure of aromatic proteins for which the potential was originally developed. In this potential the energy W of the system, given by Eq. (1), equals the sum of energies due to bonded and non-bonded interactions. The contributions for bonded interactions come from bond stretching (U_s), in-plane angle bending (U_θ), out of plane bending (U_γ), torsion (U_ϕ), and cross-interactions including stretch-bend ($U_{s\theta}$), angle-angle ($U_{\theta\theta'}$)

and stretch-torsion ($U_{s\phi}$). The non-bonded interactions are van der Waals (U_{vdW}) and dipole–dipole electrostatic ($U_{\mu\mu'}$).

$$U_s = 71.94K_s(r - r_0)^2 \left[1 - 2.55(r - r_0) + \frac{7}{12}(2.55(r - r_0)^2) \right]$$

$$U_\theta = 0.0219K_\theta(\theta - \theta_0)^2 \left[1 - 0.014(\theta - \theta_0) + 5.6(10^{-5})(\theta - \theta_0)^2 - 7.0(10^{-7})(\theta - \theta_0)^3 + 2.2(10^{-8})(\theta - \theta_0)^4 \right]$$

$$U_\gamma = 0.0219K_\gamma\gamma^2 \left[1 - 0.014\gamma + 5.6(10^{-5})\gamma^2 - 7.0(10^{-7})\gamma^3 + 2.2(10^{-8})\gamma^4 \right]$$

$$U_\phi = (V_1/2)(1 + \cos \phi) + (V_2/2)(1 - \cos 2\phi) + (V_3/2)(1 + \cos 3\phi)$$

$$U_{s\theta} = 2.511K_{s\theta}[(r - r_0) + (r' - r'_0)](\theta - \theta_0)$$

$$U_{\theta\theta'} = -0.021914K_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta'_0)$$

$$U_{s\phi} = -5.9975K_{s\phi}(r - r_0)(1 + \cos 3\phi)$$

$$U_{vdW} = \epsilon[-2.25(r_v/r)^6 + 1.84(10^5) \exp\{-12.00(r/r_v)\}]$$

$$U_{\mu\mu'} = \frac{14.3928[\mu\mu'(\cos \chi - 3 \cos \alpha \cos \alpha')]}{R^3 D} \quad (1)$$

Parameters r , θ and ϕ in Eq. (1) are shown in Fig. 1(a). A subscript, 0, on a variable represents its value in the configuration of the minimum potential energy for no external loads applied to the SWCNT. As depicted in Fig. 1(b), variables μ and μ' are bond centered dipole moments, χ is the angle between two dipoles, α and α' are angles made by two dipoles with the line connecting their centers, and R is the distance between their centers. If an atom is bonded to three other atoms, the angle between one of those bonds and the plane defined by those three adjacent atoms is represented by γ . Variables θ and θ' appearing in $U_{\theta\theta'}$ are two bond angles centered at the same atom. Variables r and r' involved

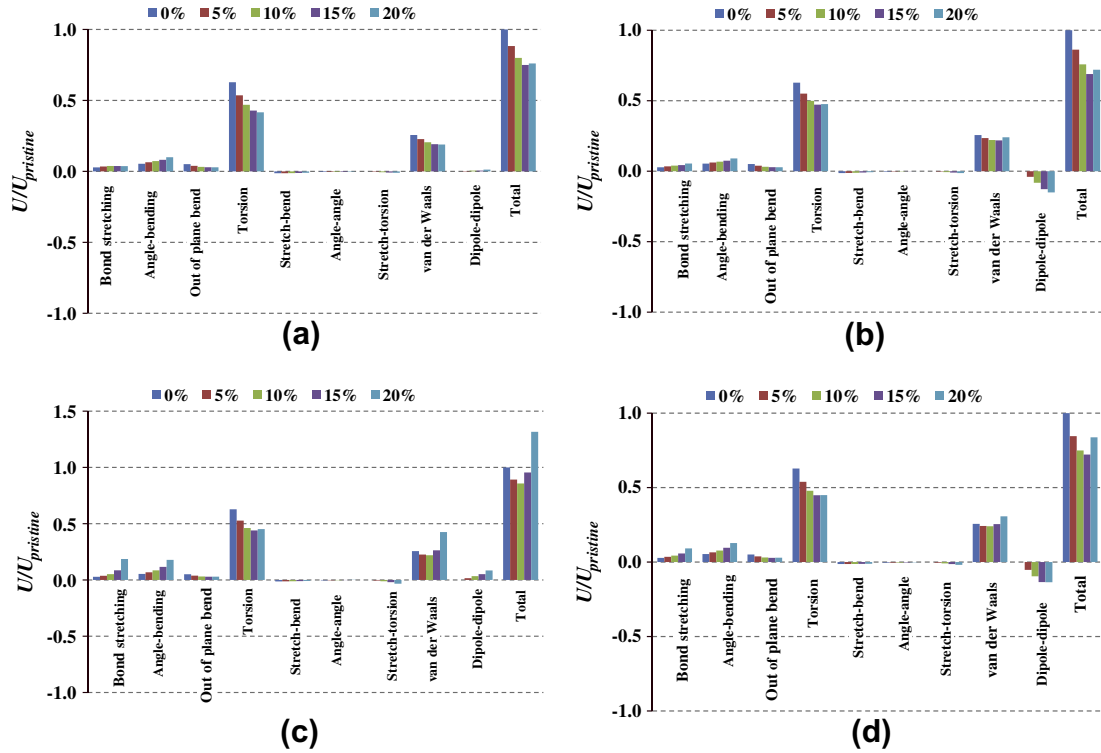


Fig. 7. Individual energy components for the relaxed configurations of the SWCNT with 0, 5, 10, 15 and 20% of randomly selected carbon atoms functionalized with (a) hydrogen, (b) hydroxyl, (c) carboxyl, and (d) amine.

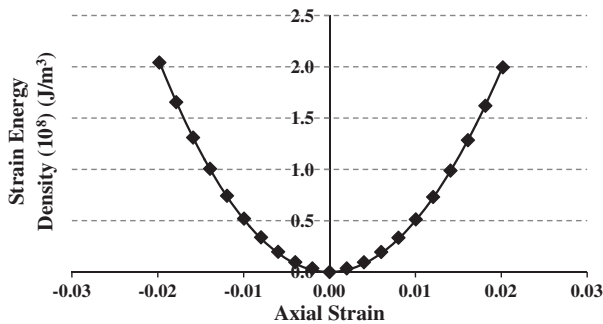


Fig. 8. Strain energy density of the pristine SWCNT vs. the axial strain computed using the MM3 potential.

in U_{s0} are the lengths of two bonds which make angle θ between them. ε and r_v are material parameters representing an energy scale factor and van der Waals distance, respectively. Values of constants K_s , K_θ , K_γ , V_1 , V_2 , V_3 , ε , r_v , K_{s0} , $K_{s\phi}$, $K_{\theta\theta'}$, and D given by Ponder [39,40] are used in this work.

2.2. Modeling of functionalized SWCNTs

Functionalization of a zigzag (10, 0) finite length SWCNT of aspect ratio 12 is considered as a model problem. The molecular structure of a functionalized SWCNT can be obtained from topologies of the pristine SWCNT and the functional group. All simulations are done with a cut-off distance of 9.5 Å and at zero Kelvin. First, the potential energy of the SWCNT is minimized by using the steepest decent algorithm with the root mean square (rms) gradient of 0.001 to obtain its relaxed configuration. The diameter

and the length of the relaxed tube are found to be 0.75 nm and 8.78 nm, respectively. The functional group is then positioned adjacent to a carbon atom of the relaxed CNT and the potential energy of the structure is minimized to obtain the relaxed configuration of the functionalized SWCNT. Note that the introduction of covalent bonds at the functionalized sites alters the hybridization of the affected carbon atoms from sp^2 to sp^3 . The percentage of functionalization is defined as the ratio of the number of carbon atoms to which atoms of a functional group are attached to the total number of carbon atoms in the CNT. Four functional groups, namely hydrogen, hydroxyl, carboxyl, and amine, have been studied. The carbon atoms to which a functional group is attached are randomly selected but the same atoms are used for different functional groups for maintaining consistency in numerical experiments. A few rings of carbon atoms near the two ends of the CNT are not functionalized to maintain their circularity for applying boundary conditions. Fig. 2 depicts schematics of the functional groups attached to a carbon atom of the SWCNT. The atoms in white, red, and blue color represent hydrogen, oxygen, and nitrogen atoms, respectively.

It should be clear from sketches displayed in Fig. 2 that the covalent bond between the carbon atom and a functional group pulls out the carbon atom radially resulting in the distortion of the CNT at the functional site. Because of this local deformations, lengths of the SWCNT between the two black vertical lines (shown in Fig. 3) may be different for the same carbon atoms functionalized with different groups. The SWCNTs functionalized with these groups are schematically depicted in Fig. 3.

2.3. Virtual tension/compression and torsion tests

Carbon atoms at ends of the pristine and the functionalized SWCNTs are not saturated which may lead to end effects during the virtual experiments. To mitigate these, boundary conditions

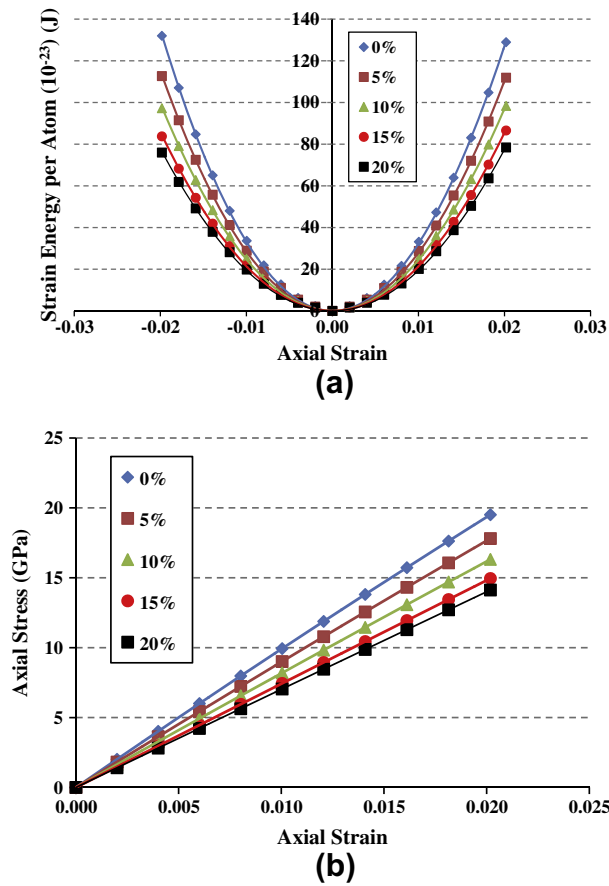


Fig. 9. (a) Variation of the strain energy per atom with axial strain, and (b) tensile axial stress-axial strain curves of -H functionalized SWCNT with the percentage of functionalization varied from 5% to 20%.

are applied on carbon atoms whose distance from an end face equals about one diameter of the SWCNT. In numerical tension/compression test of a SWCNT, carbon atoms on a ring near one end of the CNT are fixed and axial tensile/compressive displacement increments are applied to carbon atoms on the corresponding ring near the other end. After the application of each displacement increment, the potential energy of the tube is minimized and the strain energy of the deformed tube is computed by subtracting from it the potential energy of the unstrained tube. The strain energy density is computed by dividing the strain energy by the volume of the SWCNT which is taken equal to that of a continuum cylinder of length and diameter equal to those of the relaxed SWCNT and thickness equal to 0.34 nm which is the distance between adjacent layers of graphene sheets. The nanotubes are gradually deformed in simple tension/compression to 2% axial strain. It can be observed from results depicted in Fig. 3 that the functionalization induces local deformations of the SWCNT at the functionalization sites and the functionalized CNTs are not circular prismatic tubes. While computing the volume of a functionalized CNT, the average diameter of first few rings of carbon atoms near the ends (which are not attached to a functional group) is used. A polynomial function is fitted by the least squares method through the (strain energy density, axial strain) data points. The first and the second derivatives of the strain energy density with respect to the axial strain yield the corresponding average axial stress and the average Young's modulus, respectively. This procedure is the same as that used by Sears and Batra [7] to find Young's modulus of a pristine SWCNT. Also, when a CNT is deformed in tension/compression, the circumferential strain is developed in the CNT due to Poisson's effect in the graphitic plane. For

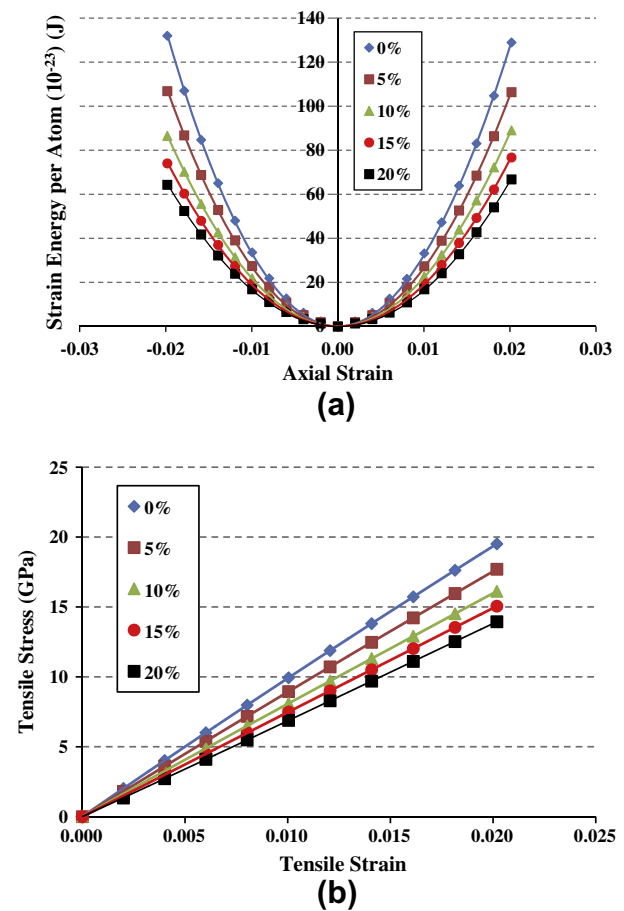


Fig. 10. (a) Variation of the strain energy per atom with axial strain, and (b) tensile axial stress-axial strain curves of -OH functionalized SWCNT with the percentage of functionalization varied from 5% to 20%.

infinitesimal deformations, the negative of the ratio of the circumferential strain to the axial strain equals Poisson's ratio. Similarly, virtual torsional tests are conducted by applying rotational rather than axial displacements to a ring of carbon atoms near one end. The first and the second derivatives of the strain energy density with respect to the shear strain correspond to the average shear stress and the average shear modulus of the SWCNT, respectively.

We note that the afore-stated approach gives average values of the elastic moduli and neglects local variations in the non-cylindrical shape of the functionalized SWCNT. However, it provides useful information for developing micromechanical models of CNT-reinforced polymeric composites. Except for functionalization with the -H group, all atoms of a SWCNT cannot be functionalized because of the size of the group. The alternative approach of assigning different thicknesses and elastic moduli to functionalized and un-functionalized carbon atoms gives an inhomogeneous continuum structure whose deformations can only be analyzed by using the 3-dimensional elasticity theory. We believe that such an approach is not warranted for designing SWCNT-reinforced polymeric composites.

3. Numerical results

3.1. Validation of functionalization

In the relaxed configuration of the functionalized SWCNTs, the equilibrium bond length between carbon atoms of the CNT and the adjoining atoms of the functional group, if present, is computed. The C-H bond length in the hydrogen functionalized CNT

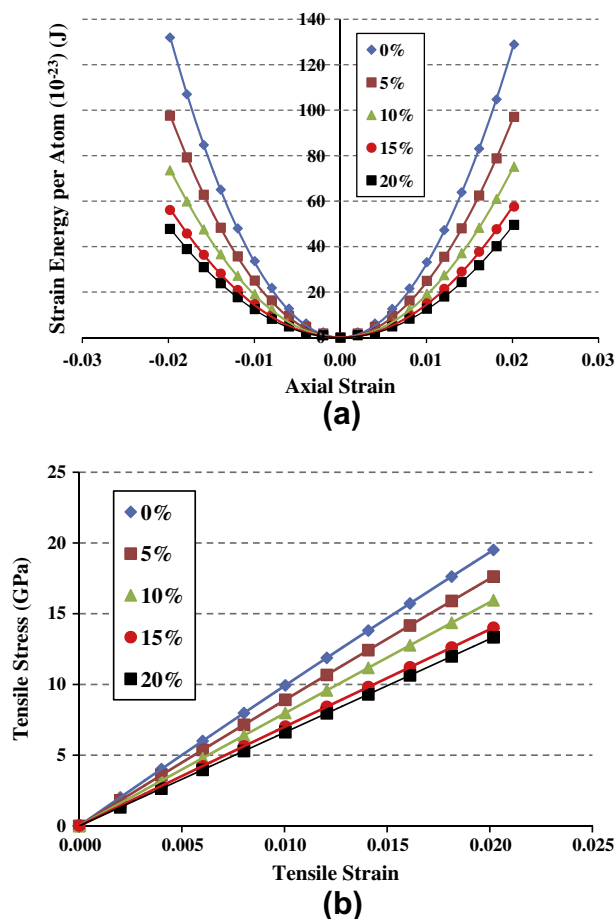


Fig. 11. (a) Variation of the strain energy per atom with axial strain, and (b) tensile axial stress-axial strain curves of $-COOH$ functionalized SWCNT with the percentage of functionalization varied from 5% to 20%.

is found to be 0.111 nm, which agrees well with that (0.111 nm) in the modified orthogonal tight binding model [41] and the 0.112 nm given by the DFT calculations [42]. Methanol (CH_3OH), acetic acid (CH_3COOH), and amino methane (CH_3NH_2) are simple structures representing covalent bonds between a sp^3 hybridized carbon and hydroxyl, carboxyl, and amine functional group, respectively. These structures are generated by employing the simplified molecular-input line-entry system (SMILES) [43,44] which is used to describe the structure of a chemical molecule shown in Fig. 4.

In order to validate the functionalization of the SWCNTs with hydroxyl, carboxyl, and amine groups, the bond angles and the bond lengths of the functionalized CNTs in the relaxed configuration of the functionalized CNTs have been measured and compared in Tables 1–3 with those in methanol, acetic acid and amino methane. It is evident that there is good agreement between the two sets of values.

3.2. Analysis of relaxed configurations

The potential energy of the system versus the number of iterations required in the steepest descent method to minimize the potential energies of $-H$, $-OH$, $-COOH$ and $-NH_2$ functionalized SWCNTs is plotted in Fig. 5(a)–(d), respectively. At the end of the minimization process, the relaxed configurations of the CNTs are obtained. For each functional group, 200 iterations suffice to minimize the potential energy of a functionalized SWCNT.

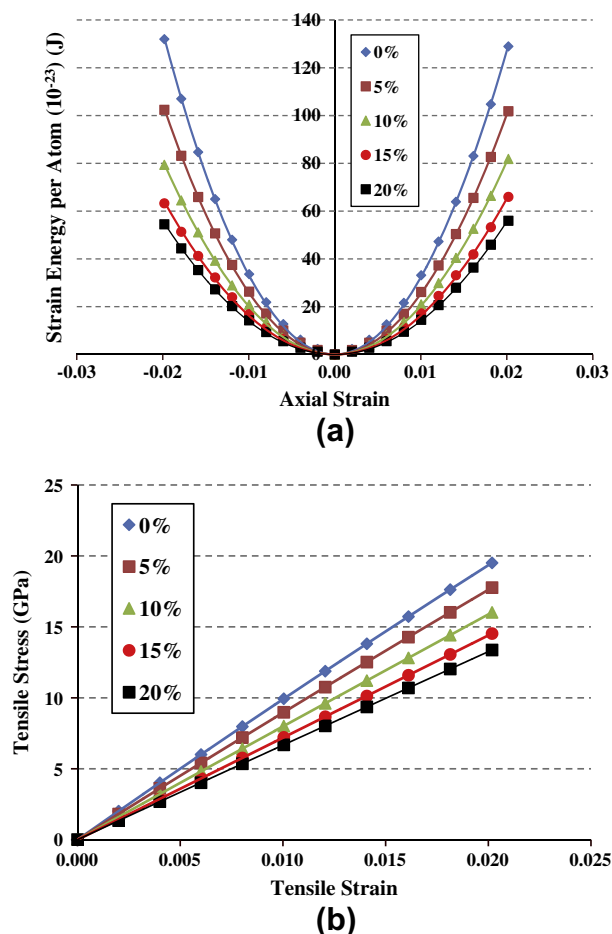


Fig. 12. (a) Variation of the strain energy per atom with axial strain, and (b) tensile axial stress-axial strain curves of $-NH_2$ functionalized SWCNT with the percentage of functionalization varied from 5% to 20%.

Table 4

Young's modulus of the SWCNT functionalized with different groups.

% functionalization	Young's modulus (TPa)			
	Hydrogen	Hydroxyl	Carboxyl	Amine
0	1.01	1.01	1.01	1.01
5	0.91	0.91	0.90	0.91
10	0.82	0.81	0.80	0.80
15	0.74	0.75	0.70	0.72
20	0.70	0.69	0.66	0.67

In Fig. 6 we have displayed potential energies of the functionalized CNTs in their relaxed configuration and in Fig. 7(a)–(d) the contribution from each term of the MM3 potential to the total potential energies of $-H$, $-OH$, $-COOH$ and $-NH_2$ functionalized CNTs, respectively. Note that potential energies plotted in Fig. 7 are normalized with respect to the potential energy of the relaxed pristine CNT.

Results presented in Fig. 6 indicate that the potential energy of the functionalized tube in the relaxed configuration is less than that of the pristine CNT and the difference in the potential energies of pristine and functionalized SWCNT increases with an increase in the percentage of functionalized carbon atoms. Possible reasons for this include (i) the functionalization breaks the π -bond of the sp^2 hybridized carbon atoms and changes the atom type from alkene to the more stable alkane, and (ii) the functionalization reduces

Table 5
Summary of theoretical predictions of the reduction in Young's modulus of SWCNTs with covalent functionalization.

Analysis method	Potential/force field	CNT	Functional group	Percentage of functionalization	Percentage reduction in Young's modulus	References
MM	MM3	(10, 0)	–H	5	10	Present study
				10	18	
			–OH	5	10	
				10	20	
			–COOH	5	11	
				10	21	
			–NH ₂	5	10	
				10	21	
			–H	10	6	
				20	12	
AFEM	2nd Generation interatomic	(9, 0)	–H	10	6	[19]
MM	COMPASS	(10, 0)	–C ₂ H ₃	8	16	[20]
				21	31	
MD	COMPASS	(10, 10)	–H	5	11	[22]
			–OH	5	16	
			–COOH	5	15	
			–NH ₂	5	14	
DFT	–	(10, 0)	–OH	6	9	[23]
				10	12	
			–COOH	6	9	
				10	14	
			–NH ₂	6	9	
				10	12	

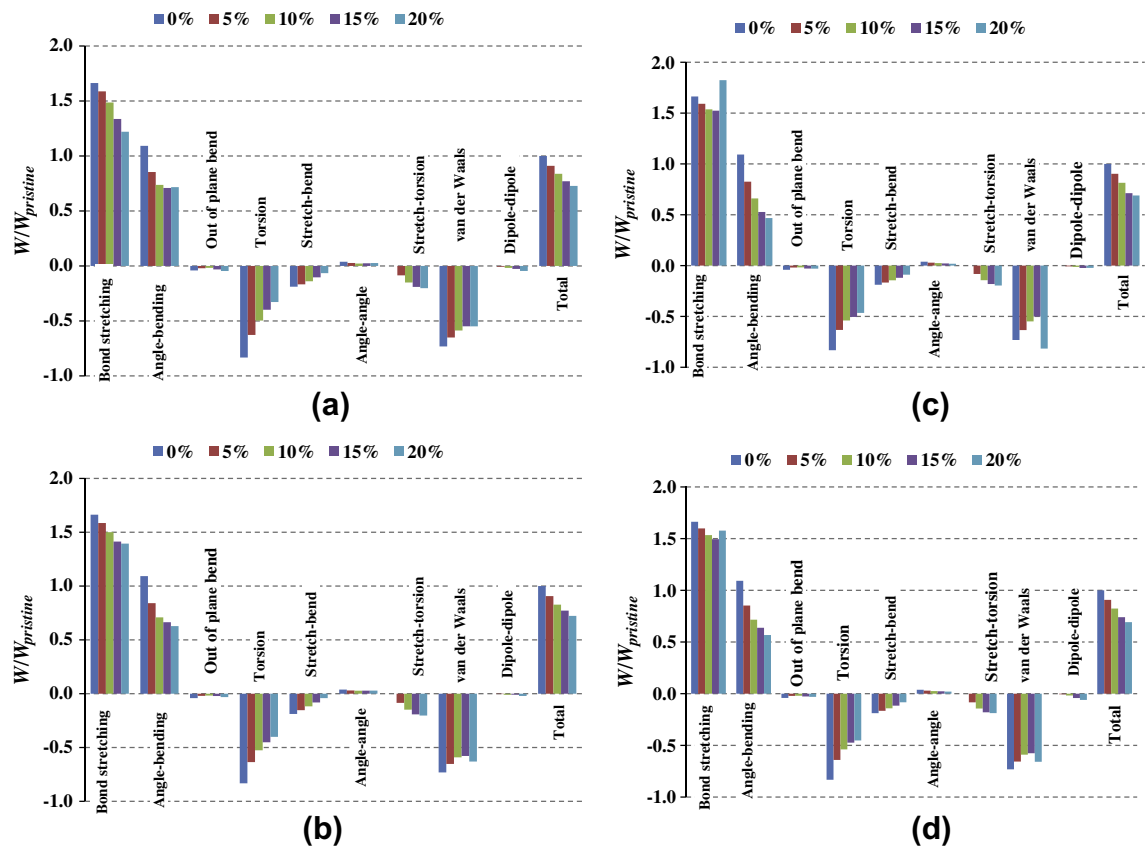


Fig. 13. Break down of the total strain energy of deformation (at 2% axial strain) into individual energy components for (a) hydrogen, (b) hydroxyl, (c) carboxyl, and (d) amine functionalized CNTs with percentage of functionalization varying from 0% to 20%.

energies associated with torsional and van der Waals components which together contribute to about 90% of the total potential energy as depicted in Fig. 7. However, with the increase in the percentage of functionalized carbon atoms, the increase in the

potential energy due to van der Waals interaction makes the potential energy curves in Fig. 6 non-monotonic. Only for the hydroxyl and the amine groups, the dipole–dipole interactions contribute noticeably to the potential energy of the system.

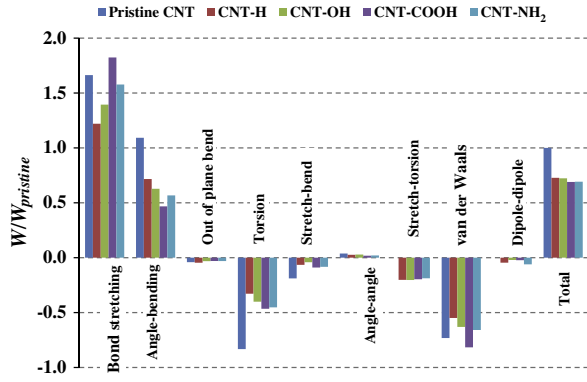


Fig. 14. Break down of the total strain energy of tensile deformation into individual energy components for the CNTs functionalized (20%) with different functional groups.

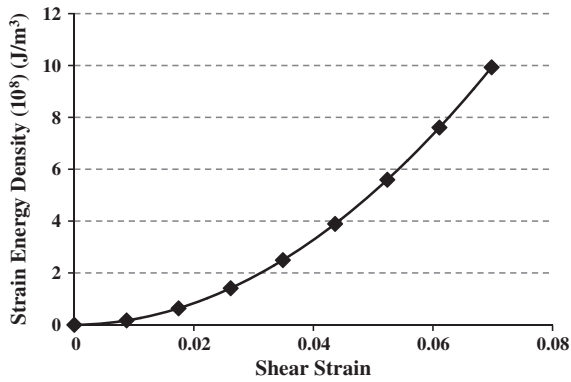


Fig. 15. Strain energy density of the pristine SWCNT vs. the shear strain computed using the MM3 potential.

Table 6
Shear modulus of the SWCNT functionalized with different groups.

% functionalization	Shear modulus (TPa)			
	Hydrogen	Hydroxyl	Carboxyl	Amine
0	0.40	0.40	0.40	0.40
5	0.36	0.36	0.35	0.36
10	0.33	0.33	0.31	0.32
15	0.31	0.29	0.30	0.31
20	0.30	0.27	0.23	0.30

3.3. Results of virtual experiments

In the calculation of Young's modulus and the shear modulus, as stated above, the thickness of both pristine and functionalized SWCNT is assumed to be 0.34 nm.

3.3.1. Young's modulus

The variation of the computed strain energy density with the axial strain for the pristine SWCNT is shown in Fig. 8, and the third order polynomial fit to the data with the regression coefficient of 1.0 is

$$W_v = -7.46(10^{11})\epsilon^3 + 5.03(10^{11})\epsilon^2 + 5.62(10^5)\epsilon \quad (2)$$

where W_v is the strain energy density in J/m³ and ϵ is the nominal axial strain. Thus, expressions for the axial stress σ and the modulus of elasticity E in Pa are

$$\sigma = -2.24(10^{12})\epsilon^2 + 1.01(10^{12})\epsilon + 5.62(10^5) \quad (3)$$

$$E = -4.48(10^{12}) + 1.01(10^{12}) \quad (4)$$

The modulus of elasticity at zero axial strain equals 1.01 TPa. It compares well with that reported in the literature [1–3]. Eq. (4) suggests that E for an axially stretched SWCNT decreases with an increase in the axial strain, and E for axially compressed SWCNT is higher than that of the axially stretched SWCNT. For the hydrogen functionalized CNT, the strain energy per atom versus the axial strain variation and the axial stress-axial strain curves for different percentages of functionalization are shown in Fig. 9(a) and (b), respectively. These plots reveal that the strain energy of deformation of the functionalized SWCNT is less than that of the pristine SWCNT, and this difference increases with an increase in the number of functionalized carbon atoms. The slope (hence the modulus of elasticity) of the axial stress-axial strain curve for the functionalized tube is less than that of the pristine tube. Moreover the modulus of elasticity decreases with an increase in the percentage of functionalization. This reduction in the modulus of elasticity could be due to the non-uniformities in the nanotube structure introduced by the functionalization that lead to localized deformation at the functionalized sites. Similar results for hydroxyl, carboxyl, and amine groups are exhibited in Figs. 10–12, respectively. For axial compression up to 2% axial strain, we did not see any sign of local buckling due to non-uniformities in the structure of the functionalized SWCNT.

Values of Young's modulus of the functionalized SWCNTs for different percentages of functionalization listed in Table 4 suggest that they do not depend much upon the functionalizing agent.

In Table 5, we have summarized similar results reported in the literature obtained using various computational methods and force fields along with those from the present study. It is clear that the present results agree with those of other researchers.

In order to better understand the effect of functionalization on Young's modulus, strain energies of deformation in the tension tests of the pristine and the functionalized CNTs have been obtained in terms of their bonded and non-bonded energy components. In Fig. 13(a)–(d) we have exhibited the contribution of different energy terms to the total strain energy of deformation at 2% axial strain for hydrogen, hydroxyl, carboxyl, and amine functionalization, respectively. These values have been normalized with respect to the strain energy of the pristine CNT. These results indicate that the functionalization mainly affects every component of the strain energy, and the change in the strain energy of the functionalized SWCNT from that of the pristine SWCNT varies with the number of functionalized carbon atoms.

Various components of the strain energy of the functionalized CNTs as a function of the functionalizing material for 20% functionalization are plotted in Fig. 14. Although the strain energy components have been found to be functions of the functionalizing material, the total strain energy of deformation is nearly independent of the functionalizing agent as evident from results plotted in the figure.

3.3.2. Shear modulus

The strain energy density of the pristine SWCNT vs. the shear strain applied in the torsion test is plotted in Fig. 15. A third order polynomial fitted through these data with the regression coefficient of 1.0 is

$$W_v = 2.66(10^{10})\gamma^3 + 2.00(10^{11})\gamma^2 + 1.57(10^8)\gamma \quad (5)$$

where γ is the shear strain. Thus, expressions for the shear stress τ and the shear modulus G in Pa are

$$\tau = 7.98(10^{10})\gamma^2 + 4.00(10^{11})\gamma + 1.57(10^8) \quad (6)$$

$$G = 1.60(10^{11})\gamma + 4.00(10^{11}) \quad (7)$$

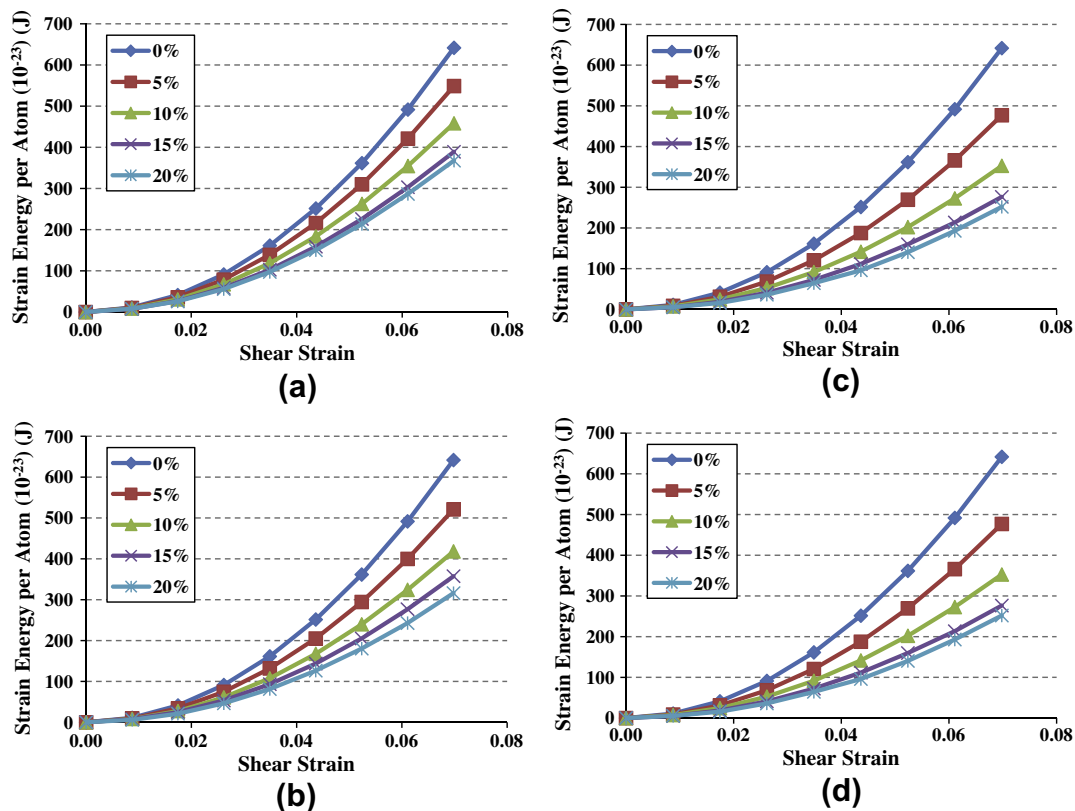


Fig. 16. Variation of the strain energy per atom with the shear strain for (a) hydrogen, (b) hydroxyl, (c) carboxyl, and (d) amine functionalized CNTs with percentage of functionalization varying from 0% to 20%.

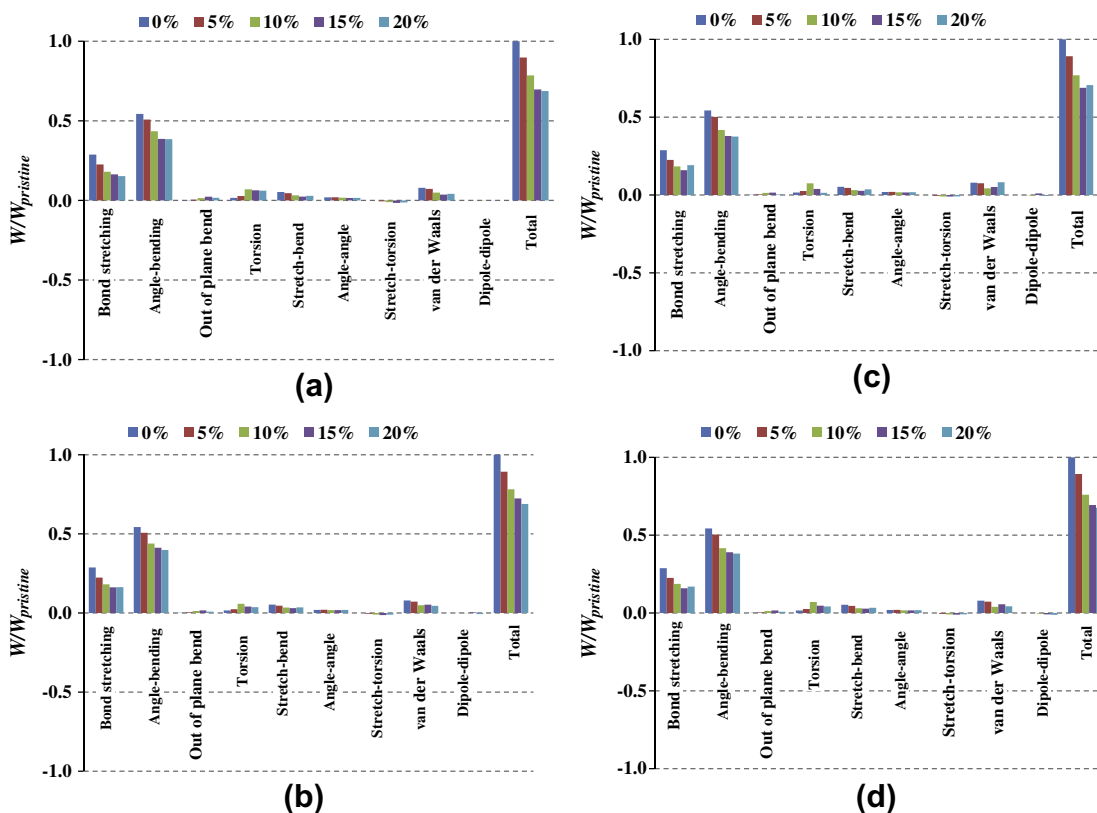


Fig. 17. Break down of the total strain energy of deformation (at 7% shear strain) into individual energy components for (a) hydrogen, (b) hydroxyl, (c) carboxyl, and (d) amine functionalized CNTs with percentage of functionalization varying from 0 to 20%.

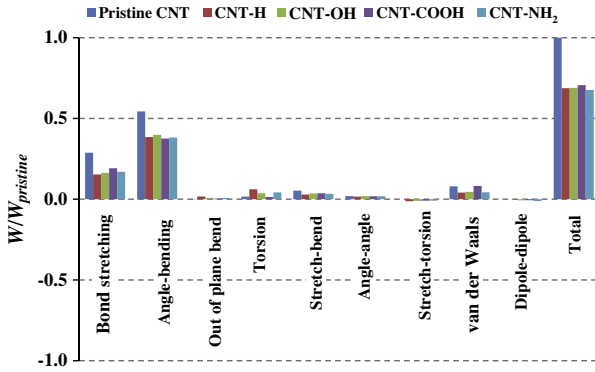


Fig. 18. Break down of the total strain energy of shear deformation into individual energy components for the SWCNT functionalized (20%) with different functional groups.

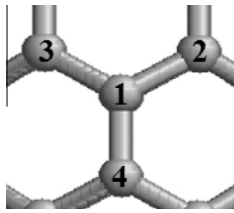


Fig. 19. A portion of the pristine SWCNT.

Table 7

Average values of E and G for five randomly selected groups of carbon atoms for 20% –H functionalized SWCNTs.

Sample	E (TPa)	G (TPa)
1	0.70	0.30
2	0.68	0.28
3	0.69	0.29
4	0.69	0.29
5	0.68	0.28
Standard deviation	0.01	0.01

Table 8

Values of various parameters for the pristine SWCNT and the SWCNT functionalized with –H group.

		Pristine CNT			When –H is attached to atom 1		
		Un-strained	Tensile (2%)	Compressive (2%)	Un-strained	Tensile (2%)	Compressive (2%)
Bond lengths	1-2 Length (nm)	0.135	0.135	0.134	0.151	0.152	0.150
	1-3 Length (nm)	0.135	0.135	0.134	0.15	0.151	0.151
	2-3 Length (nm)	0.135	0.137	0.132	0.152	0.153	0.150
Bond angles	4-1-3 Angle (degrees)	120.32	121.15	119.51	112.55	113.94	110.94
	4-1-2 Angle (degrees)	120.32	121.15	119.51	116.6	118.49	115.06
	3-1-2 Angle (degrees)	117.02	115.43	118.59	110.05	108.34	111.35
Dihedral angles	Angle between 4-1-3 and 2-1-3	–162.56	–162.96	–162.13	–132.07	–134.35	–129.69
	Angle between 4-1-2 and 3-1-2	162.57	162.96	162.13	129.81	131.95	127.50
	Angle between 3-1-4 and 2-1-4	161.97	162.03	161.98	128.63	129.47	127.62

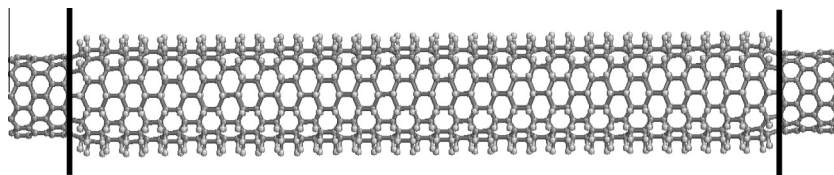


Fig. 20. Schematics of a fully –H functionalized SWCNT (Black vertical lines denote rings of carbon atoms where the boundary conditions are specified).

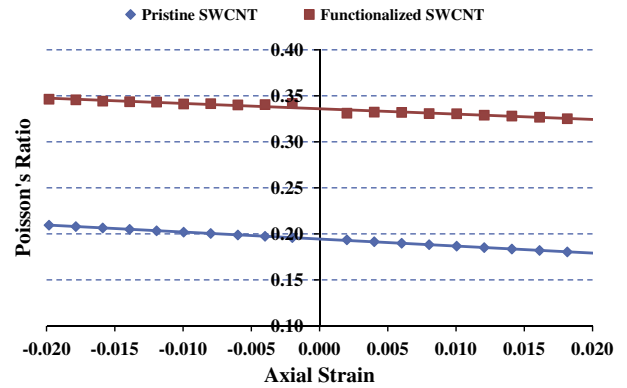


Fig. 21. Poisson's ratio vs axial strain curves for the pristine SWCNT and fully –H functionalized SWCNT.

The shear modulus at zero shear strain equals 0.4 TPa. The mean value of the shear modulus of the functionalized CNT is calculated by assuming that the average cross-sectional area is circular and is unchanged during functionalization. These values are listed in Table 6.

As discussed in Section 2.3, the computed shear moduli of the functionalized CNTs are the average values since the functionalized tubes do not have the same cross section throughout the length. Values listed in Table 6 reveal that the shear modulus of the functionalized CNT is less than that of the pristine CNT and the reduction is essentially the same for each functional group. We have plotted in Fig. 16(a)–(d) the strain energy per atom vs. the shear strain curves for –H, –OH, –COOH, and –NH₂ functionalized SWCNTs, respectively.

It can be observed from results exhibited in Fig. 16 that the strain energy of deformation of the functionalized SWCNT is less than that of the pristine SWCNT. The contribution from each term to the total strain energy (at 7% shear strain) for –H, –OH, –COOH, and –NH₂ functionalized SWCNTs, is presented in Fig. 17(a)–(d). Note that the energies depicted in the figure are normalized with respect to the strain energy of shear deformation of the pristine CNT. These results suggest that every component of the strain en-

ergy is affected by the functionalization and the difference in the strain energies of the pristine and the functionalized SWCNT increases with an increase in the number of functionalized carbon atoms.

The strain energy of shear deformation as a function of the functionalizing material is plotted in Fig. 18 for 20% functionalized SWCNTs. It is clear from these results that the strain energy does not depend on the type of the functionalizing material.

For the SWCNT functionalized with the –H group, we have summarized in Table 8 values of various parameters for the pristine and the functionalized tube. A typical portion of the SWCNT is depicted in Fig. 19. It is clear from the values listed in the table that functionalization significantly alters the bond angles but does not change the dihedral angles and the bond length. For 2% axial straining of the SWCNT, the change in bond angles and bond lengths for the pristine and the functionalized SWCNT is nearly the same. We note that the dihedral angle between atoms a–c–d and b–c–d is the angle between the planes defined by atoms {a, c, d} and {b, c, d}.

3.3.3. Results for five different randomly selected groups of carbon atoms

As stated before the functionalized carbon atoms are randomly selected. For the –H group, we conducted numerical experiments in tension and torsion for five sets of 20% randomly selected carbon atoms to which functional groups were attached. The average values of Young's modulus and the shear modulus listed in Table 7 differed from each other by less than 1% implying that the selection of carbon atoms for functionalization has virtually no effect on the mean value of the elastic moduli of functionalized SWCNT.

3.3.4. Poisson's ratio of SWCNT fully functionalized with –H

Since the cross-section of a functionalized SWCNT varies from point to point, as should be clear from the tubes plotted in Fig. 3, it is not possible to determine Poisson's ratio from results of the virtual tension test. However, if all atoms of a SWCNT are functionalized then the cross-section will be uniform as shown in Fig. 20 and one can compute Poisson's ratio.

Here, carbon atoms between rings of the SWCNT on which boundary conditions are specified have only been functionalized. Note that this method cannot be applied to find Poisson's ratio of a SWCNT functionalized fully by a carboxyl or amine group since the distance between two farthest atoms in these groups is more than the C–C bond length of a SWCNT which makes the functional groups attached to adjacent carbon atoms of the CNT intersect. Poisson's ratios of the pristine SWCNT and the fully functionalized SWCNT as a function of the axial strain are plotted in Fig. 21.

These plots suggest that for a given value of the axial strain, Poisson's ratio of the functionalized SWCNT is more than that of the pristine SWCNT, and its values at zero strain are 0.19 and 0.34 for the pristine and the functionalized SWCNT, respectively.

Values of Young's modulus of the SWCNT functionalized with –H listed in Table 4 suggest that Young's modulus decreases with an increase in the amount of functionalization. However, the rate of reduction with respect to the amount of functionalization is not constant but decreases with an increase in the amount of functionalization. For the SWCNT fully functionalized with –H group, average values of Young's modulus and the shear modulus were found to be 0.39 and 0.18 TPa, respectively. For an isotropic linear elastic material, these values of E and G give Poisson's ratio equal to $1/12$ which noticeably differs from the 0.34 obtained from results of the MM simulations. The same calculation for the pristine SWCNT gives Poisson's ratio = 0.25 which is close to the 0.19 found via MM simulations. It suggests that values of E and G for the functionalized SWCNT do not satisfy the relation, Poisson's ratio = $(E/(2G) - 1.0)$ that is valid for isotropic linear elastic materials.

We note that not all deformations obtained through MM simulations can be correlated with those from studying deformations of linear elastic, isotropic and homogeneous bodies of the same shape as the SWCNT. For example, the saturation of frequencies of inextensional modes of vibration of zigzag SWCNTs found with the MM simulations is not predicted by the linear elasticity theory, e.g., see [47].

Even though results have been computed for one SWCNT, it can be concluded from results summarized in Table 5 that elastic moduli of other SWCNTs will also decrease with an increase in the amount of functionalization.

3.3.5. Remark

The presently computed reduction in elastic moduli of a SWCNT due to functionalization provides a partial explanation of the discrepancy between theoretically predicted and experimentally determined values of elastic moduli of SWCNT-reinforced polymeric composites. Other reasons include SWCNTs not uniformly distributed and properly aligned in the composite.

Some results presented herein will appear in the book chapter [46]. Other chapters in the book discuss different aspects of nanomaterials and nanostructures.

4. Conclusions

The effect of covalent functionalization on average values of Young's modulus, shear modulus and Poisson's ratio in the graphic plane of a SWCNT has been studied. Most likely due to localization of deformation at the functionalized sites, values of Young's and the shear moduli decrease with functionalization and the reduction is nearly proportional to the percentage of functionalization. For the four functional groups studied, the reduction in the moduli is essentially the same and increases with an increase in the percentage of atoms to which functional groups are attached. Approximately 34% and 43% reduction in the values of Young's modulus and the shear modulus of the pristine SWCNT occurs for 20% of functionalization. However, the rate of decrease in the values of these moduli slows down with an increase in the percentage of functionalized carbon atoms. For example, for the SWCNT with all atoms functionalized with hydrogen, the average values of Young's modulus and the shear modulus were found to be 0.39 and 0.18 TPa, respectively, and that for the pristine tube were 1.01 and 0.40 TPa, respectively. Poisson's ratios of a pristine SWCNT and the SWCNT fully functionalized with –H group have been found to be 0.19 and 0.34, respectively.

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