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Characterizing interphase region in CNT/nylon-6 composites using molecular dynamics simulation

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Abstract. The load transfer mechanisms and effective mechanical properties of carbon nanotube (CNT)-reinforced polymer nanocomposites are strongly influenced by the interfacial region (interphase) between the embedded CNT and the polymer. In this article, elastic properties of an effective interphase present in nanocomposites are evaluated from molecular dynamics (MD) simulation studies of individual CNT, the polymer and the CNT/polymer nanocomposite. Different configurations of single-walled CNT are embedded in a nylon-6 matrix at different volume fractions of the CNT and the mechanical properties of the nanocomposites are evaluated. Subsequently, the elastic modulus of the interphase is evaluated using an inverse three-phase rule of mixtures, in which the volume fraction of the interfacial region is calculated based on the equilibrium van der Waals distance between the CNT and the polymer matrix. Based on the MD simulation results, a semi-empirical model has been developed to predict the effective interphase modulus for its applicability in continuum modelling of nanocomposites.

Keywords. Carbon nanotube; nylon-6; nanocomposite; interphase; molecular dynamics; semi-empirical model.

1. Introduction

Nanostructured composites have garnered major research interest for structural applications in recent years because of their unprecedented mechanical properties. Carbon nanotubes (CNTs) are perhaps the most widely used nanofillers, possessing high elastic modulus, multifunctionality, physical characteristics and other mechanical properties [1]. In general, different theoretical and experimental studies have indicated that insertion of CNTs into the polymers has effectively improved the elastic properties of nanocomposites [2–4]. However, theoretical predictions have some discrepancies with experimental results, which can be attributed to several reasons. One important reason is insufficient knowledge of interfacial characteristics between the CNT and the polymer, which affect the mechanical performance of CNT-reinforced composites (CNTRCs). The interface is defined as the surface boundary between the CNT and the matrix and is equal to the equilibrium van der Waals (VDW) distance between CNT and the cross-linked polymer structure. While the interphase (interfacial region) is defined as the region developed at the CNT/matrix interface and includes the interface plus a region of finite thickness on either both sides of the interface or on the matrix side of the interface. The mechanical properties of the interphase are distinct from those of CNT and the bulk polymer, and are difficult to estimate. Several researchers have paid attention to the effects of the interphase regions between CNTs and the polymer [5–11]. However, appropriate models concerning the interphase effects on the mechanical performance of nanocomposites are still lacking, and, not surprisingly, the published data on interphase effects are often contradictory.

Han and Elliott [12] observed that molecular dynamics (MD) predictions of effective properties of CNTRCs were considerably higher than those calculated using the general macroscopic rule of mixtures and concluded that interfacial effects cannot be ignored while predicting the effective properties of CNTRCs having strong interfacial interactions. Strong interfacial interaction in CNTRC can be attributed to various reasons, one of them being more crystallinity of the polymer on the CNT surface. MD simulations by Chowdhury and Okabe [8] have also demonstrated an effective stress transfer from the polymer to the nanotubes in polymer matrix composites, indicating the presence of a stiff interphase whose modulus is greater than that of the polymer matrix. On the other hand, studies by Gohil and Shaikh [13] have shown that interfacial stiffness does not have a significant effect on the stiffening of the fibre-reinforced composite in the longitudinal direction. Bhuiyan *et al* [14] have reported the presence of a soft interphase, which has a modulus lower than that of the polymer matrix and can be attributed to inefficient load transfer from the polymer to the nano-reinforcements.

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Arash *et al* [15] estimated the elastic properties of interphase by observing the fracture behaviour of CNT/PMMA composites using MD simulation. The study revealed that interfacial bonding relies on the aspect ratio of CNTs, and by increasing the aspect ratio, the properties of the interface are significantly improved. However, for both short and long CNTs, the Young's modulus of the interphase region was lower than that of the PMMA matrix. Banerjee *et al* [16] studied the role of the interphase on mechanical properties of single-walled CNT (SWCNT)-reinforced composites using the finite element method (FEM). They reported that the matrix/CNT interphase can be characterized in terms of a weak boundary layer (WBL) and that the low value of fracture stress at the WBL is the main reason for the low real-time values of elastic moduli of CNT-reinforced composites. Malekimoghadam and Icardi [17] examined a multi-scale hybrid model comprising CNTs, carbon fibre, interphase and matrix. They found that the addition of a small amount (about 2 wt%) of CNTs into the matrix reduced the interfacial radial stress, which is responsible for debonding. It was also reported that the non-bonded interphase merely affected the interfacial properties of hybrid composites, but no impact was observed on Young's modulus.

Studies using continuum mechanics have obtained some observations in the context of the interface in CNT-reinforced composites. In order to bridge the gap between the analytical model and atomic level analysis, Guru *et al* [18] parametrically studied the effect of the interphase using FEM and reported variation in the longitudinal elastic modulus of the composite at different thicknesses and stiffnesses of the interphase. Amraei *et al* [11] proposed a closed-form mathematical model to predict the transverse isotropic elastic properties of the interphase by assuming the interfacial elastic properties varying radially. It was shown that the thickness of the interphase plays a remarkable role in the overall mechanical properties of the nanocomposites. Moreover, the interphase thickness depends on the diameter of SWCNT and increases with increasing SWCNT diameter.

Although continuum approaches for nanocomposites such as the finite element method and micromechanical analysis are fast modelling techniques, these methods fall short in properly modelling interfacial interactions at the atomic level. Usually, in literature on continuum modelling based on three-phase representative volume element, the modulus of the interphase is arbitrarily chosen between the CNT modulus and the polymer modulus without any consistent reason. In some studies [12], a large discrepancy between MD predictions and micromechanical predictions of the effective properties can also be attributed to inconsistency in choosing values of SWCNT modulus and CNT volume fraction in the micromechanical equations. While the SWCNT modulus was taken based on the transverse cross-sectional area per tube in a hexagonal periodic SWCNT bundle, the CNT volume fraction was calculated by taking into account *in-situ* VDW separation distance between the CNT and the matrix, whose value is significantly less than the equilibrium separation distance between graphenes. In order to reduce ambiguity in terms of interphase parameters, this article tends to quantify the elastic modulus of an effective interphase directly from the MD simulation studies of SWCNT, polymer, and SWCNT/polymer nanocomposite. The nylon-6 polymer, which is the commercial name of thermoplastic polyamide 6 (PA6), is taken as the matrix. Different configurations of SWCNT are embedded in the nylon-6 matrix at different volume fractions of the CNT and the mechanical properties of the nanocomposites are evaluated. Subsequently, the elastic modulus of the interphase is evaluated for each case using an inverse three-phase rule of mixtures, in which the volume fraction of the interfacial region is calculated based on the equilibrium distance between the CNT and the polymer matrix due to the VDW interaction. Based on MD simulation results, a semi-empirical model has been developed to predict the effective interphase modulus, and the model results are compared with the MD predictions.

2. MD simulation

MD simulations of CNT/nyon-6 nanocomposites having different configurations and volume fractions of SWCNTs are carried out using the commercial package 'Materials Studio' and their mechanical properties are evaluated. Since the objective here is to estimate the modulus of an effective interphase, MD simulations are also used to calculate the mechanical properties of nyon-6 polymer and different configurations of SWCNTs. In this study, the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field is used, which is one of the most appropriate force fields for simulating polymers and polymer composites [19].

2.1 *MD simulation of CNT/nylon system*

A single-walled armchair nanotube (n,n) (n = 4, 6, or 10) was built and placed in the centre of a periodic cell simulation box whose cross-sectional area (A_{cell}) was calculated based on the CNT volume fraction (V_{NT}). V_{NT} is taken as the ratio of the cross-sectional area of a solid cylinder having a radius equal to the mean radius of the nanotube (R_{NT}) to the cross-sectional area of the simulation box. The length of the CNT (L_{NT}) is kept the same as that of the periodic simulation box (L_{cell}) such that the SWCNT is infinitely long and aligned. L_{cell} is taken to be sufficiently high. Next, a nylon-6 chain having 12 repeat units was constructed and the polymer was packed around the CNT by taking an initial density of 1 g cm^{-3}. The Compass force field was used to pack the polymer around the CNT. Figure 1 shows the amorphous packing of SWCNT in the

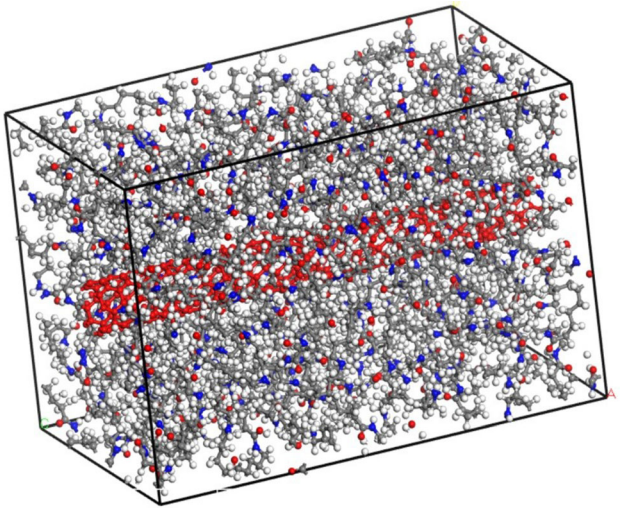

Figure 1. Packing of SWCNT and nylon-6.

nylon-6 matrix. In the next step, geometry optimization was done using an iterative process of smart algorithm to minimize the total energy of the SWCNT/polymer system. After the completion of the optimization process, the system is allowed to equilibrate using an isothermal-isochoric (NVT) ensemble at a room temperature of 298 K for 50 ps. Afterward, the structure was put into an isothermal-isobaric (NPT) ensemble at 298 K temperature and 1 atm pressure for 50 ps in order to obtain density convergence and an equilibrated simulation cell. A time step of 1 fs was used in the simulations. Figure 2 demonstrates the potential energy as well as the total energy histories during the process of the NPT ensemble for a particular case of the SWCNT(4,4)/nylon system at 2.4 vol% of SWCNT (V_{NT} = 0.024). It is seen that the potential energy attains a stable condition well before 50 ps and that the current molecular structure is in equilibrium and suitable for the characterization of the mechanical properties. Afterward, MD minimization was performed and the VDW separation distance (h_{vdw}) was calculated using the radial distribution function. The VDW separation distance was found to vary from 0.24 to 0.33 nm for different configurations and volume fractions of SWCNT. The radial distribution function for the case of the SWCNT (4,4)/nylon system at 2.4 vol% of SWCNT is plotted in figure 3.

In the next step, mechanical properties of the structure are computed by applying constant strain to the simulation cell with a strain amplitude of 0.003. The strain is applied by uniformly expanding the dimensions of the periodic cell in the direction of the deformation and re-scaling the new coordinates of the atoms to fit within the new dimensions. The structure is then re-minimized keeping the cell parameters fixed, and the resultant stress is measured.

3. Interphase characterization method

In the literature, the values of CNT Young's modulus obtained by different researchers are different for several reasons, including the effect of geometric structures of SWCNTS on their elastic moduli. Several studies [20] have shown that the values of Young's moduli of SWCNTs are weakly affected by the tube radius and tube chirality when the cross-sectional area, A_{NT} of SWCNTs is taken as $2\pi R_{NT} t_{NT}$; t_{NT} being the CNT wall thickness. In these studies, different wall thickness values have been used to calculate the Young's moduli, the most common being t_{NT} = 0.34 nm, which provided the values of Young's modulus ranging from 0.9 to 1.3 TPa. With a wall thickness value of t_{NT} = 0.0617 nm, the Young's modulus was obtained to be 4.88 TPa [21]. Since the polymer matrix does not penetrate the CNTs, in continuum mechanics-based studies the SWCNT tube is treated as a solid cylinder for the estimation

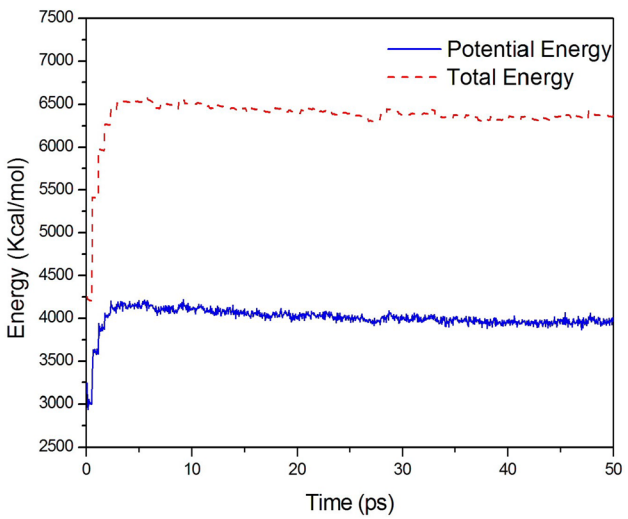

Figure 2. Variation of potential energy during NPT ensemble for the SWCNT(4,4)/nylon system at 2.4 vol% of SWCNT.

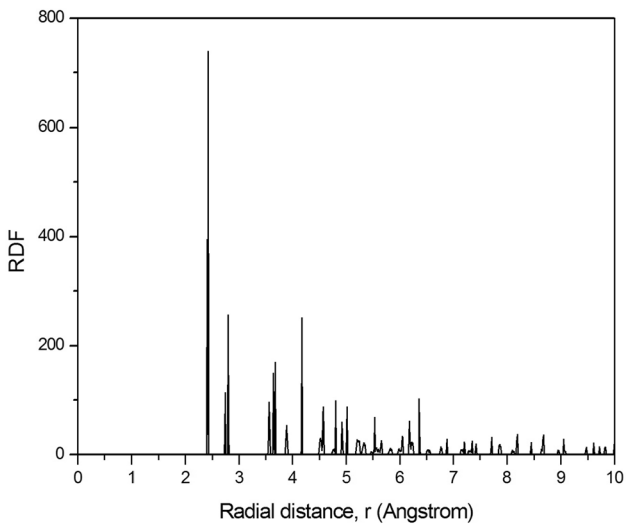

Figure 3. Radial distribution function (RDF) for the SWCNT(4,4)/nylon system at 2.4 vol% of SWCNT.

of CNT volume fraction and the equivalent Young's modulus is calculated.

In two-phase micromechanical models [12], CNT volume fraction is generally calculated by taking into account the equilibrium VDW separation distance between the CNT and the matrix using the formula

$$V_{\mathrm{NT}} = \frac{\pi\left(R_{\mathrm{NT}} + \frac{h_{\mathrm{vdw}}}{2}\right)^2}{A_{\mathrm{cell}}} \tag{1}$$

In equation (1), V_{NT} includes the entire CNT cross-section plus one-half of the VDW separation distance.

In the present three-phase micromechanical model consisting of CNT, matrix and the interphase, Young's moduli of SWCNTs (E_{NT}) are evaluated based on the cross-sectional area of a solid cylinder having a radius R_{NT}, the mean radius of the nanotube. The thickness of the interphase is taken to be either equal to the VDW separation distance or a multiple of this distance. Accordingly, the volume fractions of the three phases (SWCNT, interphase and matrix) are calculated by equation (2).

$$V_{\mathrm{NT}} = \frac{\pi R_{\mathrm{NT}}^2}{A_{\mathrm{cell}}},\ V_{\mathrm{i}} = \frac{\pi(R_{\mathrm{i}}^2 - R_{\mathrm{NT}}^2)}{A_{\mathrm{cell}}} \quad \text{and}$$
$$V_{\mathrm{m}} = 1 - V_{\mathrm{NT}} - V_{\mathrm{i}} \tag{2}$$

In equation (2), R_{i} is the outer radius of the interphase so that $R_{\mathrm{i}} = R_{\mathrm{NT}} + t_{\mathrm{i}}$, t_{i} being the thickness of the interphase.

The mass fraction of the CNT in the three-phase model can be calculated by equation (3)

$$w_{\mathrm{NT}} = \frac{V_{\mathrm{NT}}\rho_{\mathrm{NT}}}{V_{\mathrm{NT}}\rho_{\mathrm{NT}} + \mathrm{V_m}\rho_{\mathrm{m}}} \tag{3}$$

in which ρ_{NT} is the density of the SWCNT calculated based on the cross-sectional area of a solid cylinder having a radius R_{NT}, and ρ_{m} is the matrix density. Both ρ_{NT} and ρ_{m} for the equilibrated simulation cell are calculated during the MD simulation.

The elastic modulus of the effective interphase (E_{i}) can be estimated using an inverse three-phase rule of mixtures (ROM), which is given by equation (4).

$$E_{\mathrm{i}} = \frac{E_{\mathrm{c}} - V_{\mathrm{NT}}E_{\mathrm{NT}} - V_{\mathrm{m}}E_{\mathrm{m}}}{V_{\mathrm{i}}} \tag{4}$$

In equation (4), E_{NT}, E_{m} and E_{c} are calculated using MD simulations.

3.1 *Effective interphase model*

Based on the MD simulations of individual SWCNT, polymer and SWCNT/polymer nanocomposite, a semi-empirical interphase model in terms of non-bonded interaction energy present at the CNT/matrix interface has also been developed for predicting the effective interphase modulus of nanocomposites. The model may find use in continuum modelling based on a representative volume element consisting of three phases.

It is well known that the extent of interaction between the CNT and the surrounding matrix can be characterized in terms of the non-bonded interaction energy present at the CNT/matrix interface [22]. This non-bonded energy can, thus, provide an indication of the properties of an equivalent interface having a dimension equal to the non-bonded separation distance. The non-bonded interaction energy between the CNTs and the polymer, U_{i}, can be calculated by subtracting the potential energies of the CNT and the polymer from the potential energy of the nanocomposite using the formula

$$U_{\mathrm{i}} = U_{\mathrm{c}} - (U_{\mathrm{NT}} + U_{\mathrm{m}}) \tag{5}$$

in which U_{NT}, U_{m} and U_{c} are the potential energies of the CNT, matrix and nanocomposite, respectively. The potential energy of the nylon-6 is calculated from the simulation cell after the CNT is removed and only the polymer molecules are left. Similarly, the potential energy of the CNT is evaluated from the cell consisting of only the CNT.

U_{i} can be related to the non-bonded separation distance, t_{i} using a power law of the form

$$U_{\mathrm{i}} = kt_{\mathrm{i}}^{-n} \tag{6}$$

in which k is a constant and n is the exponent. The interaction force, F_{i}, can now be determined as the negative of the derivative of U_{i} with respect to the separation distance t_i, as shown in equation (7).

$$F_{\mathrm{i}} = -\frac{\partial U_{\mathrm{i}}}{\partial t_{\mathrm{i}}} = nkt_{\mathrm{i}}^{-(n+1)} \tag{7}$$

U_{i} can be interpreted as the energy of a tapered bar connecting the CNT with the polymer and having a length equal to L_{NT} and width equal to $2\pi R_{\mathrm{NT}}$ at one end and $2\pi R_{\mathrm{i}}$ at the other end. From elasticity theory, the strain energy of such a tapered bar is given as

$$U = \frac{F_{\mathrm{i}}^2}{4\pi E L_{\mathrm{NT}}} \ln\left(1 + \frac{t_{\mathrm{i}}}{R_{\mathrm{NT}}}\right) \tag{8}$$

in which E is the elastic modulus of the tapered bar that is subjected to an axial force F_{i}. Equating equations (6 and 8), and substituting from equation (7), the elastic modulus of the bar can be calculated as

$$E = \frac{n^2 U_{\mathrm{i}}}{4\pi L_{\mathrm{NT}} t_{\mathrm{i}}^2} \ln\left(1 + \frac{t_{\mathrm{i}}}{R_{\mathrm{NT}}}\right). \tag{9}$$

E in equation (9) provides an estimate of the elastic modulus of the equivalent interphase E_i.

4. Results and discussion

The mechanical properties of different configurations of SWCNT, nylon-6 matrix and SWCNT/nylon composites are predicted using MD simulation studies. This is followed by predicting the properties of the interphase using the inverse three-phase ROM and the developed semi-empirical model.

Prior to this, verification of the model using available literature results is in order.

4.1 *Validation of the model*

For the sake of model validation, a CNT/PMMA composite system is considered, whose predicted elastic properties are elaborated in literature [12]. The MD results for the Young's moduli and their micromechanical predictions reported by the authors [12] are listed in table 1. In this article, the CNT volume fraction was calculated using equation (1) and the SWCNT modulus was taken based on the transverse cross-sectional area per tube in a hexagonal periodic SWCNT bundle. A large discrepancy between MD results of effective properties and their micromechanical predictions may be attributed to the fact that the *in-situ* VDW separation distance between the CNT and the matrix used in the calculation of V_{NT} was significantly less than the equilibrium separation distance between graphenes used in the calculation of the SWCNT modulus. When both the SWCNT modulus and the CNT volume fraction are evaluated based on the cross-sectional area of a solid cylinder having a radius R_{NT} (mean radius of the nanotube) in the present study, the deviation of micromechanical model predictions from MD results is significantly reduced from about 24% to about 8% or less (table 1). The effective modulus of the interphase for CNT/PMMA composites can now be estimated using equation (3) at different CNT volume fractions. In this equation, the VDW separation distance for the calculation of interphase thickness is taken to be 0.18 nm in accordance with the earlier work [12]. The calculated interphase moduli of CNT/PMMA composites by considering different interphase thicknesses (0.18, 0.34 and 0.51 nm) are shown in table 2 at different volume fractions of (10,10) SWCNT. At the interphase thickness of 0.18 nm, the interphase moduli are predicted to be 61, 135, and 113 GPa at V_{NT} = 0.12, 0.17 and 0.28, respectively. It is observed that the interphase modulus decreases appreciably with increase in the thickness of the interphase.

4.2 *SWCNT/nylon-6 composites*

The MD prediction of the Young modulus of amorphous nylon-6 (E_m) was found to be 2.72 GPa, which is in the experimental range of 2.6–3.0 GPa. E_{NT} values for (4,4) SWCNT, (6,6) SWCNT and (10,10) SWCNT were calculated from MD simulations to be 2.8, 1.6 and 0.95 TPa, respectively. The Young's moduli of SWCNT/nylon-6 composites (E_c) calculated by MD simulation for different configurations and volume fractions of the SWCNT are shown in table 3. CNT reinforcement has significantly improved the elastic modulus of the neat nylon-6 polymer and, since the volume fraction of CNT includes the hole inside the CNT, for the same volume fraction, the reinforcing effect of CNT significantly increases with a decrease in the tube radius. The variation of the nanocomposite elastic modulus with the volume fraction of CNT is almost linear for all configurations of SWCNT, as plotted in figure 4. Table 3 also depicts the micromechanical predictions of the nanocomposite modulus using the two-phase ROM, whose deviations from MD results vary from about 0.3% to about 4% for different CNT configurations and volume fractions.

Figure 5 shows how the Young's modulus of the nanocomposite varies with the mass fraction of the SWCNT for different SWCNT configurations. Comparing the effect of tube chirality on the nanocomposite modulus at a constant mass fraction of the CNT to that effect at a constant volume fraction of the CNT, the former is found to be significantly less.

4.3 *Prediction of interphase modulus*

The interphase modulus is now calculated for different combinations of the SWCNT/nylon-6 system in which the interphase thickness, t_i is varied from a value of h_{vdw} to

Table 2. Prediction of interphase modulus (in GPa) of CNT/PMMA composite at different volume fractions of long (10,10) SWCNT.

	Interphase thickness		
CNT volume fraction (V_{NT})	0.18 nm	0.34 nm	0.51 nm
0.12	61.2	30.6	19.5
0.17	135.5	66.3	41.1
0.28	113	55.5	34.6

Table 1. Numerical results of Young's modulus (in GPa) of CNT/PMMA composite at different volume fractions of long (10,10) SWCNT.

		Two-phase ROM [12]		Two-phase ROM (this work)		
CNT volume fraction (V_{NT})	MD [12]	Results	Deviation from MD	Effective V_{NT}	Results	Deviation from MD
0.12	94.6	71.9	24.0%	0.094	91.3	3.5%
0.17	138.9	105.8	23.8%	0.13	128.3	7.6%
0.28	224.2	171.7	23.4%	0.22	209.7	6.5%

Table 3. Predicted elastic moduli, E_c (in GPa) of SWCNT/nylon-6 composites for different configurations and volume fractions of the SWCNTs.

CNT configuration	CNT volume fraction (V_{NT})	MD prediction	Two-phase ROM	Deviation from MD
SWCNT(4,4)	0.024	73.1	70.7	3.2%
	0.048	141.7	139.2	1.8%
	0.073	209.2	208.6	0.3%
	0.097	277.3	276.5	0.3%
SWCNT(6,6)	0.031	53.8	51.8	3.7%
	0.061	101.4	99.7	1.6%
	0.093	152	150.4	1.0%
	0.12	203	201.2	0.9%
SWCNT(10,10)	0.041	42.8	41.2	3.7%
	0.081	81.1	79.6	1.9%
	0.12	121	119.1	1.6%
	0.16	156	154.6	0.9%

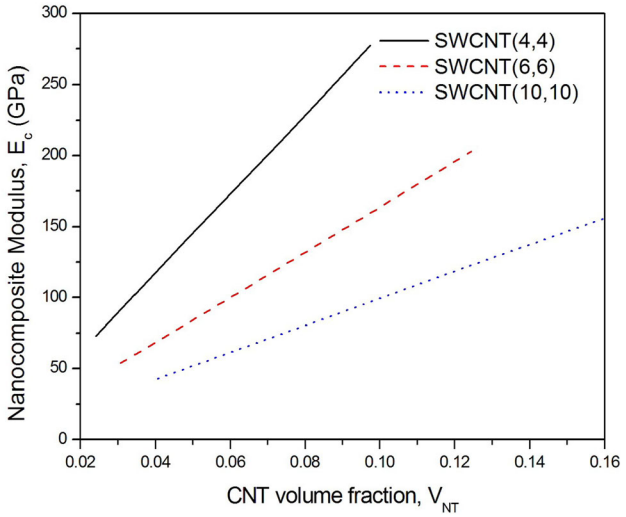

Figure 4. Variation of the nanocomposite elastic modulus with the volume fraction of SWCNT for different CNT configurations.

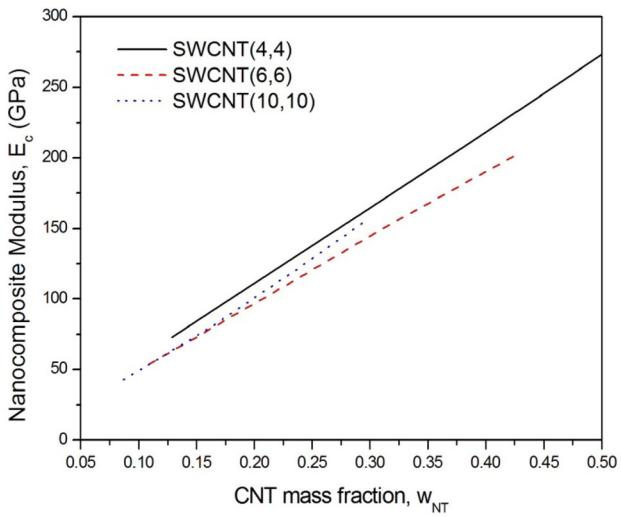

Figure 5. Variation of the nanocomposite elastic modulus with the mass fraction of SWCNT for different CNT configurations.

some higher values. Both the three-phase inverse ROM and the semi-empirical model are used to quantify the interphase modulus.

4.3a *Using three-phase inverse ROM:* The variation of effective interphase modulus with volume fraction of CNT is plotted in figure 6 for different configurations of SWCNT. It is observed that although the elastic modulus of nanocomposite E_c varies linearly with CNT volume fraction, the variation of effective interphase modulus E_i is non-linear. The interphase moduli averaged over all the volume fractions considered are listed in table 4 for different configurations of SWCNT and at different interphase thicknesses.

For all the cases considered, E_i is found to be well above the matrix modulus E_m, indicating the presence of a stiff interphase. Moreover, when the interphase thickness is taken to be equal to h_{vdw}, E_i is approximately one order of magnitude higher than the matrix modulus E_m. Although direct experimental measurement of the interphase thickness or the interphase modulus of nanocomposites has not been reported in the literature, the predicted values are consistent with earlier studies [18,23,24]. The presence of a stiff interphase can be attributed to the increase in crystallinity and density of the polymer at the CNT interface and an improvement in CNT properties because of the VDW interactions between the CNT and the polymer. Interphase modulus is also found to be a little different for different chirality of the SWCNT and increases with an increase in the radius of the CNT. Further, the interphase modulus decreases with an increase in the volume fraction of the SWCNT and also with an increase in the interphase thickness. These findings are consistent with the results reported earlier [11].

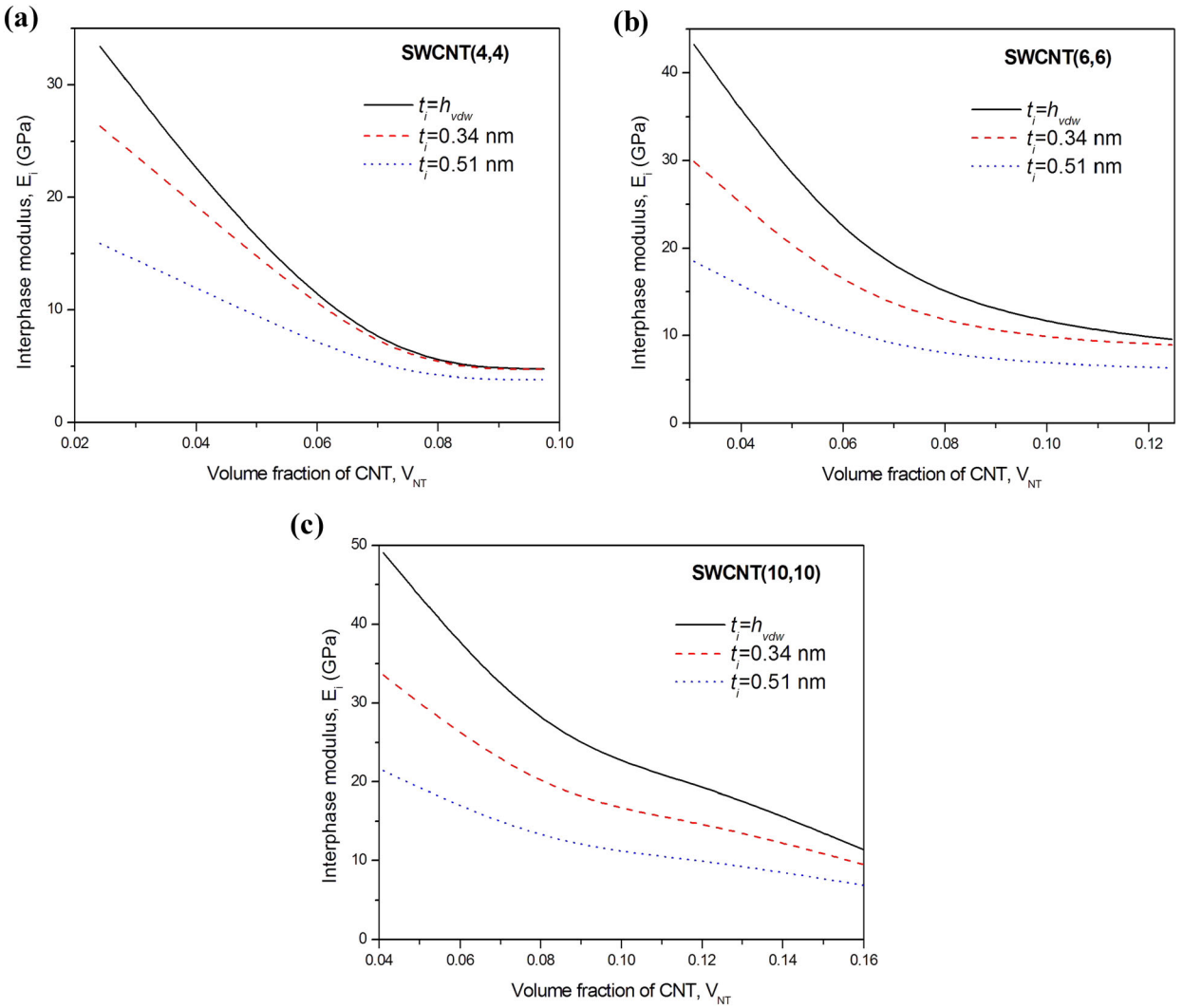

Figure 6. Variation of the effective interphase modulus with the volume fraction of SWCNT for different CNT configurations.

Table 4. Average interphase moduli (in GPa) (averaged over CNT volume fractions) of CNT/nylon composites at different interphase thicknesses.

CNT configuration	Interphase thickness		
	$t_i = h_{vdw}$	t_i = 0.34 nm	t_i = 0.51 nm
SWCNT(4,4)	14.9	12.8	8.4
SWCNT(6,6)	20.9	15.7	10.3
SWCNT(10,10)	26.3	19.0	12.6

4.3b *Using semi-empirical model:* U_I values (expressed in kcal mol^{-1} as well as in Joule) of SWCNT/nylon-6 composites calculated by MD simulation for different configurations and volume fractions of the SWCNT are depicted in table 5. For exponent $n = 6$ (the exponent used in VDW interaction energy), effective interphase moduli

Table 5. Non-bonded interaction energy between the SWCNT and the polymer for different configurations and volume fractions of the SWCNTs.

CNT configuration	CNT volume fraction (V_{NT})	U_i (kcal mol^{-1})	U_i ($J \times 10^{18}$)
SWCNT(4,4)	0.024	–212	–1.47
	0.048	–216	–1.50
	0.073	–209	–1.45
	0.097	–210	–1.45
SWCNT(6,6)	0.031	–334	–2.31
	0.061	–346	–2.40
	0.093	–350	–2.42
	0.12	–326	–2.26
SWCNT(10,10)	0.041	–496	–3.43
	0.081	–513	–3.55
	0.12	–492	–3.41
	0.16	–535	–3.70

Table 6. Effective interphase moduli calculated for different combinations of SWCNT/nylon-6 composites, using the semi-empirical model.

CNT configuration	CNT volume fraction, V_{NT}	Interphase modulus, E_i (GPa)		
		$t_i = h_{vdw}$	t_i = 0.34 nm	t_i = 0.51 nm
SWCNT(4,4)	0.024	14.3	11.2	6.5
	0.048	12.3	11.4	6.6
	0.073	11.7	11.1	6.4
	0.097	11.5	11.1	6.4
	Average	12.5	11.2	6.5
SWCNT(6,6)	0.031	19.4	13.2	7.8
	0.061	19.1	13.6	8.1
	0.093	17.6	13.8	8.2
	0.12	14.2	12.9	7.7
	Average	17.6	13.4	8.0
SWCNT(10,10)	0.041	19.4	13.0	8.0
	0.081	19.4	13.5	8.3
	0.12	18.0	13.0	8.0
	0.16	17.7	14.0	8.6
	Average	18.6	13.4	8.2

calculated using equation (9) are depicted in table 6 for different combinations of the nanocomposites.

The results show that the predicted effective interphase modulus is almost uniform for all the volume fractions of CNT when a constant interphase thickness is used. A comparison of the results in tables 4 and 6 indicates that the interphase modulus values, predicted by the semi-empirical model at the interphase thickness equal to h_{vdw}, are in the range of those estimated using the three-phase inverse ROM that is based on MD predictions of the mechanical properties of CNT, polymer and CNT/polymer nanocomposite.

5. Conclusions

The elastic modulus of an effective interphase in a CNT-reinforced polymer nanocomposite is evaluated directly from the MD simulation studies of individual SWCNT, the polymer and the SWCNT/polymer nanocomposite. Different configurations of SWCNT are embedded in a nylon-6 polymer at different volume fractions of the CNT and the mechanical properties of the nanocomposites are evaluated. Subsequently, the elastic modulus of the interphase is evaluated for each combination of SWCNT/nylon composites using an inverse three-phase ROM, in which the volume fraction of the interfacial region is calculated based on the equilibrium distance between the CNT and the polymer matrix due to the VDW interactions between them. It is observed that the effective interphase modulus varies non-linearly with CNT volume fraction. For all the cases considered, the interphase modulus is found to lie well above the elastic modulus of the matrix. The interphase modulus is also found to be different for each chirality of the SWCNT and reduces with an increase in the volume fraction of the SWCNT. Further, the interphase modulus decreases with an increase in the interphase thickness.

A semi-empirical interphase model was subsequently developed to predict the effective interphase moduli of the nanocomposites. The model is based on the non-bonded interaction energy present at the CNT/matrix interface, which is determined using MD simulations. The results predicted by the semi-empirical model are consistent with those predicted using the inverse three-phase ROM. This semi-empirical model can be used to characterize the interphase in the continuum modelling of nanocomposites, which is based on a representative volume element consisting of three phases including an interphase.

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References

[1] Coleman J N, Khan U, Blau W J and Gun'ko Y K 2006 *Carbon* **44** 1624
[2] Qian D, Dickey E C, Andrews R and Rantell T 2000 *Appl. Phys. Lett.* **76** 2868
[3] Chen X L and Liu Y J 2004 *Comput. Mater. Sci.* **29** 1
[4] Chwał M and Muc A 2016 *Compos. B Eng.* **88** 295
[5] Frankland S J V and Harik V M 2003 *Surf. Sci.* **525** L103
[6] Barber A H, Cohen S R, Keing S and Wagner H D 2004 *Comp. Sci. Tech.* **64** 2283
[7] Haque A and Ramasetty A 2005 *Compos. Struct.* **71** 68
[8] Chowdhury S C and Okabe T 2007 *Compos. Part A Appl. Sci. Manuf.* **38** 747
[9] Shokrieh M M and Rafiee R 2010 *Compos. Struct.* **92** 647
[10] Han F, Azdoud Y and Lubineau G 2014 *Comput. Mater. Sci.* **81** 641
[11] Amraei J, Jam J E, Arab B and Firouz-Abadi R D 2019 *Polym. Compos.* **40** E1219
[12] Han Y and Elliott J 2007 *Comput. Mater. Sci.* **39** 315
[13] Gohil P and Shaikh A A 2009 *J. Reinf. Plast. Comp.* **29** 685
[14] Bhuiyan M A, Pucha R V, Karevan M and Kalaitzidou K 2011 *Comput. Mater. Sci.* **50** 2347
[15] Arash B, Wang Q and Varadan V K 2014 *Sci. Rep.* **4** 1
[16] Banerjee D, Nguyen T and Chuang T J 2016 *Comput. Mater. Sci.* **114** 209

[17] Malekimoghadam R and Icardi U 2019 *Compos. B Eng.* **177** 107405
[18] Guru K, Sharma T, Shukla K K and Mishra S B 2016 *J. Nanomech. Micromech.* **6** 04016004
[19] Farazin A and Mohammadimehr M 2020 *Adv. Nano Res.* **9** 83
[20] WenXing B, ChangChun Z and WanZhao C 2004 *Physica B* **352** 156
[21] Vodenitcharova T and Zhang L C 2003 *Phys. Rev. B* **68** 165401
[22] Tsai J L, Tzeng S H and Chiu Y T 2010 *Compos. B Eng.* **41** 106
[23] Herasati S, Zhang L C and Ruan H H 2014 *Int. J. Solids Struct.* **51** 1781
[24] Rafiee R and Pourazizi R 2015 *Comput. Mater. Sci.* **96** 573