Enhancement of pullout energy in a single-walled carbon nanotube-polyethylene composite system via auxetic effect

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1. Introductions

Carbon nanotubes (CNTs) have been considered as an ideal reinforcement for high-performance polymer composite materials, owing to their high aspect ratio, low density, nano-scale, and more importantly, excellent mechanical properties [1–3]. CNTs are stiff and strong, exhibiting Young’s modulus in a range of 1–2 TPa and fracture stress as high as 50 GPa, yielding a density-normalized strength ~50 times larger than that of steel wires [4,5]. Conventional CNT reinforced polymer nanocomposites have been fabricated by directly mixing the CNTs into polymer matrices followed by solution casting or injection molding [6]. Though progress has been made in the past few years, several critical issues, such as achieving homogenous dispersion and high content of CNTs in the polymer matrix, still prevent CNT/polymer composites from their use in wide range applications.

Free-standing CNT sheets, commonly referred to as buckypaper, is a macroscopic planar structure comprising of continuous CNT networks [7]. In a format unlike the individual CNTs, this porous fibrous material has been developed with the aim to exploit and homogenize the excellent properties of CNTs, e.g., the superior mechanical properties, from a nano-scale to a macro-scale, for various engineering applications. Buckypaper based polymer composites can render

solutions to the dispersion and content issues faced by the traditional CNT/polymer composites. With resin infused into the porous structure of the buckypaper, nanocomposites with high CNT loading (as high as 70 wt%) can be obtained [8], avoiding of the process of CNT dispersion [9–11]. According to the rule of mixture, higher mechanical, as well as conductive properties of the composites have been obtained by researchers due to the much higher CNT loading [6]. However, the mechanical properties of buckypaper and its composites are still far from individual CNTs. The main reason has been ascribed to the lack of effective inter-tube stress transfer abilities. CNTs in the buckypaper interact with each other by weak van-der-Waals forces and mechanical entanglements.

Inter-tube bridging of CNTs is a reliable way to improve the inter-tube stress transfer abilities [12]. Using an atomic force microscope, a 30-fold increase of the bending modulus of a CNT bundle was observed by Kis et al. [13], due to the inter-tube bridging generated by the moderate electron-beam irradiation inside a transmission electron microscope. Buehler et al. [14] studied the mechanical performance of CNT bundles with the inclusion of a binding polymer, and found that the ultimate tensile stress was increased by fourfold, and the modulus by fivefold. Ventura et al. [15] and Cha et al. [16] introduced inter-tube covalent bridging into the CNT network structures, and observed an obvious enhancement of tensile strength, bringing the buckypaper closer to practical applications. Yet, few studies have been conducted on the influence of inter-tube bridging on the mechanical properties of the buckypaper/polymer compos-
ites so far. In the CNT/polymer composites, CNTs reinforce the matrix through several key mechanisms of energy dissipation, especially for fiber pullout and crack bridging [17]. Hence, the mechanical properties of the buckypaper composites could be evaluated by investigating the pullout energy of the embedded CNTs. However, measurement of either the pullout energy or force for an embedded CNT could be a challenging and time consuming task, and only limited experimental results have been reported [18,19]. Experimental techniques to identify an embedded CNT interconnection and perform the pullout are even more challenging to develop.

Alternatively, molecular simulation methods, including molecular mechanics and molecular dynamics (MD) simulations, have been employed as an effective approach to investigate the interfacial interaction of CNT/polymer composite systems [20–23]. Liao and Li [20] found that the interfacial interactions between CNTs and the polystyrene matrix mainly consist of electrostatic and van-der-Waals interactions, with interfacial shear stresses at slip condition equal to 160 MPa, 32% of the estimated 500 MPa interfacial strength for the CNT/polyurethane composite system, identified by Wagner et al. [24]. The interfacial bonding existing in CNTs reinforced epoxy composites was also investigated by Gou et al. using a combination of computational and experimental methods [21], and a CNT–matrix interfacial shear stress up to 75 MPa was reported. Tube–matrix interfacial interactions of covalently surface-functionalized CNTs have been investigated by several groups. Zheng et al. [22] have looked at the interfacial characteristics between polymer matrix and CNTs grafted with –COOH, –CONH2, –C6H11, or –C6H5 groups, by performing tube pullout simulations. The results showed that the functionalization of as little as 5.0% of the surface carbon atoms increased the tube–matrix interfacial bonding and shear stress dramatically, as high as 1700% by –C6H5 groups. Frankland et al. [23] investigated the influence of the chemical cross-links between a single-walled carbon nanotube (SWCNT) and polymer matrix on the matrix–tube shear strength using MD simulations. From those MD results, it is possible that the interfacial shear strength can be enhanced by an order of magnitude with the formation of cross-links involving less than 1% of the tube-surface carbon atoms.

In this study, we reported a MD simulation study on the composite system of SWCNTs embedded polyethylene (PE). Influence of inter-tube bridging on the mechanical properties of the buckypaper composites was theoretically calculated by calculating the tube pullout energies. Energy dissipating mechanisms during the pullout process were discussed.

2. Methods

2.1. Force-field

The MD simulation was conducted using a molecular model developed with the commercial software package Materials Studio® (Accelrys Inc). The force-field of the condensed phase optimization molecular potentials for atomistic simulation studies (COMPASS) was used to perform the computations [25]. The functional form of the COMPASS force field potential can be decomposed into two components. One is with-bond energy, which is associated with bond, angle, torsion, Wilson out-of-plane internal coordinates, and cross-coupled internal coordinates. The other component is related to non-bond energy including Coulombic electrostatic interaction and van-der-Waals’ energy [25–27]. The force-field of COMPASS enables an accurate prediction of the various gas-phase and condensed-phase properties of most of the common organic and inorganic materials, and has been used in other references to study the interfacial characteristics of CNT/polymer composite systems [22,28].

2.2. Molecular model

In the MD simulation, the model of the overall composite system consisted of a super-cell (representative volume element (RVE)) with the dimension of 80 Å × 80 Å × 110 Å and more than 5 × 10⁴ atoms. The RVE was composed by a bundle of two fragments of SWCNT totally embedded inside the amorphous PE matrix (as shown in Fig. 1). A single chain of PE, with 20 repeating units of –CH₂– groups, represented the matrix of the composite. The (10, 10) armchair SWCNT, with a diameter of 13.56 Å and a length of 98.38 Å was selected as a representative CNT structure. The molecular model of SWCNT bundle was employed for that CNTs often aggregate into bundles, and the inter-tube bridging also largely occurs between neighboring CNTs within bundles. The unsaturated boundary effect of the SWCNT was avoided by adding hydrogen atoms at both ends of the tube. The wall–wall distance between the two parallel SWCNTs was 5 Å. Configuration of the composite system was initiated by randomly generating PE molecular chains surrounding the SWCNTs using an initial density of 0.9 g/cm³. To ensure a reasonable molecular configuration, the composite system was placed into an NVT ensemble simulation at the temperature of 300 K, and equilibrated for 40 ps with a time step of 0.5 fs, while keeping the nanotube rigid. Further equilibrium of the system was obtained for another 40 ps with a time step of 1 fs with non-rigid nanotubes to create a zero initial stress state.

Previous studies showed that the CNT interconnections could be formed by covalent functionalization [12,15,29,30]. Although the mechanisms concerning the chemical functionalization of the CNTs are not completely clear, there are clear indications that the potential function allows the formation of chemical bonds with...
appropriate atomic rehybridization between the nanotube and bridging linkers [13]. We have therefore first grafted acyl-chloride groups onto the surface of SWCNTs, and then formed the CNT interconnection by introducing an inter-tube linker with multi-amino-groups that react with the acyl-chloride groups and form amide linkages. Three organics with different geometrical configurations, two long chain aliphatic diamines \((\text{CH}_2)_3\text{N}_2\text{H}_4\) and \((\text{CH}_2)_{10}\text{N}_2\text{H}_4\), and the aromatic Phenylenediamine (PDA) were specially chosen as the covalent linkers. Models of the SWCNT interconnections were constructed by bridging two carbon atoms at exactly the middle segment of the tube wall with the chosen covalent bridging linkers (Fig. 2). Composite systems with the SWCNT interconnections embedded in were also built following the same procedures.

### 2.3. Pullout simulation

Tube pullout simulations were performed by moving several layers of atoms indicated by the frame in Fig. 1a, which were kept rigid, at the left end of one of the SWCNTs along the axial direction at a constant pullout velocity of 0.002 Å/fs. This velocity value was achieved by pulling the rigid end at an increment of 0.1 Å per step, with each displacement followed by 100 relaxation steps with a time step of 0.5 fs [31]. The boundary condition applied to the system assume that all the atoms of the matrix outside the boundary surface are fixed with no movement and zero velocity [32]. The dimension of the boundary surface has a baseline value set as \(60 \times 40 \text{ Å}^2\) along the axial direction (shown in Fig. 1b). The pullout energy, \(E_{\text{pullout}}\), is defined as the energy difference between the original system and the pulled-out configuration [20]. A default bond-length tolerance factor of 1.15 was used in the molecular simulations, meaning that the cut-off distance between two atoms is 115% of the sum of their covalent radii [33].

### 3. Results and discussion

To test the effect given by the RVE dimensions, pullout simulations with a boundary surface dimensions of \(60 \times 40 \text{ Å}^2\), \(70 \times 50 \text{ Å}^2\) and \(80 \times 60 \text{ Å}^2\) were performed and the results are shown in Fig. 3. The pullout energy can be related to the pulling force, \(F_{\text{pull}}\), by the following equation:

\[
F_{\text{pull}} = \frac{\partial E}{\partial d}
\]

where \(E\) is the energy dissipated during a tube displacement of \(d\). The pulling forces along the tube axis estimated from the pullout energies are presented in the inset of Fig. 3. The pulling force curve was quite similar to the fore-displacement curve generated from a tube pullout experiment using the tip of a scanning probe microscope [19], indicating that the simulation results were credible. The dimension of the boundary surface together with the diameter of the SWCNT can be used to calculate the area density of the tube, namely, \(12.0\%, 8.3\%\) and \(6.1\%\) for the selected boundary dimensions. It is noted that very close results were obtained for the pullout energies and pulling forces of different boundary dimensions, with variations less than 5%. The results indicated that during the pullout process, the CNT only interacted with a thin layer of matrix around it. Hence, only the simulations based on the boundary surface dimension of \(60 \times 40 \text{ Å}^2\) have been subsequently performed. Pullout energies of the composite systems embedded with isolated SWCNTs and SWCNT interconnections with different inter-tube linkers are plotted against the displacements of the SWCNT when extracted from the matrix (Fig. 4). Only the pullout energies before the broken of inter-tube linkers (cut-off) were recorded for the composite systems embedded with SWCNT interconnections.

With reference to Fig. 4, it is clear that the tube pullout process consists of two stages: the first stage corresponds to the pullout energy increased rapidly from 0 to 600–700 kcal/mol before the pullout distance of about 5 Å, and the second one exhibits an abrupt drop of increasing speed of the pullout energy. The progressive development of stretching, necking and debonding featured largely in the first stage. When the SWCNT is pulled out initially,
the tube segment outside the matrix moved to the loading end at a rate faster than that of the embedded tube segment due to the smaller resistance. Hence, near the matrix/tube/air edges, the tube wall shows some significant stretch and necking due to the Poisson’s ratio contraction [32]. The combined stretching and necking causes significant tube–matrix debonding, as shown in Fig. 5a. Meanwhile, the pulling force spreads over the whole tube and the tube–matrix debonding propagates along the tube axis until reaching full tube length. This mechanism “peels” the tube wall off the matrix and dissipates large amount of energy, resulting in rapidly increased overall pullout energy. However, as the debonding propagates, the force required for the succedent tube pullout gradually decreases. The calculated pulling forces for the four composite systems are presented in the inset of Fig. 4, and a clear tendency of decrease in the forces can be found. The first stage continues till the stress and debonding propagate over the whole tube. In this stage, the pullout energies for the different composite systems are similar. During the second stage, the tube “peeled off” from the surrounding matrix is pulled out against the matrix in a sliding mode, which is less energy dissipative, resulting in the slowly increased pullout energy. In this stage, the tube necking also propagates near the pulling end of the tube, however, without causing additional tube–matrix debonding, as shown in the snapshots of simulation in Fig. 5b–d. Hence, the tube necking does not contribute much to the pullout energy in the second stage.

As shown in Fig. 4, during the second pullout stage, composite systems with different fillers exhibit different pullout energy increasing rate. The highest rate is observed for the PDA-linker system of about 11.59 kcal/mol Å, followed by the (CH2)3N2H4-linker system of about 8.75 kcal/mol Å, and finally by the (CH2)10N2H4-linker of about 5.86 kcal/mol Å and the non-linker system of about 0.65 kcal/mol Å. The pullout energy can be related to the interfacial shear stress, $\tau_i$, by the following equation:

$$E_{\text{pullout}} = \int_{x=0}^{x=d} 2\pi r(L-x)\tau_i dx = 2\pi rL\tau_id - \pi\tau_id^2$$

where $r$ and $L$ are the outer radius and the length of SWCNT, respectively, $x$ is the coordinate along the longitudinal tube axis, and $d$ is the shear displacement of the SWCNT. The shear strength, $\tau_i$, estimated from the molecular simulations is 46.48 MPa, 63.45 MPa, 90.26 MPa and 100.85 MPa for the non-linker, (CH2)10N2H4-linker, (CH2)3N2H4-linker, and PDA-linker systems, respectively. The calculated tube–matrix shear stress is close to the previous simulation results reported by Liao (160 MPa) [20] and Gou et al. (75 MPa) [21].

Fig. 4. Pullout energies of the composite systems embedded with isolated SWCNTs, and SWCNT interconnections with (CH2)3N2H4, (CH2)10N2H4, and PDA. Inset shows the pulling forces generated from the pullout energies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. Snapshots of the simulated system without inter-tube linker at pullout displacements of: (a) 4 Å, (b) 12 Å, (c) 20 Å and (d) 28 Å, the arrows indicate the wall necking, and (e) inter-tube bridging linker induced wall collapse and wall enlarging. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
and is about 10–20% of the interfacial strength (500 MPa) obtained by Wagner et al. [24] in the CNT/polyurethane composite system using the fragmentation test method.

We ascribe this phenomenon to three different energy dissipative mechanisms. Initially (first mechanism), as the SWCNT is extracted out, the branch-like inter-tube linker would block the pullout due to the mechanical joggling [12], with a stress concentration on the SWCNT wall formed at the linker end (Fig. 5e). Along the loading direction, a small wall collapse occurs due to a localized compression effect, while a slight wall enlarging is present simultaneously at the linker end location against the loading direction due to a stretching effect. The compression-induced wall collapse has also been observed using TEM image on the compressed SWCNT [34], and this collapse causes further tube–matrix debonding which dissipates energy. With an opposite effect, the tube wall enlarging increases the wall–matrix interaction and provides additional resistance to the pullout process. The localized tube wall enlarging corresponds to a local negative Poisson’s ratio (auxetic) effect, which has been observed in SWCNT with metastable non-reconstructed defects [35], and also in nanotube bundles due to relative glide of CNT filaments [36]. It is also worth noting that the negative Poisson’s ratio effect is responsible for large energy pullout increase in meso-scale composites epoxy matrices with auxetic ultra high molecular weight polyethylene fibers [37]. Combination of the wall collapse and enlarging (auxetic) effects leads to the higher pullout energy for the composite systems with inter-tube linkers (Fig. 4).

The second mechanism providing the pullout effects observed in these simulations is the following. During the pullout process, the inter-tube linker embedded in the matrix would “cut through” (penetrate) the matrix as the tube is pulled forward, indicating that the type of inter-tube linker is a critical factor that should be taken into account when designing the SWCNT interconnection. Chain length and atom numbers of the inter-tube linkers of PDA and (CH$_2$)$_3$N$_2$H$_4$ are almost the same. However, the aromatic ring of PDA provides enhanced contact area with the matrix, which leads to more resistance during the pullout, resulting in a higher pullout energy and a shorter linker-broken distance than that of the (CH$_2$)$_3$N$_2$H$_4$ system. The linker made by (CH$_2$)$_{10}$N$_2$H$_4$ has a much larger contact area than the other two linkers, while the corresponding pullout energy increase of the composite system has a slower speed compared to the other two systems. This behavior can be explained by the transforming configurations of the (CH$_2$)$_{10}$N$_2$H$_4$ during the pullout process. The initial inter-tube wall–wall distance (5 Å) is remarkably shorter than the length of the linker of (CH$_2$)$_{10}$N$_2$H$_4$, hence the linker becomes “compressed” to fit in the narrow gap between the tubes (Fig. 6a). The load transfer is not effective through this bulked linker. As the pullout process progressing, the linker is extended as shown in Fig. 6b and c, and the larger the elongation of the linker, the higher is its apparent stretching stiffness. Therefore, the load transfer efficiency increased until the chain is fully extended, resulting in a more rapid increase of pullout energy and its rate, especially at the pullout distance of about 15–20 Å (as indicated by the circle in Fig. 4).

As the third mechanism, in mechanical performance afforded by the three inter-tube linkers is also reflected by the combining “pullout” displacement of the SWCNT at the other end of the linker (as schematically shown in Fig. 7a). As the SWCNT is pulled out from the matrix, the SWCNT at the other end of the linker is also pulled out under the stress transferred through the linker, but with a much smaller displacement. With reference to Fig. 7b, it can be observed that the SWCNT in the non-linker system almost does not move, while the tube in the systems with inter-tube linker is pulled out for a small displacement. The load transfer efficiency by the inter-tube linker changes with the type of bridging functional group. The aliphatic chain provides

![Fig. 6. Configurations of the inter-tube bridging linker of (CH$_2$)$_{10}$N$_2$H$_4$ at different pullout displacements: (a) 0 Å, (b) 10 Å and (c) 20 Å. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 7. (a) Schematic image for the combining pullout of the SWCNT at the other end of the linker; and (b) displacement of the SWCNT at the other end of the inter-tube linker during the pullout process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image2)
a lower resistance against the matrix than the aromatic ring structure, because of its equivalent lower contact surface with matrix. Hence the displacement distance of the tube in the composite system with (CH2)3N2H4 is higher than the one observed with the PDA linker. During the pullout, the inter-tube linker made of (CH2)3N2H4 is elongated to a maximum distance of about 15–20 Å. As a result, the displacement of the system with (CH2)3N2H4 starts at the pullout distance of about 15–20 Å, which is much later than the systems having short linkers such as PDA and (CH2)3N2H4. All the three additional energy dissipative mechanisms brought in by the inter-tube linker contribute to the significantly higher pullout energy with an improvement of as high as 19.6%, 14.6% and 24.6% for composite systems with linkers of PDA, (CH2)3N2H4 and (CH2)3N2H4, respectively. The higher pullout energy and the bridging effect will prevent the crack propagation more effectively than an isolated SWCNT. As a result, the toughness of the composite system with SWCNT interconnection is improved. The micro-mechanisms observed in this work offer useful insights also in the experimental findings from our previous work [12]. The energy dissipative mechanisms indicate that the inter-tube linkers with aromatic rings which provide larger contact area with the matrix, or longer chains which increase pullout energies over a larger pull-out displacement are preferred.

It worth pointing out that, although the interconnection of the SWCNTs can improve the efficiency of the load transfer, the functionalization process might also introduce defects on the walls of the pristine nanotubes, which will deteriorate the mechanical properties of the SWCNTs [38]. Therefore, only tubes with the appropriate low level of functionalization may be considered as ideal candidates for composite reinforcement.

4. Conclusions

The influence of wall–wall inter-tube bridging on the tube–matrix interfacial interaction of the SWCNT–PE composite system has been studied using the MD simulation method. Molecular models of composite systems have been constructed by embedding isolated SWCNTs and SWCNT interconnections into a PE matrix. Tube pullout simulations have been performed and the pullout energies were recorded to evaluate the mechanical properties of the nano-composites with the bridged reinforcements. The simulation indicated that the inter-tube bridging could significantly enhance the tube pullout energy. Three energy dissipative mechanisms contributed to this: linker-stress induced tube deformation, linker–matrix penetration, and the pullout of the accompanying tube at the other end of the linker. The simulation also indicates that inter-tube linker with aromatic ring dissipates a higher level of pullout energy compared to analogous bridging groups made of aliphatic chains for the same maximum tensile displacement. The inter-tube linker with long aliphatic chain also dissipates a higher level of energy during the whole pullout process due to its larger linkerbroken distance.

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