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Exploring the interface between single-walled carbon nanotubes and epoxy resin

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ABSTRACT

A significant mechanical reinforcement of epoxy matrices with carbon nanotubes (CNTs) requires a very strong covalent interfacial bonding between the tube and the resin, diglycidylether of bisphenol A (DGEBA). Using classical molecular dynamics (MD) and density functional theory (DFT), various methods of improving covalent binding to CNTs are applied on four major categories: CNT diameters, dopants, defects, and functional groups. The diameter category includes (n, 0) CNTs with n = 5, 7, 9,11, 13, 15; the dopant category includes B-, N-, and Si-doped CNTs; the defect category includes CNTs with mono-vacancies, Stone-Wales, and more complex nitrogen terminated monovacancies and divacancies; the functional group category includes CNTs with atomic oxygen, hydroxyl, amine, carboxyl, and a combination of oxygen and hydroxyl. The computation of binding energies (BE), affinity indices (AI), and shear fracture forces on all configurations converged to the conclusion that smaller tubes, Si-doped CNTs, CNTs functionalized with a combination of oxygen and hydroxyl, and CNTs with monovacancies show the strongest indication for mechanical reinforcement in their respective categories.

1. Introduction

Structural materials with extremely high specific strength and stiffness are an enabling technology for next generation aerospace vehicles [1]. In aeronautics, the drive towards environmentally responsible aviation will require large decreases in fuel burn per passenger mile flown. While aerodynamic and engine efficiency improvements are critical factors, reduction of structural mass, achieved with the use of new advanced composites, will also contribute to enhanced aircraft efficiency. Similarly, mass reduction at constant or improved performance levels is an important objective in space exploration missions. Mass is already a serious limiting factor for launches to low Earth orbit. For future missions, which may include flight to cislunar space and Mars, mass is a far more critical barrier. In fact, a number of conceptual missions are either unaffordable or impossible with state of the art structural materials. Recent advances in the commercial availability of high strength carbon nanotube yarns [2] and fibers [3] have made this material an interesting option for use as reinforcement in advanced composites. The fabrication and optimization of CNT fiber reinforced composites is still an early stage technology and a number of issues remain to be understood and resolved. This paper addresses one of these, the CNT-matrix interface, which is the primary pathway for load transfer.

Polymer thermosets and carbon nanotubes are located at opposite ends of the spectrum of materials' mechanical properties. The Young's modulus of the former is low [4] (~2 GPa), the Young's modulus of the latter is among the highest [5] (~10^3 GPa). Additionally, because of their great flexibility, low thermal expansion, great elongation (up to 20% elongation to failure), high tensile strength (up to ~60 GPa), high aspect ratio (length up to 10^3 times the diameter) and high absorbance, carbon nanotubes are ideal candidates for mechanical reinforcement in polymer thermosets. Experimentally, the addition of CNTs into polymer matrices (polyamides [6], epoxy [7], polyethelene [8], etc…) has not met the reinforcement expectations because of the ineffectiveness of the processing methodologies and the lackluster performance of the matrix-CNT load transfer. Indeed, a successful reinforcement is

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conditional on good solubility which CNTs do not satisfy due to their hydrophobic nature. This is a compounding factor to both the matrix-CNT covalent bonding and load transfer. Computational attempts [9,10] to understand and circumvent the insolubility of CNTs in liquid polymers have converged to the existence of a (3–5 Å) matrix-CNT non-covalent interfacial region. This large, non-covalent interfacial region is bad for mechanical reinforcement of composites insofar as there is poor load transfer between the polymer and the CNT.

In order to promote the covalent crosslinking, the interaction between CNTs and one of the most common epoxy resin base, DGEBA ($C_{21}H_{26}O_4$ diglycidylether of bisphenol A), is analyzed in terms of binding energy, affinity index, and shear fracture forces. The covalent binding is quantified for four categories of different local chemistry alterations: CNT diameters, dopants, defects, and functional groups. The dopants considered are: silicon [11], boron [12], and nitrogen [11]; the types of defects considered are: monovacancies [13], nitrogen terminated monovacancy [14], nitrogen terminated divacancy [15,16] and Stone-Wales [13,17]; the functional groups considered are: oxygen [18], carboxyl [19,20], hydroxyl [13,19,20], and amine [13,19]. A combination of oxygen and hydroxyl was also considered due to experimental evidence where record strength of CNT composite strength was achieved [18,20]. The analyses are carried out using classical molecular dynamics using a ReaxFF potential (MD/ReaxFF) and density functional theory (DFT). The next sections elaborate on the computational tools of the analysis, present the results, and discuss the significance thereof.

2. Methodology

2.1. Configurations

Fig. 1 shows different local chemical situations on a (9, 0) CNT where the same activated DGEBA end is used to bind the polymer to the CNT in all configurations [21]. Silicon (Si), boron (B), and nitrogen (N) dopants, substituting a single carbon atom on the CNT, are considered both in direct connection to the DGEBA molecule, and in adjacent connection to a CNT-DGEBA bond. Dopant configurations are abbreviated Si-D, Si-A, N-A, N-D, B-A, and B-D, where the '-D' and '-A' suffixes refer to the dopant being direct or adjacent as pictured in Fig. 1. All defective CNTs are bonded to the DGEBA with the most chemically active atom, namely, the monovacancy (1V) is bonded to DGEBA with the two-coordinated carbon atom, the three-nitrogen atom terminated monovacancy (3NV) is bonded to DGEBA with one of the nitrogen atoms, the four-nitrogen atom terminated divacancy (4ND) is bonded to DGEBA with one of the nitrogen atoms, the Stone-Wales defect (SW) is bonded to DGEBA with a carbon atom belonging to both seven-membered rings.

Each functionalized CNT is linked to the DGEBA molecule in a manner similar to comparable crosslinks in the literature. Specifically, hydroxyl [13,19,20] (OH), and amine [13,19] (NH_2) are bonded to the carbon atom nearest to the CNT-DGEBA bond; carboxyl [19,20] (COOH) directly binds to the DGEBA molecule with the oxygen atom connected to C; oxygen [18] (O) directly binds to the DGEBA molecule; the combination of O and OH [18, 20] (O-OH) is connected to the DGEBA molecule by juxtaposing the previous individual connections. The diameter dependence is analyzed on (5, 0), (7, 0), (9, 0), (11, 0), (13, 0), and (15, 0) tubes because of the proven higher reactivity of zigzag tubes [13] (compared to armchair tubes).

2.2. Models

The CNT-DGEBA interfacial bonding is evaluated with binding energies, affinity indices and fracture forces. All molecular dynamics (MD) calculations are performed with the large-scale atomic/molecular massively parallel simulator [22] (LAMMPS) using the parameterizations of the Reax Force Field (ReaxFF) for fullerene [23] and silicon carbide [24] with a timestep of 0.25 fs.

The CP2K software package used to perform all DFT calculations [25] implements the quickstep method on a mix of Gaussian and plane wave basis sets [26], thereby allowing for a very efficient representation of the wave function in systems as large those in Fig. 1. The well-established PBE exchange-correlation functional [27] and the Goedecker-Teter-Hutter (GTH) pseudopotentials with the complimentary GTH double zeta polarization Gaussian basis set [28,29] are used for all atomic species. A 280 Rydberg plane-wave and the efficient orbital transformation method (for wavefunction optimization) [30] are used in structure relaxations as well as electronic calculations.

Binding energies are calculated with covalent CNT-DGEBA connections (see Fig. 2a) through molecular dynamics (MD) at room-temperature and density functional theory (DFT) at zero temperature as the difference between the energy of the optimized CNT-DGEBA connection and the energy of the CNT and DGEBA, optimized separately. In the MD binding energy formula (Equation (1)), energies of CNT and DGEBA, taken separately (E_{CNT}, E_{DGEBA}) or covalently bonded ($E_{CNT} - E_{DGEBA}$), are obtained performing with two consecutive equilibration processes on the respective structures.

The first is a canonical (NVT) ensemble at 300 K with Nosé-Hoover thermostat for 100 ps. In the second process, the Nosé-Hoover thermostat is removed and the system runs for 25 ps with the rescaling of velocities to minimize temperature fluctuations.

$$\begin{aligned} BE_i &= E_{CNT-DGEBA} - (E_{CNT} + E_{DGEBA}) \\ \mu_{BE} &= n^{-1} \sum_{i=100ps:25fs:125ps} BE_i \\ \sigma_{BE} &= \left(n^{-1} \sum_{i=100ps:25fs:125ps} (BE_i - \mu_{BE})^2 \right)^{\frac{1}{2}} \end{aligned} \quad (1)$$

During the second equilibration process, the binding energy, BE_iin Equation (1), is calculated every 25 fs and the resulting average (μ_{BE}) and standard deviation (σ_{BE}) are extracted (see Equation (1) with $n = 1000$ being the number of frames). The average binding energy is used as an indicator of the CNT-DGEBA stability.

The affinity index quantifies the average distance between the CNT and the DGEBA molecule when free to interact during the equilibration process (see light-green area in Fig. 2d). It has been defined by Jihua Gou [10] as the average distance between epoxy atoms and CNT atoms as a way to characterize van-der-Waals (vdW) interactions with CNTs. However, the implementation of Jihua Gou's definition on the doped, defective and functionalized CNTs (see Fig. 1), led to results inconsistent with both MD and DFT binding energies because several atoms stuck out of the CNT. Because the cylindrical distribution function is an effective method of characterizing CNT interfaces [31], it can be used to define the affinity index as the distance between the first time it drops down to 0 and the first time it goes above 0 (around the interfacial region). The CNT-DGEBA interfacial region of Fig. 2b has been zoomed into Fig. 2d to further clarify the concept. While the CNT shell (light-blue shell containing CNT atoms) and the DGEBA shell (light-blue shell containing DGEBA atoms) contain a positive number of atoms, the light-green region in between (depletion shell) contains no atoms and its extent (affinity index AI) indicates the minimum CNT-DGEBA interface gap distance. The amount of dopants, functional