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Atomistic modeling of thermomechanical properties of SWNT/Epoxy nanocomposites

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Abstract

Molecular dynamics simulations are performed to compute thermomechanical properties of cured epoxy resins reinforced with pristine and covalently functionalized carbon nanotubes. A DGEBA-DDS epoxy network was built using the 'dendrimer' growth approach where 75% of available epoxy sites were cross-linked. The epoxy model is verified through comparisons to experiments, and simulations are performed on nanotube reinforced cross-linked epoxy matrix using the CVFF force field in LAMMPS. Full stiffness matrices and linear coefficient of thermal expansion vectors are obtained for the nanocomposite. Large increases in stiffness and large decreases in thermal expansion were seen along the direction of the nanotube for both nanocomposite systems when compared to neat epoxy. The direction transverse to nanotube saw a 40% increase in stiffness due to covalent functionalization over neat epoxy at 1 K whereas the pristine nanotube system only saw a 7% increase due to van der Waals effects. The functionalized SWNT/epoxy nanocomposite showed an additional 42% decrease in thermal expansion along the nanotube direction when compared to the pristine SWNT/epoxy nanocomposite. The stiffness matrices are rotated over every possible orientation to simulate the effects of an isotropic system of randomly oriented nanotubes in the epoxy. The randomly oriented covalently functionalized SWNT/Epoxy nanocomposites showed substantial improvements over the plain epoxy in terms of higher stiffness (200% increase) and lower thermal expansion (32% reduction). Through MD simulations, we develop means to build simulation cells, perform annealing to reach correct densities, compute thermomechanical properties and compare with experiments.

Keywords: molecular dynamics, polymeric material, nanocomposites, epoxy

(Some figures may appear in colour only in the online journal)

1. Introduction

Carbon nanotubes (CNTs) have been researched extensively in the last 20 years due to their outstanding mechanical [1–3], electrical [4–6] and thermal properties [7–8]. Due to these exceptional properties, forming CNT/polymer nanocomposites has become an attractive option to improve the properties of the polymer. This work will focus in particular on single wall carbon nanotubes (SWNTs). SWNTs are an atom thick single layer of graphene with a cylindrical structure with an elastic modulus around 1 TPa [9]. The thermomechanical properties of epoxy-based composite materials are highly dependent on the interface between the fiber and epoxy. It is experimentally difficult to characterize this interface, making molecular modeling an essential tool for relating molecular interfacial structure to bulk thermomechanical properties. Molecular dynamics (MD) allows for the effects of mechanical and thermal loading to be isolated and visualized in regions of interest where it may not be possible with experiments. In this work, MD is used in order to explore the effects on the mechanical and dilatometric properties by adding pristine and covalently functionalized SWNTs to cross-linked polymers.

There has been numerous experimental studies on the effects of adding SWNTs to epoxies [10–23]. To take full advantage of the mechanical and thermal properties of the SWNTs, attempts have been made to covalently functionalize the nanotube to the epoxy. Functionalization allows for better dispersion and interfacial bonding of the SWNTs to the polymer matrix, and has shown to give significantly improved mechanical properties [12–18]. Attempts to study SWNT-epoxy systems via molecular dynamics are limited. Liang *et al* used MD to study the interactions between SWNTs and EPON 862 (DGEBF) resin and EPI-CURE W (DETDA) curing agent [24]. Gou *et al* expanded this work by studying and comparing affinities between SWNT and DGEBA (diglycidylether of bisphenol A) with curing agent DETA (diethylenetriamine) [25]. Zhu *et al* studied SWNT/EPON 862 composites, and found stress–strain relations in the direction parallel to the nanotube for continuous and discontinuous CNTs [26]. Mohan *et al* predicted the effects of carbon vacancy defects on a SWNT and EPON 862 cross-linked with EPI-CURE W composite [27]. Recently, Varshney used MD to study the thermal conductivity of functionalized SWNT/epoxy composite, where the epoxy was EPON 862 and cross-linking agent was DETDA [28]. To the author’s best knowledge, there has not yet been a molecular dynamics study on the mechanical or dilatometric effects of covalent functionalization on a SWNT/Epoxy nanocomposite. Molecular scale simulations provide the ability to isolate the effects of the SWNT on the composite system in greater detail than experimentation. Epoxies have an amorphous structure and building complex cross-linked molecular configurations with accurate properties is challenging [29]. Using an amorphous cross-linked structure that has been experimentally verified [30], MD will be used to obtain full elastic stiffness matrices and thermal expansion vectors for pristine nanotube/SWNT and covalently functionalized/SWNT composite systems. The effects of randomly oriented nanotube/epoxy composites will be simulated by rotating and averaging the properties in every direction.

2. Materials

Diglycidyl ether of bisphenol A (DGEBA) is the epoxy chosen for this study. The curing agent used is diamino diphenyl sulfone (DDS). The epoxy molecules were cross-linked (cured) with 3–3′ DDS. The structure of the epoxy and the amine can be seen in figure 1. The epoxy monomer has two epoxide (oxirane ring) groups with a total functionality of two, each epoxide

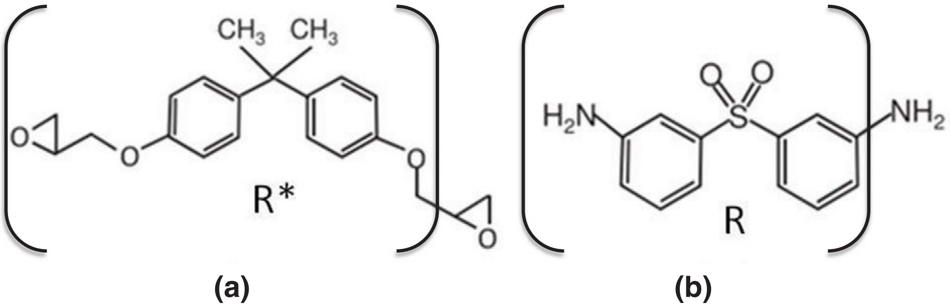

Figure 1. (a) Chemical structure of epoxy resin, DGEBA and (b) The amine monomer diamino diphenyl sulfone. Brackets give the notation for R and R* in figure 2.

has a cross-linking functionality of one towards the amine curing agents. The DDS monomer has two amine groups and a total functionality of four, each amine group with a functionality of two towards epoxy molecules. A typical amine stoichiometric ratio for synthetic epoxy is approximately 2:1 or 33.3 mol% amine. The polymer is formed by bonding of the epoxide group in DGEBA and the amine groups in the DDS. To form a cross-link, the primary amine group reacts with the epoxide group, creating a bond between the terminal carbon of the epoxide group and the nitrogen of DDS. The carbon–oxygen bond breaks between the terminal carbon and the oxygen from the epoxide, and forms and alcohol (-OH) link. The cross-linked structure seen in figure 2(a) can undergo another reaction with a different epoxy molecule, forming the final cross-linked structure seen in figure 2(b).

3. Material modeling

For industrial grade epoxies, a conversion 70–95% is typically seen when measured through near-infrared (NIR) Spectroscopy [31]. In order to create accurate models for molecular dynamics simulations, a number of approaches have been used to build cross-linked polymer networks with greater than 70% cross link conversions. The majority of these approaches can be characterized based on whether unreacted monomer mixtures are cross-linked all-at-once (one-step) or over time (multi-step). For one-step cross-linking, sites are first randomly selected and then pairs of sites within a capture radius are cross-linked together [32, 33]. In multi-step cross-linking, every reactive pair that satisfies a length criteria are cross-linked iteratively, with equilibration and the length criteria increasing with every iteration [34–36]. Multi-step methods prevents and relieves network strains, but they are computationally expensive. In 2007, Christensen introduced a new method to build epoxy networks using a ‘dendrimer’ growth approach [29, 37]. In this approach, the thermoset resin is modeled by starting with a single monomer and then cross-linking a second layer of monomers around it. In the next step, a third layer of monomers are cross-linked to the second layer. In this way, generations (layers) of monomers are added to a seed structure that grows in size at every pass. The principal advantages of the dendrimer growth method are the complete avoidance of artificial network strain during curing and the low computational cost of the growing procedure.

The ‘dendrimer’ growth approach was used to build the epoxy network in Materials Studio [38] containing 36 amine groups and 71 epoxy groups as seen in figure 3. The system contains 4601 atoms and is sufficiently complex to accurately capture the amorphous nature of the polymer. All simulations in this work are performed under periodic boundary conditions, and the Consistent Valance Force Field (CVFF) [39] potential was used for bonded and non-bonded

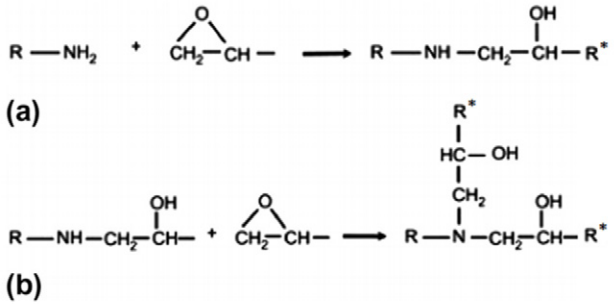

Figure 2. Epoxy-amine cross-linking through reaction of epoxide group and amine group.

interactions in LAMMPS [40]. This force-field has been used in a previous study to accurately predict thermodynamic properties of epoxy [41]. 75% of available epoxy sites were cross-linked, which is representative of many structural epoxies. To verify the accuracy of the initial dendrimer structure; the dilatometric curve simulated by MD has been compared to experimental results, and the full elastic stiffness matrix was generated by conducting tensile and shear tests via MD to verify the structure is isotropic.

To equilibrate the structure, the initial dendrimer first is optimized by minimizing the energy using conjugate gradient (CG) minimize for 10 000 iterations. MD was then performed over several annealing cycles using an NPT ensemble. Dynamics was first performed well above glass transition temperature (600 K and 1 atm) for 500 ps. Next, dynamics was run well below T_g (1 K and 1 atm) for 500 ps, followed by CG. This was done for ten cycles, at which point the potential energy was sufficiently minimized such that density converged to within 0.5% across consecutive annealing steps. A final density of $1.17\,\mathrm{g\ cc^{-1}}$ at 1 atm and 1 K is obtained after convergence.

To build the CNT/Epoxy nanocomposites, a vacancy was created in the epoxy by moving atoms radially outward from a chosen point, and an single walled armchair nanotube (4,4) was inserted in the space. Moving atoms caused many bonds to displaced from their equilibrated length, so the same annealing process ran previously via a sequence of conjugate gradient (CG) minimization and dynamics above and below T_g was used to minimize potential energy until the density converged. A functionalized SWNT/Epoxy composite was created by covalently bonding the nanotube to the DDS molecule. One of the two amine groups of the DDS is attached to the carbon nanotube, as shown in figure 4(a). The other amine group reacts with the epoxide, as shown earlier in figure 2. The degree of cross-linking for the epoxy is unaffected, as sites that were previously not reacted with the epoxy were selected to bond covalently to the nanotube. Again, equilibration was performed via a sequence of the conjugate gradient (CG) minimization and annealing until the density was seen to converge. The functionalized system containing four covalent bonds to the epoxy can be seen in figure 4(b). Experimentally, carbon nanotubes with amino groups covalently bonded to their side walls have been prepared by use of fluorinated SWNTs [17, 18, 42, 43].

4. Model verification

Tension (*x*, *y* and *z* directions) and shear tests (*xy*, *yz* and *xz* in the positive and negative directions) were performed via MD to obtain the stiffness matrices at various temperatures. Strains were applied and the stress was averaged over three samples. These results were used to

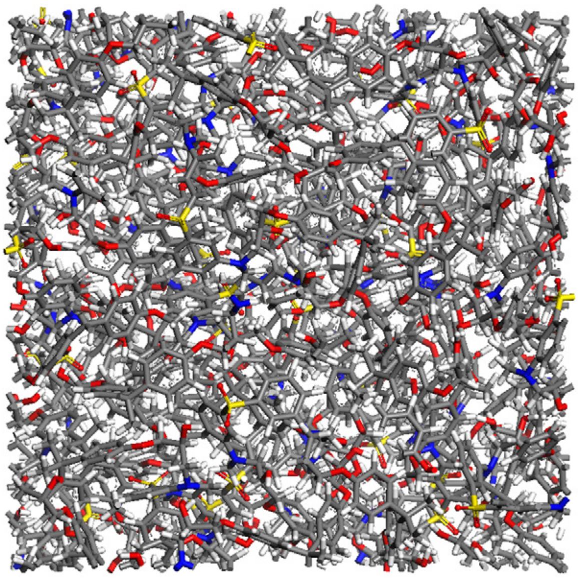

Figure 3. The dendrimer structure of epoxy after energy minimization.

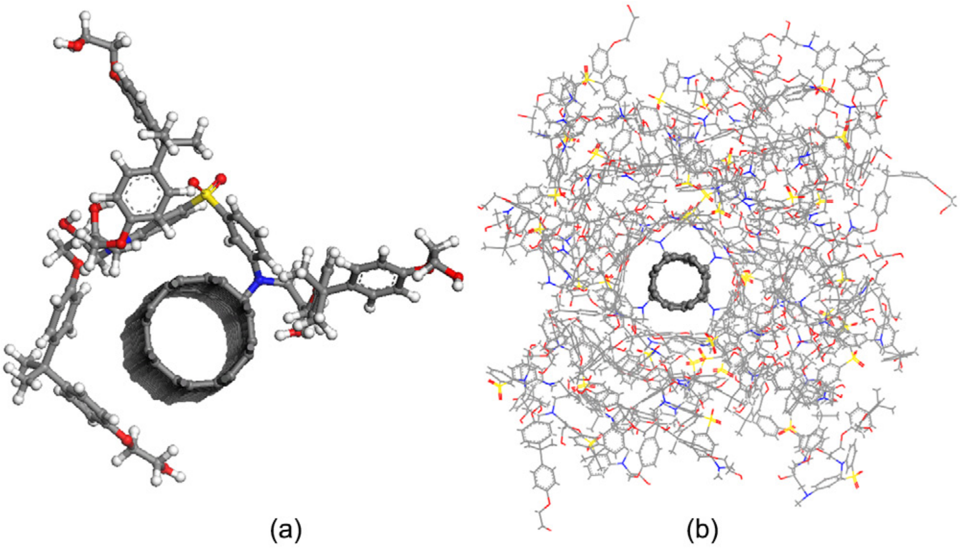

Figure 4. (a) Nanotube functionalization to amine and subsequent cross-linking to epoxy. (b) Functionalized Carbon nanotube and epoxy nanocomposite.

solve for the 36 constants in the elastic stiffness matrix. The epoxy is verified to be isotropic by rotating the resulting stiffness matrix in all directions, using the transformation law for a fourth-order tensor, as shown in figure 5(a). Rotation tensors were chosen such that they took into account all independent rotations of a transversely isotopic system when accounting for symmetries. The isotropic properties of epoxy can be seen in figure 5(b). It has been measured experimentally that for an 80% degree of cure for DGEBA-DDS resin system the tensile elastic modulus is 3.1 GPa at room temperature (300 K) [44]. Additionally, for tests

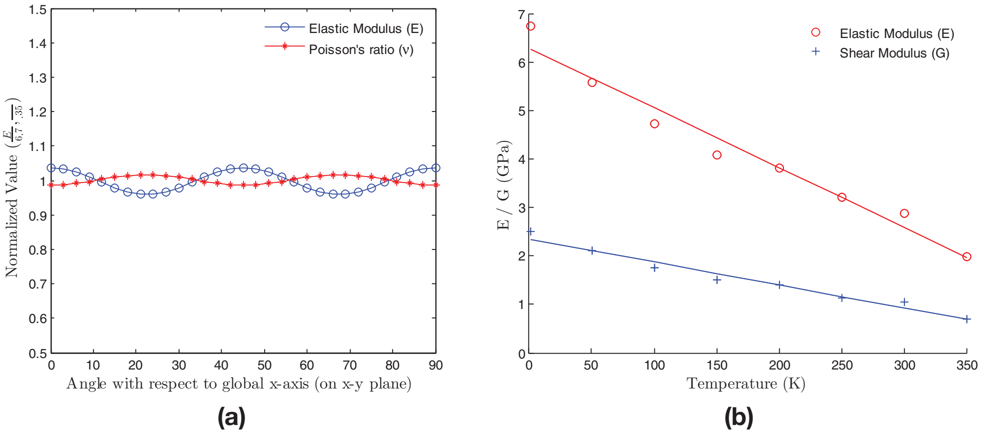

Figure 5. (a) Variation of elastic properties along various directions in the x–y plane. (b) Elastic Modulus and Shear modulus for epoxy model.

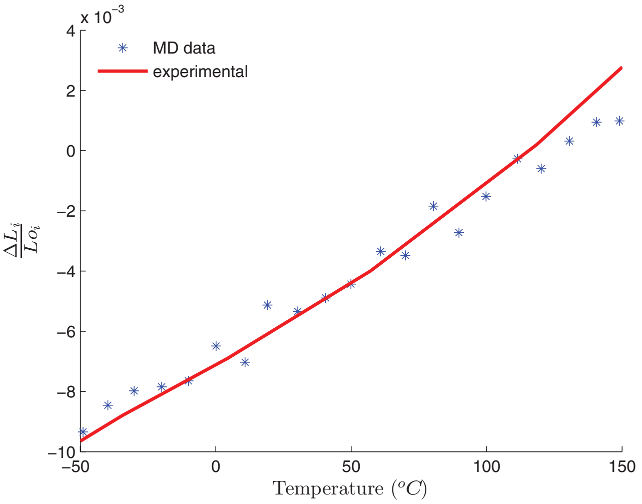

Figure 6. MD calculations of thermal expansion is superposed with experimentally measured dilatometric curves reported in [46].

in compression at room temperature and quasi-static loading rates, a Poisson's ratio of 0.37 has been measured experimentally [45]. Despite the high strain rate of MD experiments, the Young's Modulus and Poisson's ratio at 300 K are found to be 2.9 GPa and 0.35 respectively, which compares well with the quasi-static experimental results.

The thermal expansion coefficient for the neat epoxy was obtained via an NPT simulation. The change in cell length with varying temperature is plotted with an experimentally measured dilatometric curve measured by Tcharkhtchi *et al* [46]. The experimental curve is in very good agreement with the MD calculated data, seen in figure 6. The linear coefficient of thermal expansion between −50 °C to 150 °C is measured to be $54.4 \pm 2.7\ \mu\ ^\circ\mathrm{C}^{-1}$ from this figure, with error bars shown later in figure 14. Thermal expansion at higher temperatures is plotted in figure 7 to show the glass transition temperature, which falls within the experimental range of 425–495 K for DGEBA/DDS [46].

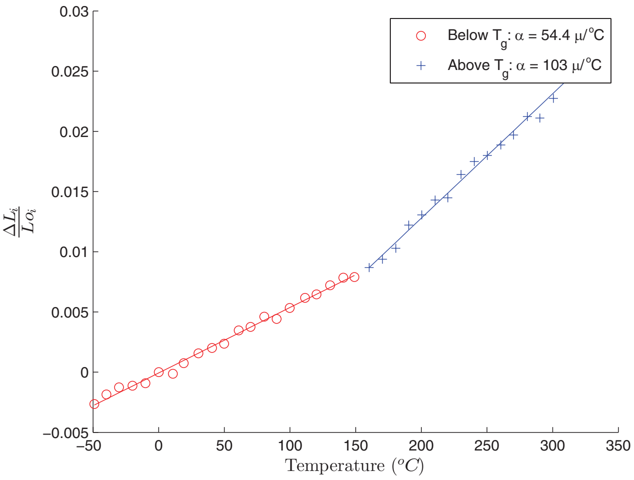

Figure 7. Thermal expansion for neat epoxy showing the glass transition temperature.

Table 1. Material properties- pristine SWNT/Epoxy composite.

Temperature (K)	E_{xx}(GPa)	E_{zz}(GPa)	ν_{xy}	ν_{zx}	G_{xy}(GPa)
1	7.2	72	0.49	0.32	2.4
50	6.2	71	0.52	0.32	2.1
100	5.9	70	0.54	0.36	2.0
150	5.1	70	0.55	0.36	1.7
200	4.7	69	0.59	0.37	1.5
250	3.7	68	0.67	0.40	1.3
300	2.7	68	0.75	0.43	0.87
350	2.0	67	0.75	0.45	0.77

5. Results

Similar to epoxy, tension and shear tests are run for the pristine and covalently functionalized SWNT/epoxy composite systems to obtain the full stiffness matrices. Both nanocomposite systems are found to be transversely isotropic and the properties of the pristine SWNT/epoxy system and the covalently functionalized SWNT/epoxy systems are seen in tables 1 and 2, respectively. As expected, both systems see dramatically increased stiffness in the z-direction due to the inclusion of the nanotube. By comparing the properties of the covalently functionalized SWNT/epoxy composite to that of the pristine SWNT/epoxy composite, it is seen that the nanocomposite becomes much more stiff in the direction transverse to the nanotubes (E_{xx}), as highlighted in figure 8. It can be readily seen here that the directions transverse to the nanotube show substantial improvement due to functionalization (40% at 1 K), where the pristine nanotube system only sees minor improvements in transverse stiffness due to van der Waals effects (7% at 1 K) [25]. It is worth noting that functionalization causes sp^3 hybridization carbon sites on the sidewalls of the nanotube, and this lowers the stiffness of the composite system along the nanotube (E_{zz}), as seen in tables 1 and 2. It has been shown theoretically, however, that even a high degree of functionalization on the sidewall of the SWNT will only decrease the mechanical strength by 15% [47]. There are negligible differences in the in-plane Poisson’s ratio (ν_{xy}) between the functionalized and non-functionalized systems. There is a

Table 2. Material properties- covalently functionalized SWNT/Epoxy composite.

Temperature (K)	E_{xx}(GPa)	E_{zz}(GPa)	ν_{xy}	ν_{zx}	G_{xy}(GPa)
1	9.4	70	0.49	0.30	3.3
50	8.7	69	0.50	0.30	2.9
100	8.0	69	0.54	0.31	2.8
150	6.6	68	0.54	0.31	2.5
200	6.0	67	0.57	0.32	2.2
250	4.9	66	0.58	0.35	1.8
300	4.0	66	0.63	0.38	1.6
350	3.0	65	0.67	0.38	0.86

clear reduction in the out of plane Poisson's ratio (v_{zx}), meaning that there will be less contraction in the plane of isotropy (x–y) when the system is pulled along the nanotube direction (z) due to the nanotube functionalization. Finally, the shear modulus in the plane of isotropy (G_{xy}) has noticeably increased due to the covalent bonding to the SWNT.

A tension test in the plane of isotropy (x–y), where each atom was colored by its per-atom stress at various strain levels, is shown for the covalently functionalized SWNT/Epoxy nanocomposites in figure 9(a), and for the pristine SWNT/Epoxy nanocomposite in figure 9(b). MD results are statistical, and so the stress evolution of an individual atom is meaningless. However, when considering the stresses of every atom in the system at lower strain levels, the high stress (red) and low stress (blue) atoms tend to cancel, where at higher strain levels there are less low stress (blue) atoms. When averaging over all of the atoms and accounting for the volume, the average stress increases linearly with increasing strain as seen previously in figure 5(b). Figure 9(a) shows that at higher strains the atoms bonding the epoxy to the nanotube experience higher average stresses, demonstrating that stress is being transferred to the nanotube, leading to the higher stiffness levels seen in figure 8 when comparing the covalently functionalized SWNT/Epoxy nanocomposite to the pristine SWNT/Epoxy nanocomposite.

The thermal expansion vectors are founds for SWNT/epoxy composite systems. The thermal expansion in the plane of isotropy (x–y) and nanotube (z) directions for the SWNT/epoxy composite with pristine nanotubes are shown in figure 10. Since the structure is transversely isotropic, the results in the x and y directions are identical and the linear coefficient of thermal expansion is measured to be $55.3 \pm 5.1\ \mu\ ^{\circ}\mathrm{C}^{-1}$, which is approximately the thermal expansion coefficient of neat epoxy. This result is expected since there is no functionalization to the nanotube, so the epoxy is free to expand in the x–y plane. The expansion in the z-direction is found to be $6.9 \pm 1.4\ \mu\ ^{\circ}\mathrm{C}^{-1}$, where the thermal expansion is constrained by the nanotube which has a longitudinal coefficient of thermal expansion of $-1.2\ \mu\ ^{\circ}\mathrm{C}^{-1}$ [48]. For the covalently functionalized SWNT/Epoxy composite, the thermal expansion in the plane of isotropy (x–y) and nanotube (z) directions can be seen in figure 11. There is a negligible effect of the covalent bonding for thermal expansion on the x–y direction. However, even with only 4 covalent bonds the thermal expansion is reduced to $4.3 \pm 1.2\ \mu\ ^{\circ}\mathrm{C}^{-1}$ in the nanotube direction. This represents a 42% reduction when compared to the pristine SWNT/epoxy composite.

To create an isotropic composite epoxy system, the effects of randomly oriented nanotubes in the epoxy were explored. To achieve this, the stiffness tensor and thermal expansion vector are rotated and averaged over all possible orientations. The resulting system is isotropic and so can be compared with epoxy, done for the Young's Modulus in figure 12, shear modulus figure 13, and the linear coefficient of thermal expansion in figure 14. Adding randomly oriented nanotubes results in a very large increase in the elastic modulus for both the functionalized nanotube epoxy composite (200% increase at 1 K) and pristine nanotube epoxy composite

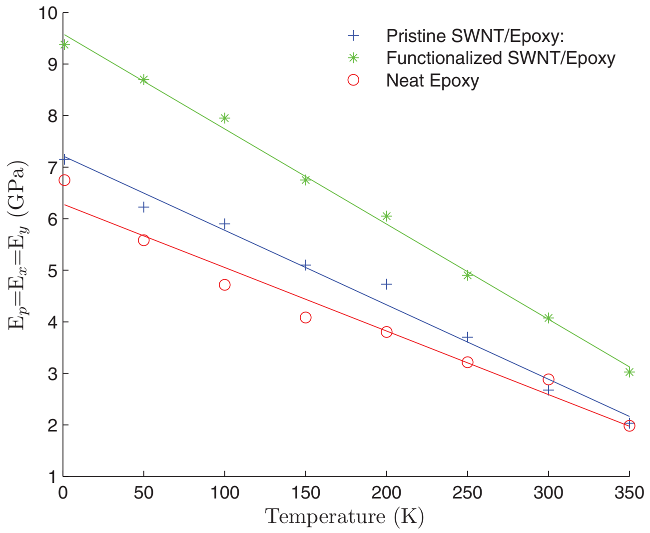

Figure 8. Elastic modulus in the plane of isotropy for the composite systems and plain epoxy (fully isotropic).

(180% increase at 1 K) when compared to neat epoxy. The coefficient of thermal expansion are seen to be reduced by 30% to $39.3 \pm 2.0\ \mu\ ^\circ\mathrm{C}^{-1}$ for the pristine SWNT/Epoxy composite system and 32% to $37.2 \pm 1.4\ \mu\ ^\circ\mathrm{C}^{-1}$ for the covalently functionalized SWNT/Epoxy composite system.

For all of the MD results shown in this paper, three different equilibrated structures were averaged, and properties for each structure were averaged across multiple time steps. This leads to two different types of errors due to averaging: time step averaging and sample-to-sample averaging. For the thermal expansion results, both sources of error are summed and the resulting error bars have been reported. For the transversely isotropic thermal expansion in figures 10 and 11, the cell length in the plane of isotropy and nanotube directions are used to calculate the linear coefficient of thermal expansion. For the thermal expansion of the equivalent isotropic systems, seen in figure 14, volume data is used to calculate the linear coefficient of thermal expansion.

Experimentally, it has been found that covalent functionalization of the SWNT to the epoxy will increase the tensile modulus when compared to neat epoxy [17–18]. Pristine nanotube and epoxy composite systems show a lesser improvement in mechanical properties than functionalized nanotubes due a lack of interfacial bonding across atomically smooth carbon nanotube surfaces [12–14]. Functionalization allows the load to be transferred to the nanotube from the polymer matrix and prevent slipping between the nanotube and the polymer [49]. It is important to note that the MD results shown here represent a material with a very high weight percentage of nanotubes (8 wt% SWNT) with perfectly dispersed, pristine, continuous nanotubes due to periodic boundary conditions. Studies have shown that an increasingly large wt% of nanotubes continues to increases the modulus of polymer/SWNT composites [13, 50, 51]. In particular, Zhu *et al* saw a 30% increase with 1 wt% functionalized SWNT in a EPON 862 and Curing Agent W composite system, and a 70% increase with 4 wt% SWNT [13]. Wang *et al* showed an increase of 60% in the modulus with just 1 wt% nanotubes that were covalently functionalized [16]. It has been shown at very high loading of non-covalently

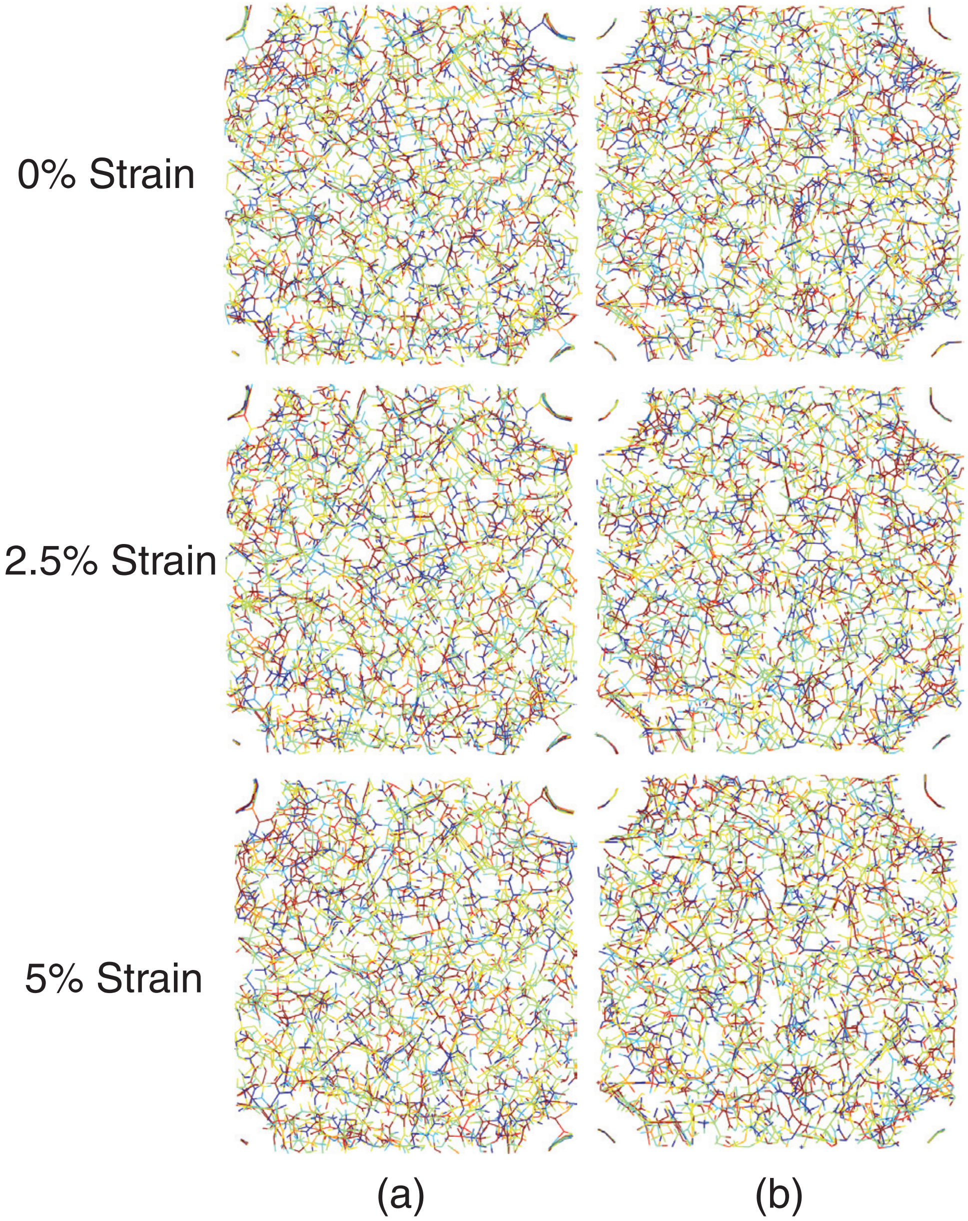

Figure 9. Atoms colored by high stress (red) and low stress (blue) at various strain levels for the a. covalently functionalized SWNT/Epoxy nanocomposite and b. pristine SWNT/Epoxy nanocomposite.

functionalized SWNTs, 20.5 wt% and 39.1 wt%, tensile modulus increases by 166% and 408% respectively [21].

Pizzutto *et al* measured the thermal dilatation of 0.25 wt% carboxylated single-walled carbon nanotubes without covalent functionalization. In the linear region of 25 °C–65 °C, the linear coefficient of thermal expansion measured to be 62 μ °C^{-1} for the plain epoxy, and 44 μ °C^{-1} for the SWNT/epoxy composite [11]. Adding in the SWNTs reduced the linear

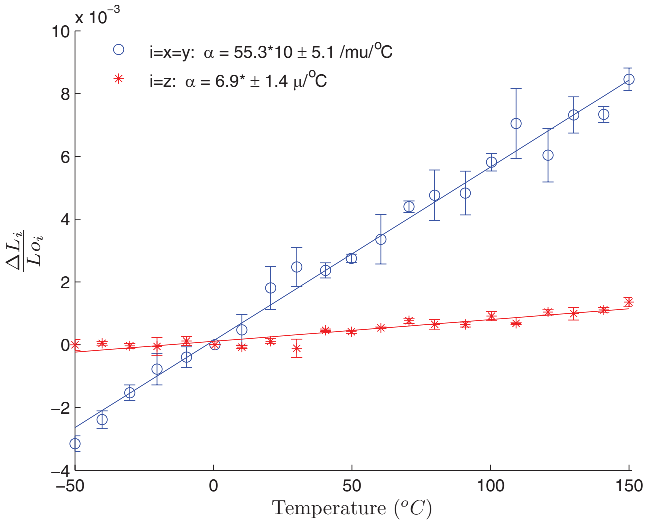

Figure 10. Thermal expansion for pristine nanotubes/Epoxy nanocomposites in the z-direction (along nanotube) and averaged in the x–y direction.

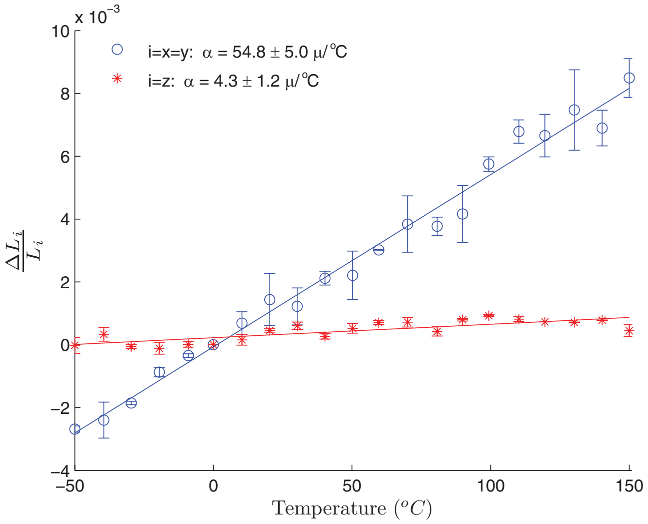

Figure 11. The thermal expansion for covalently functionalized SWNT/Epoxy nanocomposites in the z-direction (along nanotube) and averaged in the x–y direction.

coefficient of thermal expansion by 29%. For the MD simulation of the pristine SWNT/Epoxy system, as seen in figure 14, the linear coefficient of thermal expansion has decreased from 55.2 μ °C^{-1} for the neat epoxy to 39.1 μ °C^{-1}, a similar reduction of 30%. Wang *et al* studied functionalized SWNT-epoxy composites, and in the linear region of 50°C–120 °C, saw reduction in thermal expansion from 60 μ °C^{-1} for pure epoxy to 40 μ °C^{-1} for oxidated single wall nanotubes that showed covalent functionalization, a reduction of 33% [19]. This is very similar to the 32% reduction shown for functionalized nanotube seen in this study. A summary of experimental comparisons to the MD results for thermal dilatation is shown in figure 15.

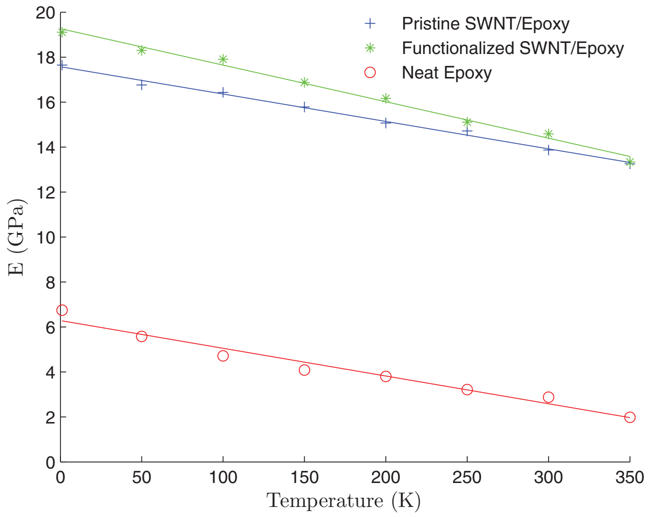

Figure 12. Young's Modulus for for an isotropic non-functionalized SWNT/epoxy composite, isotropic functionalized SWNT/epoxy composite and neat epoxy.

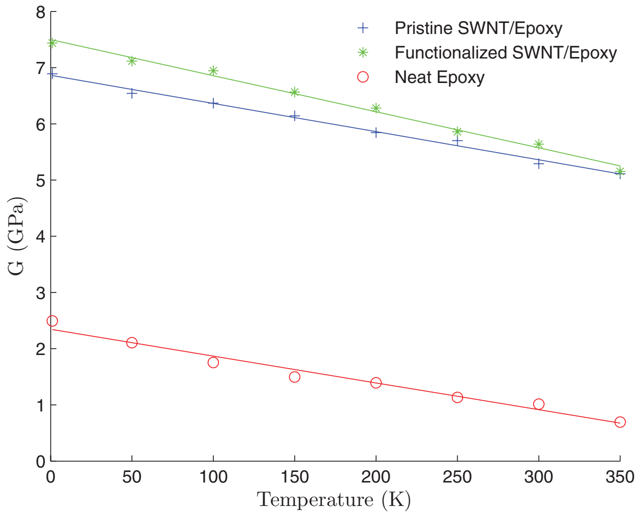

Figure 13. Shear Modulus for an isotropic non-functionalized SWNT/epoxy composite, isotropic functionalized SWNT/epoxy composite and neat epoxy.

6. Conclusions

Molecular dynamics have been used to analyze the thermal and mechanical properties of SWNT/epoxy nanocomposites by adding functionalized and pristine carbon nanotubes to cross-linked polymers. The epoxy model built using a 'dendrimeric' approach was verified by obtaining the correct density, showing the system to be isotropic, and by comparing the thermal expansion to experiments. The change in the mechanical and thermal expansion properties was studied along and perpendicular to the nanotube for both epoxy/SWNT nanocomposites, and the full stiffness matrices and thermal expansion vectors were obtained.

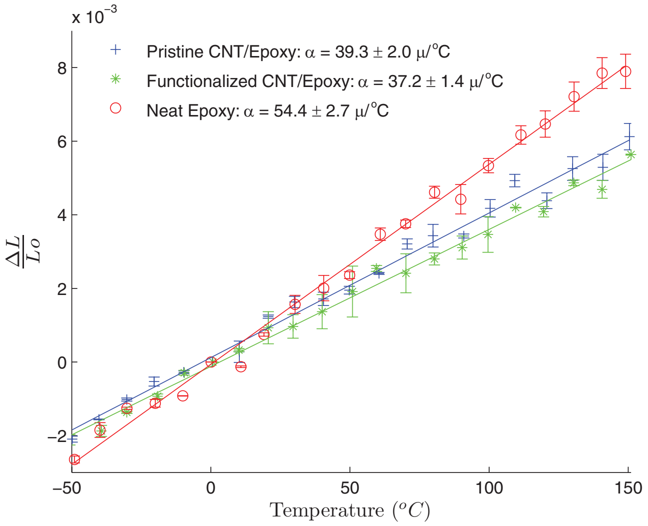

Figure 14. Thermal expansion for an isotropic non-functionalized SWNT/epoxy composite, isotropic functionalized SWNT/epoxy composite and neat epoxy.

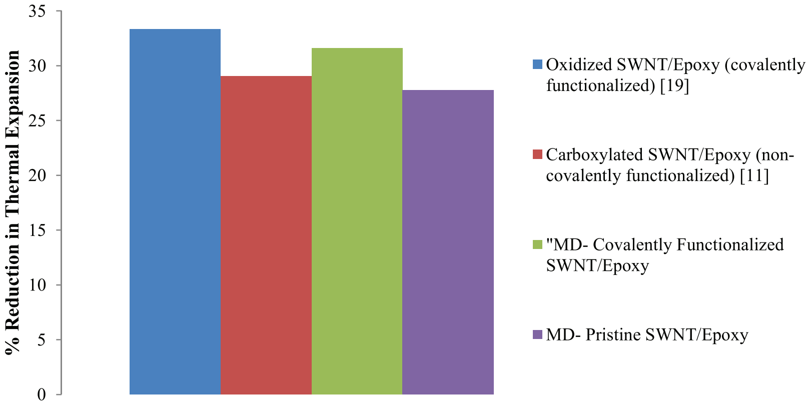

Figure 15. Percent Reduction in linear coefficient of thermal expansion due to the addition of nanotubes to epoxy [11, 19].

As expected, there was huge increase in stiffness along the nanotube direction for both the pristine SWNT/epoxy and functionalized SWNT/epoxy composites. The direction transverse to the nanotube saw a 40% increase in stiffness due to covalent functionalization over neat epoxy at 1 K whereas the pristine nanotube system only saw a 7% increase due to van der Waals effects. The thermal expansion along the nanotube was significantly decreased due to the negative coefficient of thermal expansion of a SWNT. An additional 42% reduction in thermal expansion in the direction of the nanotube was realized for the covanently functionalized SWNT/epoxy composite when compared to pristine SWNT/epoxy composite. The thermal expansion transverse to the nanotube showed negligible change compared to to the neat epoxy for both nanocomposite systems. The stiffness matrices and thermal expansion vectors were rotated over every possible configuration to simulate the effects of an isotropic system of randomly oriented nanotubes in the epoxy. The nanocomposite systems showed substantial improvements over the plain epoxy in terms of higher stiffness (200% for the covalently functionalized SWNT/Epoxy composite) and lower thermal expansion (32% reduction for the covalently functionalized SWNT/Epoxy composite). The increase in stiffness and reduction in thermal expansion were verified by comparison with experiments. Future work will consist of investigating other thermomechanical properties for the nanocomposite systems, such as thermal conductivity [52]. Additionally, it is of interest to the authors to study the effects of curing conversion, the degree of functionalization and bond distribution, as well as the effects of varying the chirality and number of walls of the nanotube.

Acknowledgments

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