MOLECULAR DYNAMICS SIMULATIONS OF AN EPOXY – DEFECTIVE SWCNT COMPOSITE SYSTEM

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Introduction

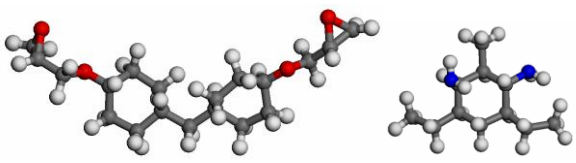
Computational techniques such as molecular dynamics (MD) simulations have emerged as an alternative to the traditional experimental and theoretical methods of estimating mechanical properties of the Epoxy – Carbon Nanotube composite systems. However, differences have been observed between results obtained from experiments and those obtained from MD simulations with the experimental results being lower. This paper presents the effect of carbon vacancy defects in the single wall carbon natotube (SWCNT) on the Young's modulus of the EPON 862-DETDA-SWCNT composite evaluated through molecular dynamics simulations performed with Accelrys and Materials Studio.

Since their discovery, Carbon nanotubes (CNT) have gained significant attention because of their superior chemical, mechanical and thermo-physical properties. Inclusion of CNTs in polymer matrices have shown significant improvement of properties compared with the properties of the parent polymers, however, defects in these CNTs have also been observed to have detrimental effects on the mechanical properties of the composites.

Methodology

All molecular models were created and simulated in Materials Studio/Discover by Accelrys. The potential energy of the models was characterized by the COMPASS force field with the non-bond energies characterized by the Vander Walls and Coulomb's interactions.

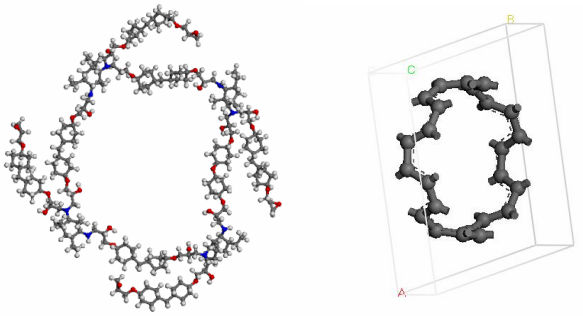
Figure 1 shows the molecular structures of EPON 862 and DETDA.



a. b.

Figure 1. (a) EPON 862 and (b) DETDA molecular structures from Materials Studio

The recommended weight ratio of EPON 862 to DETDA for a fully cured composite during processing is 100:26.4. Because EPON 862 has a molecular weight of 312, and DETDA has a molecular weight of 178, the molecular ratio of the fully cured composite was approximated to 2 molecules of EPON 862 to 1 molecule of DETDA. The fully cured composite was therefore constructed with 8 molecules of EPON 862 and 4 molecules of DETDA as shown in Figure 2a. Figure 2b shows a unit cell of the SWCNT cell



a. b.

Figure 2. (a).Fully cured (8:4) EPON 862 cross linked with DETDA (b)SWCNT unit cell.

Three composite models with SWCNT weight percentages between 7% and 12% were used in the investigations. The three molecular models of the defective SWCNT (DSWCNT) cured epoxy system used had the following configurations and weight percentages:

1. 3 unit cells of DSWCNT and 2 fully cured epoxy matrix corresponding to the CNT weight percentage of 11.28-11.58% at this configuration.
2. 4 unit cells of DSWCNT and 3 fully cured epoxy matrix corresponding to the CNT weight percentage of 10.34-10.49% at this configuration.
3. 4 unit cells of DSWCNT and 4 fully cured epoxy matrix corresponding to the CNT weight percentage of 7.95-8.08% at this configuration.

The models were minimized to obtain the lowest energy configuration. A cascade of the steepest descent minimization method and the Fletcher-Reeves method were used for the minimization. The minimized models were then equilibrated with the NVT ensemble for 100ps at 298 K. A sample simulation cell is shown in Figure 3.

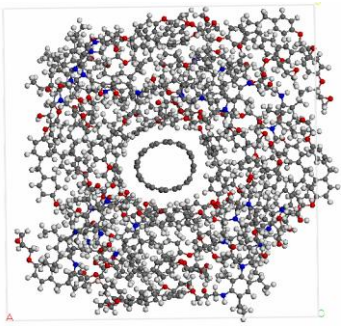


Figure 3. Simulation cell showing the CNT embedded in the fully cured epoxy matrix

Simulated annealing was used to mimic the curing cycle of EPON 862-DETDA-SWCNT composite and to ensure that the final configuration had the lowest energy possible. A characteristic property of simulated annealing is lowering the temperature slowly in stages to allow thermal equilibrium to be attained at each stage. The cell was heated to 498 K, and the temperature was dropped to 298 K in steps of 10 K using the NPT ensemble with a specified pressure of 0.0001 GPa (1 atm). MD simulations were run at each temperature for 200 ps with a time step of 1 fs. The final structure of each step was used as the starting structure of the next step. The density was noted at each step. At 298 K, an analysis of the elastic properties was performed by saving 10 trajectories and using them for the estimation.

Defect Types

The effect of 2 and 4 carbon vacancy defects in the SWCNT on the mechanical properties of the composite were studied. Incorporation of the 2 defects was accomplished by removing two adjacent vertical carbon atoms on one side of the nanotube. Because of the short length of the nanotube removal of the 4 defects was accomplished by removing two adjacent vertical carbon atoms on opposite sides of the nanotube. Figure 4 shows an image of the DSWCNT with 2 adjacent carbon atoms removed

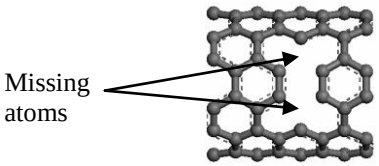


Figure 4. SWCNT with 2 missing adjacent carbon atoms

With the SWCNT having a density of 1.9 g/cm^3 and the epoxy resin having a density of 1.2 g/cm^3, the rule of mixtures densities of the composites were calculated. To obtain the Young's modulus at the exact densities for each of the models, simulated annealing runs were conducted at three different lattice configurations for each model and interpolated to the exact density. The corresponding Young's modulus was then evaluated.

Results

Table 1. Percentage reduction in Young's modulus with the introduction of defects

CNT weight % (No defect)	**Young's Modulus [GPa]**	
	% reduction with 2 defects in composite	**% reduction with 4 defects in composite**
11.87	17.9 (2.78% defects in CNT)	29.6 (5.56% defects in CNT)
10.69	15.7 (2.08% defects in CNT)	25.1 (4.17% defects in CNT)
8.24	13.6 (2.08% defects in CNT)	21.9 (4.17% defects in CNT)

Table 1 can be interpreted as follows: For the 11.87% SWCNT composite, introduction of 2.78% of defects into the SWCNT resulted in 17.9% overall reduction in the Young's modulus of the composite while introduction of 5.56% of defects into the CNT resulted in 29.6% reduction in the Young's modulus of the composite. For the 10.67% SWCNT composite, introduction of 2.08% of defects into the SWCNT resulted in 15.7% overall reduction in the Young's modulus of the composite while introduction of 4.17% of defects into the CNT resulted in 25.1% reduction in the Young's modulus of the composite. For the 8.24% SWCNT composite, introduction of 2.08% of defects into the SWCNT resulted in 13.6% overall reduction in the Young's modulus of the composite while introduction of 4.17% of defects into the CNT resulted in 21.9% reduction in the Young's modulus of the composite.

Conclusion

This study showed that 2 carbon vacancy defects in the SWCNT resulted in a reduction in Young's modulus of between 13-18% as compared with the pure models of the EPON 862-DETDA-SWCNT while four vacancy defects resulted in a reduction of between 21-30% reduction as compared with the pure models of the composite.