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CHEMICAL BONDING OF POLYMER ON CARBON NANOTUBE

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ABSTRACT

Recently, carbon nanotubes are considered as nanoscale fibers, which can strengthen polymer composite materials. Nanotube-polymer composite materials can be used for micron scale devices with designed mechanical properties and smart polymer coating to protect materials under extreme physical conditions such as microsatellites. To explore these possibilities it is important to develop a detailed atomic scale understanding of the mechanical coupling between polymer matrix and embedded nanotubes. In this work we study the chemical bonding between polymer molecules and carbon nanotubes (CNTs) using molecular dynamics. Study shows that the bonding between polyethylene and a CNT is energetically favorable. Chemical bonds can be formed at multiple sites, which make the mechanical load transfer from the polymer chain to the tube more favorable. We will discuss about the resulting mechanical coupling between the CNTs and polymer matrix to develop efficient nano-composite materials.

INTRODUCTION

Because of their unusual mechanical [1,2] and electronic properties [3,4], there are extensive studies on carbon nanotube (CNT) as a nano-fiber to improve the performance of a matrix or to achieve new properties [5-8]. One distinguished property of a CNT is its high strength, coming from the strong sp^2 bonds, which makes CNTs good candidates as reinforcement fibers to matrix. The other advantage of a CNT as a fiber is its large surface area, which is good for chemical bonding or adhesion, an important factor for a good composite. One essential issue in the reinforcement of a fiber composite material is that the embedded fibers must have large enough aspect ratio so that there is enough load transfer through the interfacial shear stress and consequently the full strength of the fiber can be used. For a micrometer long CNT with diameter in nano-meter scale, the aspect ratio can be 1000 or higher, which is much larger than usual common fibers. There are experiments using TEM to investigate CNTs (both multi-walled and single-walled CNTs) as reinforcement fibers in polymer matrix [6,8]. Although people found load transfers exist between CNTs and polymer matrix with cases of showing signs of quite large load transfers in some polymer-CNT composites [9], which suggest possible chemical bonding between CNTs and polymers, it is not clear what is the mechanism of the load transfer. It is thus important to understand the mechanism of load transfers at atomic level to facilitate the development of high performance CNT-polymer composites.

MOLECULAR DYNAMICS SIMULATIONS

When chemical bonding is present, the interfacial shear energy between a fiber and a matrix is typically in range of 50 to $300J/m^2$ [10]. If only Van der Waals interactions are

Table I: MD simulations of chemical bonding of hydrogen atom on several carbon systems using Tersoff-Brenner potential compared with DFT calculations [12].

Hydrogen @		C_{60}	CNT(10,0)	Graphite
Bond Energy(eV)	TB potential	-3.68	-3.00	-2.29
	DFT	-3.18	-2.39	-1.63
Bond Length(Å)	TB potential	1.085	1.087	1.092
	DFT	1.115	1.127	1.142

present, such shear energy will be in range of 50 to 350mJ/m^2 [11]. Consequently strong chemical bonding is expected to be important for high performance of fiber composites. In this work, we will study the possibility of the chemical bonding between CNTs and polymer matrix to improve the load transfers at the interfaces.

We use molecular dynamics simulation to study the CNT-polymer system. Tersoff-Brenner potential [13, 14] is used for the carbon-carbon and hydrocarbon interactions. This potential is parameterized from the structure of graphite, diamond and several hydrocarbon systems and has been used in several simulations to study the mechanical properties of carbon nanotubes [15,16]. In Brenner's original paper, the hydrogen absorption on a diamond surface was studied using this potential [14].

Before investigating the chemical bonding between CNTs and polymers, we first test the accuracy of Tersoff-Brenner potential for the bonding of hydrogen atom on several carbon systems. In Table I, the bonding energies and C-H bond lengths of hydrogen atom on C_{60}, CNT (10,0) and graphite, are listed; and compared with the results from density functional theory (DFT) calculations [12]. DFT is considered to give more accurate description of interactions. The comparison in the table shows that the bond energies and bond lengths determined by Tersoff-Brenner potential are in good agreement with the DFT results. For both cases, the chemical bond of Hydrogen on C_{60} is found to have the largest bonding energy and shortest bond length because of the high chemical reactivity induced by the higher curvature of the local carbon-bonding configuration of C_{60}.

We now proceed to study the chemical bonding between polymers and CNTs. Polyethylene (a linear chain polymer) and CNT (10,0) are chosen for our simulations. We found polyethylene can be chemically bonded to the CNT, shown in Figure 1.
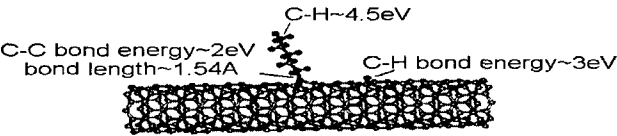

C-H~4.5eV

C-C bond energy~2eV
bond length~1.54A

C-H bond energy~3eV

Figure 1: Chemical bonding of polyethylene on CNT (10,0)

With one hydrogen atom removed and bonded to the CNT with energy 3eV, polyethylene can form sp^3 bond with a π orbital on the CNT surface. Our MD simulation shows that the C-C bond energy between the polymer chain and the CNT is 2.0 eV, and that the bond length is 1.54 Å, which is close to the bond length of C-C in the polyethylene.

It is expected that the load transfer from polymer matrix to a CNT can be enhanced with the presence of such chemical bonding. Furthermore, the load transfer is expected to increase for more than one bond attached to the CNT. More loads can be carried over by polymer chains to larger section of the CNT surface, and the larger strain energy can then be distributed over the nanotube. In this way, the multi-site bonds can act together in response to an applied mechanical load.

We use MD simulation to study whether a multi-site bonding will increase the load transfers from polymers to CNTs. Mechanical loads to a polymer chain are applied in two cases: single site bonding (Figure 2a) and double site bonding (Figure 2b). The detailed mechanical deformations of the C-C bonds within the polymer chain and at the polymer-CNT interface in response to the external load are plotted in Figure 3a and Figure 3b for both cases.

Figure 3 shows that in both cases the C-C bond within the polymer reaches its maximum deformation (i.e. the largest C-C bond length before breaking the bond) first, followed by the C-C bond at the polymer-CNT interface. The difference in the case of single site bonding and double site bonding is that in the later case, the two C-C bonds at the interface of the polymer and the CNT induce more rigid response to the mechanical load. After the C-C bonds reach their maximum deformations, mechanical loads are
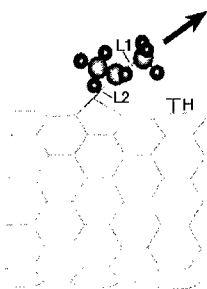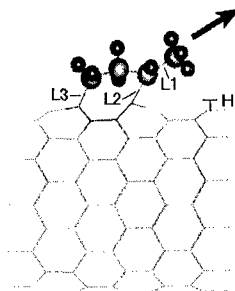

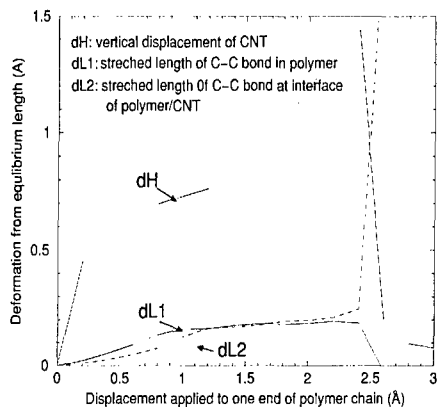**Figure 2a:** single site bonding

Figure 2b: Double site bonding

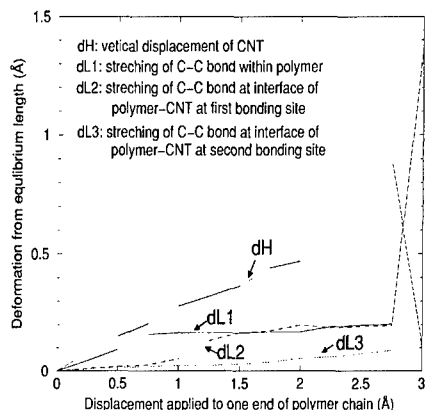**Figure 3a:** single site bonding
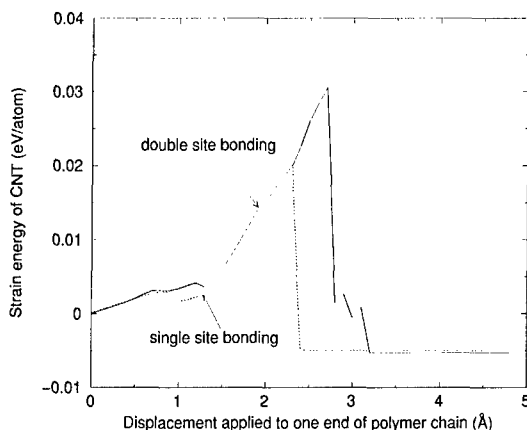

Figure 3b: double site bonding

Figure 4: Strain energy transferred to CNT by mechanical loading process

continuously transferred to the CNT until bonds are broken either at the polymer-CNT interface or within the polymer chain. In Figure 4, the strain energy transferred to the CNT as a function of the mechanical loading is plotted for both cases. It is clear that more loads are transferred in the case of double site bonding, and that the CNT-polymer interface accommodates a higher shear strain.

CONCLUSIONS

In this work, we used classical molecular dynamics with Tersoff-Brenner potential to

study the chemical bonding between polymers and carbon nanotubes. We found that it is energetically favorable for polyethylene to form chemical bonding with a CNT with bond energy about 2eV. The load transfer test using MD simulations shows that a multiple-site bonding is more favorable for load transfers.

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