

# MICROSTRUCTURE AND BONDING STRENGTH OF CARBON NANOTUBES DIRECTLY GROWN ON A CARBON FIBER SUBSTRATE

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## Abstract

*Carbon nanotubes (CNTs) are directly grown on a carbon fiber (CF) surface using chemical vapor deposition to improve the interfacial properties of the CF composite. To characterize the interfacial properties quantitatively, the microstructure of the interface and the bonding strength of the CNTs on the CF surface were systematically investigated in this study. Through the observation of the microstructure by high-resolution transmission electron microscope, the interface between the CNT and the CF surface was found to consist of the covalent bonding. This interfacial structure observed was confirmed through a molecular dynamic (MD) simulation. Finally, the bonding strength of the CNTs on the CF surface was measured by separating a bundle of CNTs from the CF surface and compared with the calculated results from MD simulation, again demonstrating that the covalent bonds were formed at the interface between CF surface and CNTs.*

## 1 Introduction

Due to their high aspect ratio, large surface area, low density, and outstanding mechanical, thermal, and electrical properties, carbon nanotubes (CNTs) have stimulated a considerable amount of research, leading to numerous potential applications [1], including field-emission displays, bio-sensors, microelectrodes, and structural composites [2]. CNTs have been incorporated into these applications in a variety of forms, e.g., dispersed in a media [3], assembled in mats or yarns [4], and anchored to a substrate [5]. For the latter case, a strong interaction between the CNTs and the substrate is required to maintain good reliability for the long-term use.

Recently, hierarchical structures by grafting CNTs onto a carbon fiber (CF) surface have been the subject of much research in an effort to improve the weak interface between the CF reinforcement and the matrix in CF-reinforced composites by utilizing CNT anchoring effect [6]. To characterize the effect of CNT anchoring on the interfacial shear strength of CFs, the interface between CNTs and the CF surface, including the bonding strength, should be investigated, however, few research have been conducted [7,8].

The bonding structure between CNTs and the substrate is determined by the growth mechanism of the CNTs. Although their growth mechanism is still not clearly understood, the most commonly accepted growth model of CNTs is the vapor-liquid-solid (VLS) model [9]. In this model, hydrocarbons are catalytically decomposed around the catalyst nanoparticles, after which carbon atoms are adsorbed into the nanoparticles. When a supersaturated state is reached, the carbon atoms precipitate into a tubular and crystalline form [10] by the tip-growth or base-growth morphology. These morphologies determine the interfacial structure between CNTs and substrates given that direct bonding between CNTs and substrate can be formed only in the tip growth mode. This is the main reason for the interface between CNTs and CF to be unique, i.e., CNTs mostly grows on CF surface in the tip growth mode.

In this study, CNTs are directly grown onto a CF surface by means of chemical vapor deposition (CVD). The microstructures of the interface between the CNTs and the CF surface are investigated using a high-resolution transmission-electron microscope (HR-TEM), based on which molecular model is constructed to explain the interface. The bonding strength is then calculated using molecular mechanics at the atomic level based on the COMPASS potential [11]. Experiments are also carried out to measure the bonding strength of a CNT to a CF.

## **2 Experimental and molecular simulation**

### *2.1 CNT growth on a CF surface using the CVD process*

Poly (acrylonitrile) based high-strength CFs (T700SC-12000-50C, Toray) with sizing agents were used after cleaning in distilled water by ultrasonic vibration. The sizing agents on the CF surface were removed using a thermal treatment. Nickel (Ni) as a catalyst for the CNT growth was coated onto the desized CF surface by means of metal sputtering with a thickness of 2 nm. The Ni films on the CFs were converted to Ni nanoparticles by an annealing process. CNTs were grown on the CF surface with acetylene gas as a carbon source and with H<sub>2</sub> and Ar. Details on these processes can be found in [12].

### *2.2 Microstructural observation*

The morphologies of CNTs grown on the CF surface were observed using field emission-scanning electron microscopy (FE-SEM, SUPRA 55VP from Carl Zeiss, Inc.). The microstructure of the interface between the CNTs and the CF surface was investigated using a high resolution- transmission electron microscope (HR-TEM, JEM-3000F from JEOL Ltd.). The specimens were prepared using a focused ion beam device (FIB, SMI3050SE from SII Nanotechnology Inc.). The CNT-grafted CF was fixed on a silicon wafer. Amorphous carbon was then deposited on the surface of the CNT-grafted CF to prevent damage during the FIB process using Ga<sup>+</sup> ions.

### *2.3 Molecular simulation of the bonding energy of CNTs on the CF surface*

The geometry of the observed interface of the CNT-grafted CF was established in molecular level using a commercial atomic simulation program (Material Studio). The detailed surface of CFs was not modeled; instead ideal graphite structure was used to model the CF surface. The junctions between the CNTs and the graphite were then established for multi-walled CNTs (MWCNTs) with 3 to 6 walls considering the actual inter-wall spacing. A unit-cell with lattice parameters of  $a=78.72\text{\AA}$ ,  $b=78.72\text{\AA}$ ,  $c=57.2\text{\AA}$ ,  $\alpha=90^\circ$ ,  $\beta=90^\circ$ , and  $\gamma=120^\circ$  was established by assuming the hexagonal packing of the CNTs. The energy of the unit-cell was minimized to find the optimized microstructure of the interface. The displacement was then applied until the interfacial structure was broken, enabling to calculate the bonding strength of CNTs on CF surface.

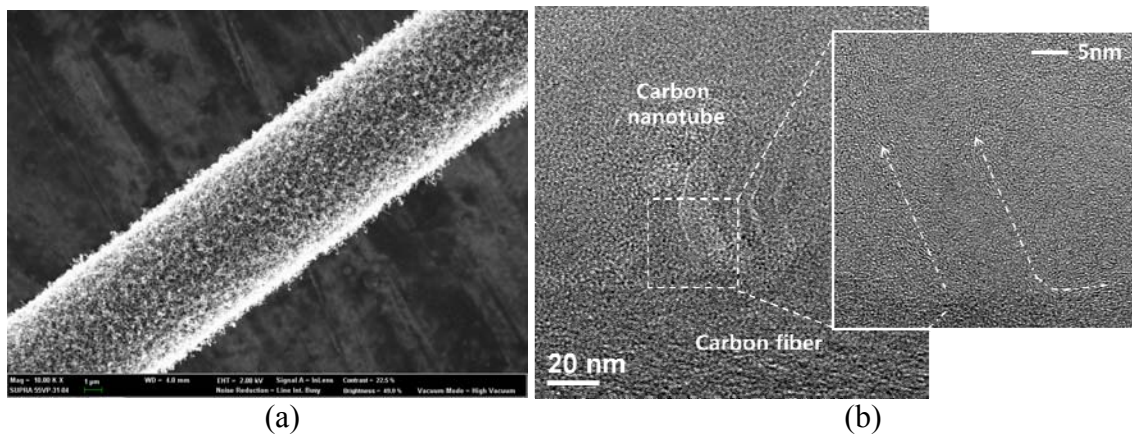
### 2.4 Bonding strength measurement of CNTs grown on a CF surface

CNT growth was controlled by introducing the catalysts only over half the length of the CF. Polyvinyl alcohol (PVA) was deposited over CF surface without CNTs grown to reduce the friction in later pulling test. The CF was then mounted into a micro-load universal machine (with a sensor of 100 g), after which the one end of the CF was pulled at a cross-head speed of 0.05mm/min. CNTs were debonded from the CF surface by applied shear force during test. All the test procedures were recorded in a video through a digital microscope (Mi-7000P from Magiceyes Co.). The debonding tests were conducted for at least six single fibers. The debonding energy was then calculated from the area of the load-displacement curve measured during the debonding test.

## 3 Results and discussion

### 3.1 Interface between CNTs and the CF surface

The CNTs were uniformly grown on the CF surface as shown in Fig. 1 (a). In this study, most of the CNTs were grown in the tip growth, which was confirmed by SEM and HR-TEM. The nanoparticles was not observed at the interface between the CNTs and the CF surface (Fig. 1 (b)) but at the tip of the CNTs. Many connections between the CNTs and the graphitic layers of the CF surface were observed at the interface, indicating that the interface was formed by covalent bonds due to possibly the diffusion and precipitation of carbon atoms via the nanoparticles into graphitic layers in CF.



**Figure 1.** SEM and HR-TEM images of CNT grafted CF. (a) the morphology of the CNTs grown on the CF surface and (b) the microstructure of the interface between the CNTs and the CF surface.

### 3.2 Bonding energy calculation of CNTs grown on the CF surface

A displacement was applied to the top of the CNT, while the graphitic layer at its opposite side were fixed. As the displacement increased, the potential energy of the unit-cell increased until the interface failure occurred, thereafter the potential energy of the unit-cell suddenly decreased. Here, the maximum energy change of the unit-cells was assumed as the bonding energy of each CNT with the graphite. According to the number of walls, the bonding energy of single CNT was calculated in Table 1.

Number of walls	Bonding energy, $E_{bonding}^0$ (kcal/mol)
3	16882
4	35564
5	45427
6	83121

**Table 1.** The bonding energy obtained from the molecular simulation.

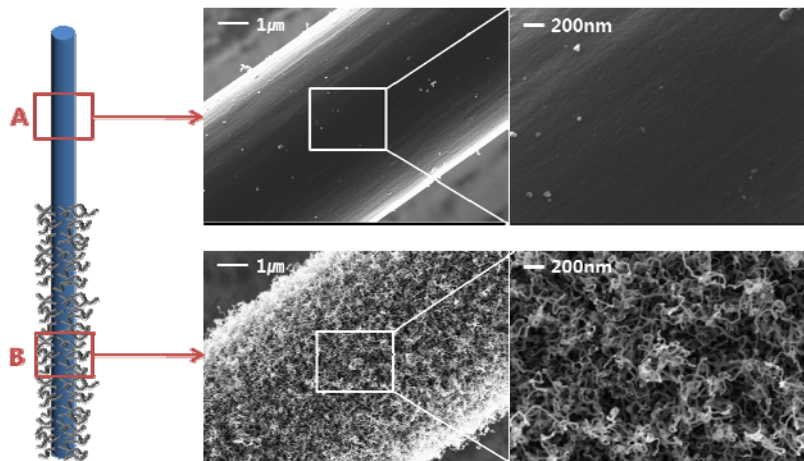
The relationship between the bonding energy and the number of CNT walls was obtained from the data in Table 1 as follows.

$$E_{bonding,N}^0 = 1466N^{2.2343} \quad (1)$$

Here,  $E_{bonding,N}^0$  is the bonding energy (kcal/mol) according to the number of CNT walls, and  $N$  is the number of CNT walls. The bonding energy of a CNT on the CF surface was calculated considering the number of CNT walls (23 walls), as obtained from the HR-TEM observation of the CNTs, finding 7.35 pJ. The interfacial bonding energy calculated was from 20 to 100 times stronger than that for a CNT on a Si or Cu substrate [13]. This result indicates that the interface may have formed by a strong bond such as covalent ones, as observed in the experiments.

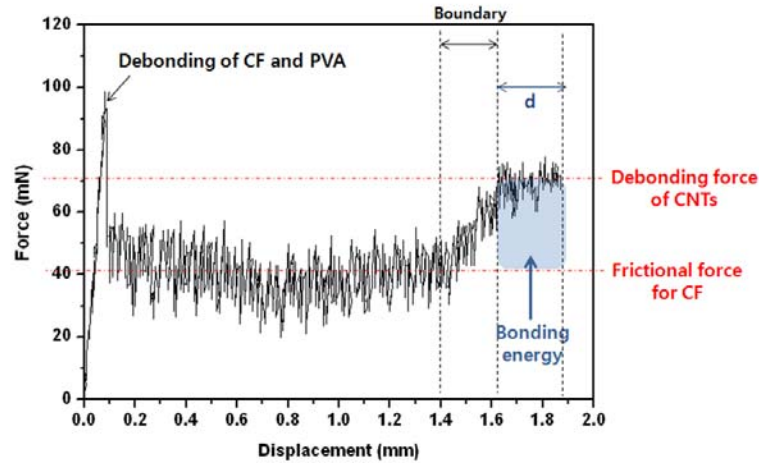
### 3.3 Bonding strength measurement of CNTs grown on the CF surface

CNT grafted CFs were prepared by introducing the nanoparticles limitedly on the CF surface. Fig. 2 shows a smooth surface for no catalyst-deposited region (Fig. 2. A) and uniformly grown CNTs on catalyst-deposited surface (Fig. 2. B).



**Figure 2.** The morphologies of CNT grafted CF used for the debonding test. Left: a schematic drawing of CNT configuration on CF surface. Right: SEM image.

The debonding testing was conducted using the procedure explained section 2.4. Fig. 3 shows a typical force-displacement curve measured during the debonding test. A debonding between the smooth surface of the CF and the PVA (used as a detaching material) occurred first, representing the initial peak force in the early region of the curve. After this debonding, only the frictional behavior of PVA against CF surface was recorded. The force started to increase when the debonding of the CNTs occurred at the boundary region. The force then became stabilized by the debonding of the CNTs in the region where the CNTs were grown uniformly.



**Figure 3.** Force-displacement curve for the debonding of CNTs from the CF surface

The total bonding energy was calculated by integrating the area of the force-displacement curve where the force shows a plateau. The bonding strength of the CNTs grown on the CF surface was calculated from the following equation (2):

$$\sigma_{bonding} = \frac{dE/dl_d}{2\pi R l_d n \times \pi r^2} \quad (2)$$

$$n = \frac{0.5}{\sqrt{3}/4a^2}$$

Here,  $\sigma_{bonding}$  denotes the bonding strength of a CNT,  $dE/dl_d$  is the total debonding force for the effective debonded area,  $l_d$  is the displacement pertaining to the uniform debonding of the CNTs,  $R$  denotes the radius of the CF,  $n$  is the number density of the CNTs grown on the CF surface,  $a$  is the distance between the CNTs, and  $r$  represents the radius of a CNT. The total bonding force was determined using the slope of the bonding energy-displacement curve. The distances between the CNTs were measured to be approximately 86 nm by investigating FE-SEM images of the CF surface after the debonding of the CNTs. The bonding strength of a CNT on the CF was finally determined to be 70.69MPa, which was much higher than that on other substrates such as SiC and metal (0.5-2.5MPa) [13]. This result gain indicates that the covalent bonding between the CNTs and the CF was formed.

#### 4 Conclusions

The microstructure of the interface and the bonding strength of the CNTs grafted on the CF surface were investigated. The interface between the CNTs and the CF surface was found to consist of covalent bonds between the CNT walls and the graphitic layers of the CF surface. The bonding energy of the CNTs was determined to be 7.35 pJ in a molecular simulation, which was much stronger than the bonding energy of CNTs grown on other types of substrates. The bonding strength of the CNTs on the CF surface (about 71 MPa) was measured by separating a bundle of CNTs from the CF surface, again demonstrating that a strong interface between CNTs and CF surface was formed.

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