# MECHANICAL PROPERTIES OF CARBON-CARBON COMPOSITES REINFORCED WITH CARBON NANOTUBES OR CARBON NANOFIBERS

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**Keywords**: *Carbon-carbon composites, mechanical properties, carbon nanotubes, carbon nanofibers, phenolic resin.*

***Abstract***

*The mechanical properties of CNTs or CNFs reinforced phenolic resin matrix composites and carbon/carbon (C/C) composites were investigated. The C/C composites were obtained by pyrolyzing the phenolic resin composites. For the phenolic resin composites, limited strength enhancement was measured. However, better reinforcing results were obtained for CNF reinforcement as compared to the CNT reinforcement due to the better interfacial bonding. CNF reinforcement also showed better results for the modulus measurement than those of CNTs. Contrary to the phenolic resin composites, CNTs showed better reinforcing results for C/C composites carbonized at 1000 and 1400 ℃. For C/C composites heat treated at 2400 ℃, the flexural strength values were lower than those at 1000 and 1400 ℃, and the difference between different reinforcements was not significant. Compared with the flexural strength, the enhancement of flexural modulus was much more significant.*

## 1 Introduction

The superior mechanical properties of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) make them the ideal candidates for composite reinforcement. Although some experimental measurements indicated the enhancement of strength with the addition of CNTs into the polymer matrix [1-4], results without or with limited strength enhancement were also reported [3,4]. Two important issues concerning the applications of CNTs and CNFs in the composite reinforcement need to be overcome. The first is the uniform dispersion of these nano-reinforcing materials in the polymer matrix. The second is the effective stress transfer from the CNTs to the composite. For the effective stress transfer, the bonding between the reinforcement and the matrix should be strong, which make the surface properties of the CNTs and CNFs important.

Compared with the CNT-polymer composites, few experimental results for the CNT- and CNF-reinfored carbon-carbon (C/C) composites were reported. In this study, the mechanical properties of C/C composites derived from the CNT- and CNF-phenolic resin composites, were studied. The effects of microstructure and diameter of the CNT and CNF on the mechanical properties of composites were discussed.

## 2 Experimental

### 2.1 Sample Preparation

CNTs and CNFs with different microstructures were used as the composite reinforcements. The CNTs have a tube or bamboo-like structure (Fig. 1(a) and 1(b)), and the CNFs, produced in our laboratory (40-60 nm), have a structure with internal conical cavities (Fig. 1(c)). Two types of CNTs with different diameter distributions, 10-20 nm and 60-100 nm, were also used to study the size effect. For the fabrication of phenolic resin-based composites, the vacuum bag hot pressing technique was used after mixing the CNTs and phenolic resin with an aid of ultrasonification and forming the B-stage sample. The as-cured phenolic resin composites were then pyrolyzed to convert into C/C composites. Carbonization of the as-cured composites was performed at 1000℃ in a horizontal tube furnace under an argon atmosphere. For composites heat treated above 1000℃, a carbonization heat treatment at 1000℃ was performed in advance. The heat treatment above 1400℃ was carried out in an Astro

1000-3060-FP20 graphite furnace under a helium atmosphere.

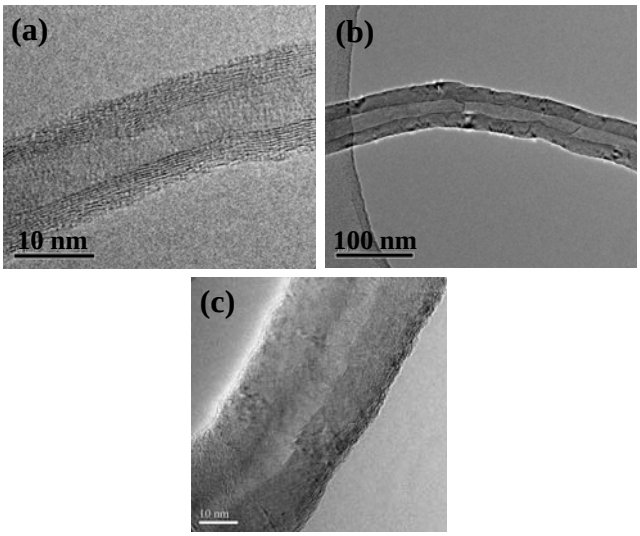


Fig. 1. TEM images: (a) CNT 10-20 nm, (b) CNT 60-100 nm, and (c) CNF.

### 2.2 Characterization

The mechanical properties and fracture behavior were studied using the three-point bending test according to ASTM D-790. The rectangular plate samples were cut from the composite panel. The dimensions of the samples were about 50 by 10 by 3 $mm^3$. The support span was 25 mm and the crosshead speed was 0.1 mm/min. The fracture surfaces of the as-cured phenolic resin composites and the corresponding C/C composites after bending tests were observed using scanning electron microscopy (SEM). The arrangement of graphene layers in the CNTs and CNFs was characterized by the high resolution transmission electron microscopy (HRTEM).

## 3 Results and Discussion

### 3.1 Phenolic Resin Composites

Fig. 2 shows the flexural strength of CNT- and CNF-reinforced phenolic resin composites. Although the strength enhancement was limited, better reinforcing results were found for CNF reinforcement as compared to the CNT reinforcement. The reason could be attributed to the CNF structure, which reveals more graphite edge planes on the outer surface and results in better bonding. In general, the flexural strength decreased with increasing loading of reinforcement due to the formation of defects in the composite fabrication process. For the CNT reinforcement, bettter results were found for the bigger diameter CNT due to the larger surface area for the smaller diameter CNT and consequently more defect formation. For the flexural modulus (Fig. 3), the CNF reinforcement also showed better results than those of CNTs. However, for the CNT reinforcement higher modulus value was measured for the smaller diameter CNT, contrary to the strength results.

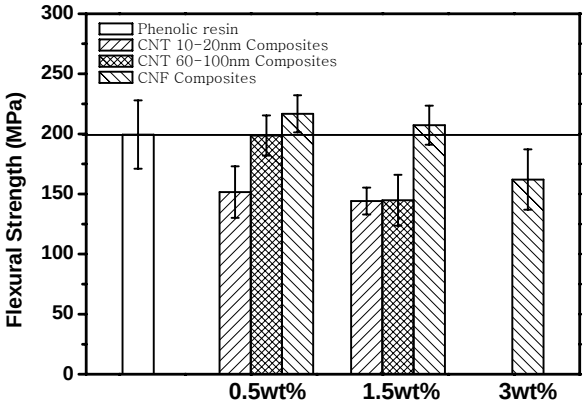


Fig. 2. Flexural strength of CNT- and CNF-reinforced phenolic resin composites.

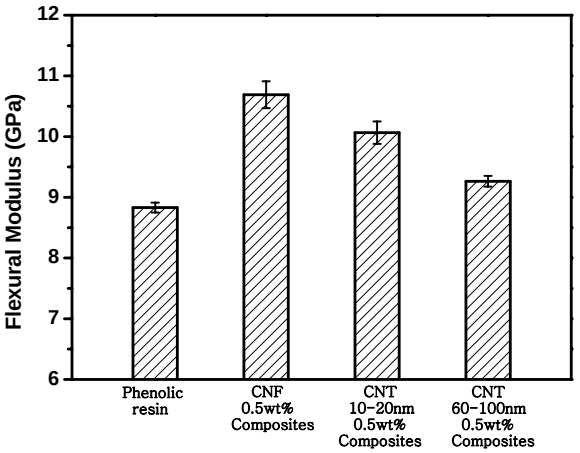


Fig. 3. Flexural modulus of CNT- and CNF-reinforced phenolic resin composites.

The SEM images of fracture surfaces of CNF reinforced phenolic resin composites are presented in Fig. 4. The CNFs tend to aggregate together although the individual fibers could still be impregnated by the resin. Therefore, reinforcement rich areas as pointed out by the bigger red arrow sign and reinforcement deficient areas (the smaller blue arrow sign) could be observed in Fig. 4(a) and

(b). The number and area of the reinforcement rich area increased with increasing CNF loading, resulting in the decrease of flexural strength [5]. Fig. 4(c) shows the fracture surface of pure phenolic resin without reinforcements. A flat fracture surface and the stripe-like pattern in the edge of the flat surface, typical of the brittle failure, were observed. Comparison with the fracture surface of phenolic resin reinforced with CNFs (Fig. 4(a) and (b)) reveals that the latter has a rougher fracture surface, which indicates that the CNF reinforcement possesses a certain potential to improve the fracture toughness of the phenolic resin [6].

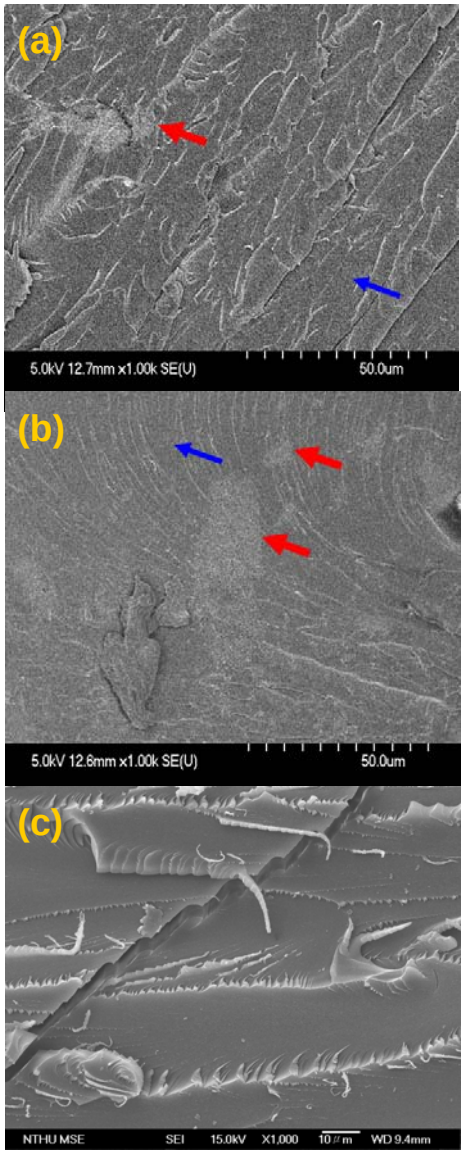


Fig. 4. Fracture surfaces of phenolic resin composites reinforced with (a) 0.5 wt% CNFs and (b) 3 wt% CNFs. (c) pure resin matrix without reinforcements.

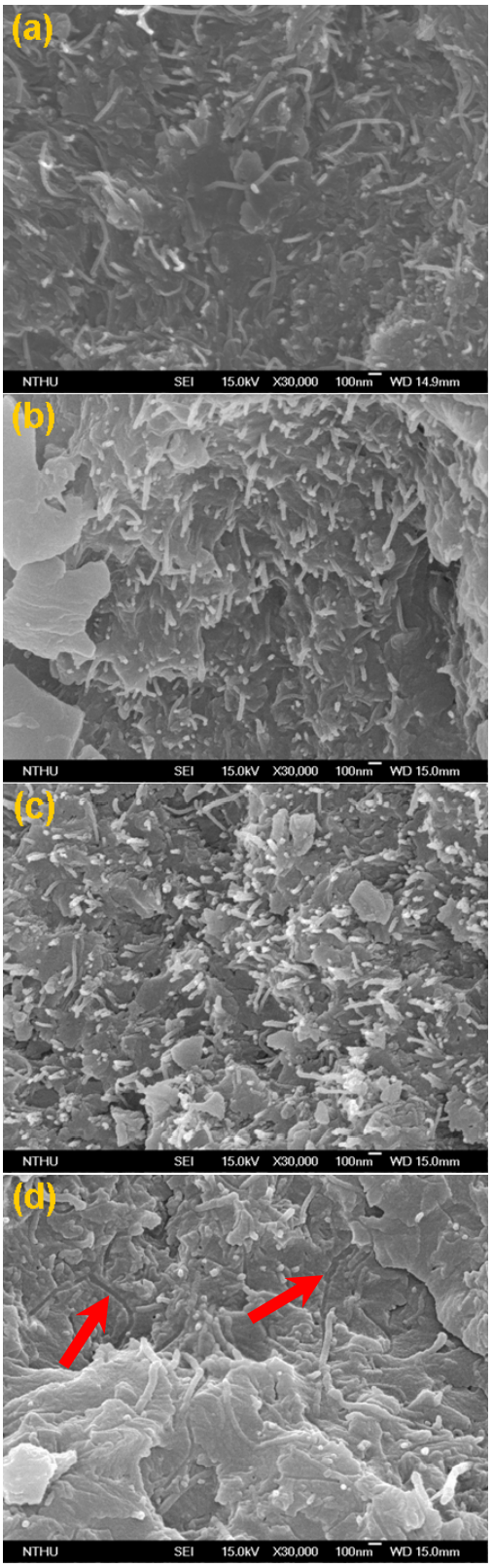


Fig. 5. Fracture surfaces of phenolic resin composites reinforced with (a) 0.5 wt% MWNT (10 nm~20 nm), (b) 1.0 wt% MWNT (10 nm~20 nm), (c) 1.5 wt% MWNT (10 nm~20 nm) and (d) 0.5 wt% MWNT (60 nm~100 nm).

Fig. 5 shows the SEM images of fracture surfaces of CNT reinforced phenolic resin composites. It must be pointed out that the fracture surfaces of CNT/phenolic resin composites also show reinforcement rich and reinforcement deficient areas as those of CNF/phenolic resin composites. The fracture surfaces presented in Fig. 5 are within the reinforcement rich area. As shown in Fig. 5(a)~(c), the density of CNT increased as the content of CNT increased from 0.5wt% to 1.5wt%. CNT pull-out could be found. It is also noted that the number of void and defect, resulting from the CNT pull-out or the process of composite fabrication, increased with increasing CNT loading. In addition to the CNT pull-out, CNT in-print denoted by the arrow sign was also observed in the composites reinforced with CNT with a larger diameter distribution (60-100 nm, Fig. 5(d)), indicating the weak interfacial bonding between CNT and phenolic resin. The weak interfacial strength is believed to be one of the important reasons reducing the strength of CNT/phenolic composites.

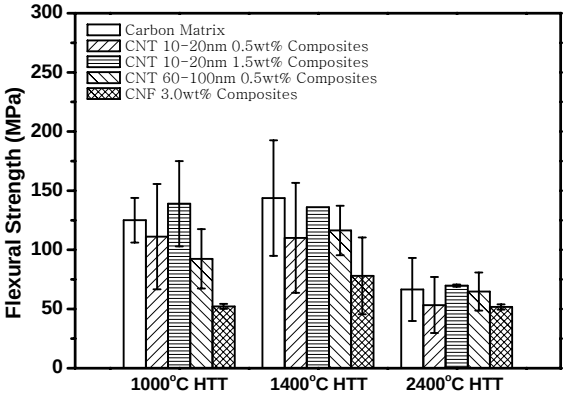


Fig. 6. Flexural strength of CNT- and CNF-reinforced carbon-carbon composites heat treated at different temperatures.

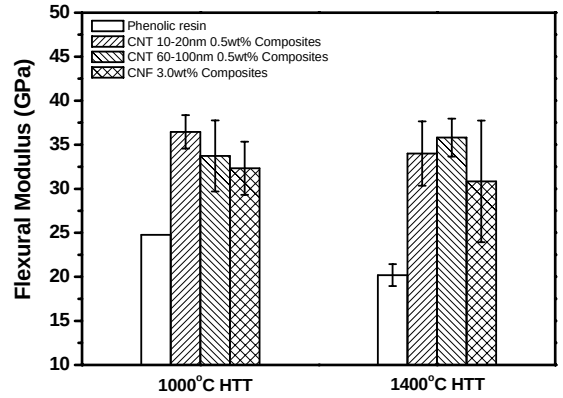


Fig. 7. Flexural modulus of carbon-carbon composites reinforced with CNTs of different diameter and heat treated at different temperatures.

### 3.2 Carbon-Carbon Composites

Fig. 6 shows the flexural strength of CNT- and CNF-reinforced C/C composites heat treated at different temperatures. Contrary to the phenolic resin composites for which CNF reinforcement resulted in higher strength due to the better interfacial bonding, CNTs showed better reinforcing results for C/C composites carbonized at 1000 and 1400℃. Above phenomenon is frequently reported in C/C composites [7,8]. It is also noted that for C/C composites carbonized at 1000℃ higher flexural strength was measured when reinforced with the smaller diameter CNT (10-20 nm), and that higher loading (1.5wt%) of the CNT(10-20 nm) led to the higher average strength. However, the influences of CNT diameter and loading on the strength decreased as the heat treatment temperature was raised. For C/C composites heat treated at 2400℃, the flexural strength values were lower than those at 1000 and 1400 ℃ , and the difference between different reinforcements was not significant. The enhancement of flexural modulus as shown in Fig. 7 was much more significant than that of flexural strength. CNT reinforcement also showed better results than those of CNFs. Furthermore, the improvement was larger for C/C composites carbonized at 1400℃ than that at 1000℃.

Fig. 8 shows the SEM images of fracture surfaces of C/C composites carbonized at 1000℃ and reinforced with CNTs of different diameter distributions. Very limited CNT pull-out was observed and consequently little reinforcing effect was also measured.

### 4 Conclusions

The mechanical properties of phenolic resin matrix composites reinforced with CNTs or CNFs and their corresponding C/C composites were investigated. For the phenolic resin composites, limited strength enhancement was measured. However, better reinforcing results were obtained for CNF reinforcement as compared to the CNT reinforcement due to the better interfacial bonding. CNF reinforcement also showed better results for the modulus measurement than those of CNTs. Contrary to the phenolic resin composites, CNTs showed better reinforcing results for C/C composites carbonized at 1000 and 1400℃. For C/C composites heat treated at 2400℃, the flexural strength values were lower than those at 1000 and 1400℃, and the difference between different reinforcements was not

significant. Compared with the flexural strength, the enhancement of flexural modulus was much more significant.

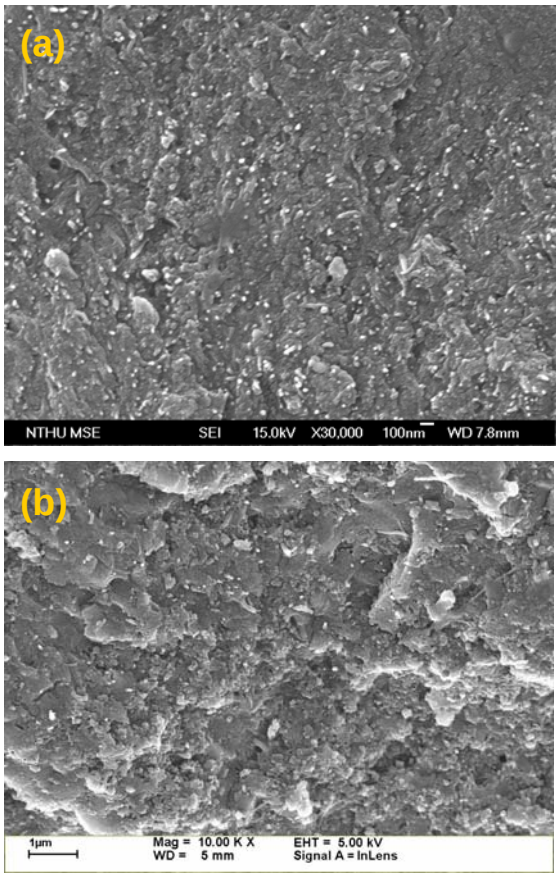


Fig. 8. Fracture surfaces of C/C composites carbonized at 1000℃ and reinforced with (a) 0.5 wt% MWNT (10 nm~20 nm) and (b) 0.5 wt% MWNT (60 nm~100 nm).

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