PREPARATION AND MECHANICAL BEHAVIOR OF PHENOLIC RESIN BASED CARBON-CARBON COMPOSITES WITH CARBON NANOTUBE OR CARBON NANOFIBER ADDITION

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Abstract

Carbon nanotubes(CNTs) or carbon nanofibers(CNFs) were mixed with phenolic resin, which was used as the precursor of carbon matrix of carbon-carbon(C/C) composites. The CNTs- or CNFs-reinforced carbon fiber fabric/phenolic resin composites were fabricated using hand lay-up and the vacuum bag hot pressing technique. The as-cured composites were then pyrolyzed to convert into C/C composites at different heat treatment temperatures. The mechanical properties of the composites were studied using the three-point bending test according to ASTM D-790 and the fracture surfaces were observed using scanning electron microscopy. The results indicated that the mechanical properties of carbon/carbon composites were influenced significantly by interfacial strength between carbon matrix and carbon reinforcements, including CNTs/CNFs and carbon fibers. A 16.7% increase was found for the flexural strength of carbon/carbon composites after 2000℃ heat treatment with a 0.5 wt% CNF addition.

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, results without or with limited strength enhancement were also reported [1,2]. 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. Recently, incorporation of CNTs or CNFs in micro-fiber reinforced polymer composites to form a hybrid multiscale composite was proposed and enhancements of mechanical behavior were reported for carbon fiber (CF)/polymer [3-6] and glass fiber/polymer [7-9] composites. The properties of carbon nanomaterials reinforced composites primarily depend on the dispersion of carbon nanomaterials in the matrix of composites. Agglomeration of nanofillers leads to the generation of potential defects and thereby deteriorates composite properties. Hence the selection of an efficient dispersion technique for nanofillers prior to the fabrication of three-phase composites is extremely

important. To date, four major approaches have been developed [10,11]: (1) infusion of a CNT-/CNF-resin mixture into the preform, (2) direct growth of CNTs/CNFs on reinforcement fabric substrates, (3) direct placement of CNTs/CNFs between layers of the preform, and (4) electrophoretic deposition of CNTs/CNFs on reinforcement fabric substrates. Discussion of these methods can be found in the literature [10,11].
Compared with the polymer matrix composites, few investigations [12] were reported on the reinforcement of carbon fiber reinforced carbon matrix (C-C) composites with the incorporation of CNTs or CNFs. Therefore, in this investigation, CNFs or CNTs reinforced three-phase (CNT or CNF/carbon fiber/carbon matrix) C-C composites were fabricated and their mechanical behavior was investigated.

2 Experimental

Fig. 1 shows the SEM images of CNTs and CNFs used in this study. The CNFs, produced in our laboratory (40-60 nm), have a structure with internal conical cavities (insert in Fig. 1(a)) and the CNTs, 10-20 nm in diameter, have a tube structure (insert in Fig. 1(b)). For the fabrication of CNT or CNF/CF fabric/phenolic resin composites, the CNTs or CNFs dispersed phenolic resin solution with a CNT/CNF content of 0.5 wt% was prepared first with the aid of ultrasonication. Then the CF fabrics were impregnated with the solution and the vacuum bag hot pressing technique was used to fabricate the composites. For the fabrication of C-C composites, the phenolic resin based three-phase nanocomposites were cut, weighed and then carbonized at 1000℃. The carbonization treatment was performed at a heating rate of 2℃/min using a three-zone tube furnace under an argon atmosphere. The hold time was 30 min. at 1000℃. For composites heat treated at 2000℃, a carbonization heat treatment at 1000 ℃ was performed in advance. The heat treatment at 2000℃ was carried out in an Astro 1000-3060-FP20 graphite furnace under a helium atmosphere. The heating rate was 5℃/min and the hold time was 30 min.
The mechanical properties and fracture behavior were studied using the three-point bending test according to ASTM D-790. The fracture surfaces of the composites after bending tests were observed using SEM. The microstructure of the composites was analyzed using TEM.

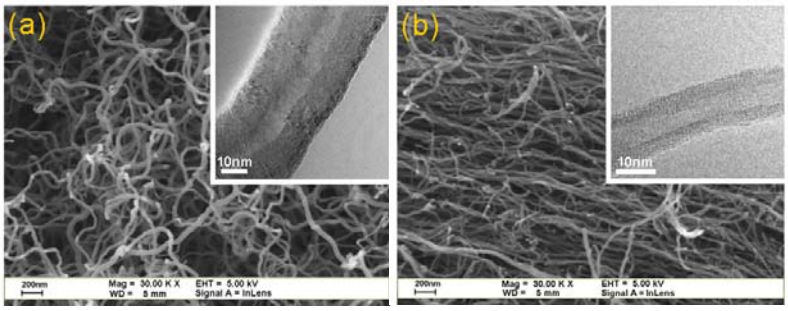

Figure 1. SEM and TEM images of: (a) CNFs and (b) CNTs.

3 Results and discussion

3.1 Formation of CNT-centered rod-like structure

Fig. 2 shows the SEM images of the fracture surface of the CNT reinforced C-C composites heat treated at 2000℃. As shown in the low magnification image (Fig. 2(a)), a lot of rod-like materials were pulled out from the fracture surface. However, these rod-like materials are not CNTs added in the phenolic resin in the preparation of the CNT reinforced composites since their sizes (~50-200 nm in diameter) are bigger than that of CNTs. High magnification image

(Fig. 2(b)) reveals that the rod-like materials are composed of the CNT in the center (as indicated by the arrow signs A) and the surrounding materials which is presumably the phenolic resin-derived carbon. It is also noted that some of the CNTs did not form the rod-like structure as pointed out by the arrow signs B. The thermosetting resin-derived carbon is known to be a non-graphitizing carbon even though the heat treatment temperature is above 3000℃. Phenolic resin-derived carbons are no exception. However, preliminary TEM study (not shown) indicates that the phenolic resin-derived carbons surrounding the CNTs have better degree of graphitization than that of the phenolic resin-derived carbons away from the CNTs. CNTs, when used as filler in a glass-like carbon matrix, has been reported to induce stress graphitization in the matrix [13,14]. However, formation of CNT-centered rod-like graphitic structure has not been reported. While a more detailed understanding is required, it is speculated that the large difference of the graphitization degree between the graphitic rods and the glassy carbon matrix results in a weak interfacial bonding, leading to the pull-out of the graphitic rods upon fracture.

As compared with the fracture surface of CNT reinforced C-C composites in Fig. 2, the number of CNF-centered rod-like structure was much less, but the pull-out length was longer as shown on the fracture surface of CNF reinforced C-C composites (Fig. 3(a)). High magnification image (Fig. 3(b)) reveals that the longer rod tended to be broken into several shorter rods but the centered CNF remained unbroken. It is also noted that the CNFs forming the rod-like structure are straighter CNFs and that crooked CNFs did not tend to form the rod-like structure as pointed out by the arrow signs C in Fig. 3(b).

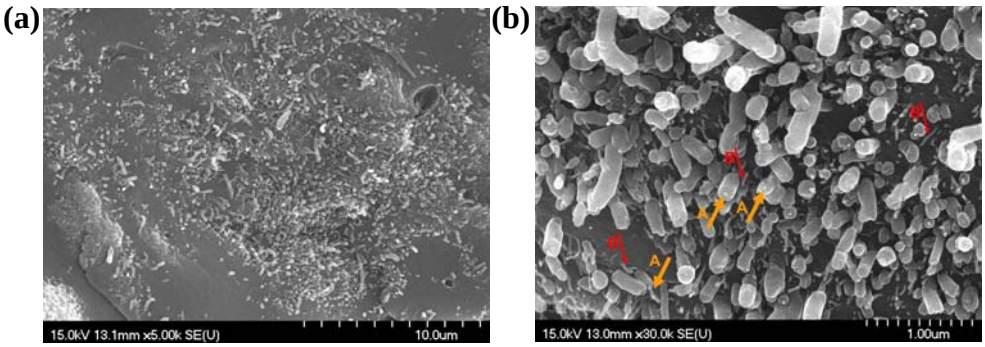

Figure 2. SEM images of fracture surfaces of CNT reinforced C-C composites: (a) low magnification and (b) high magnification.

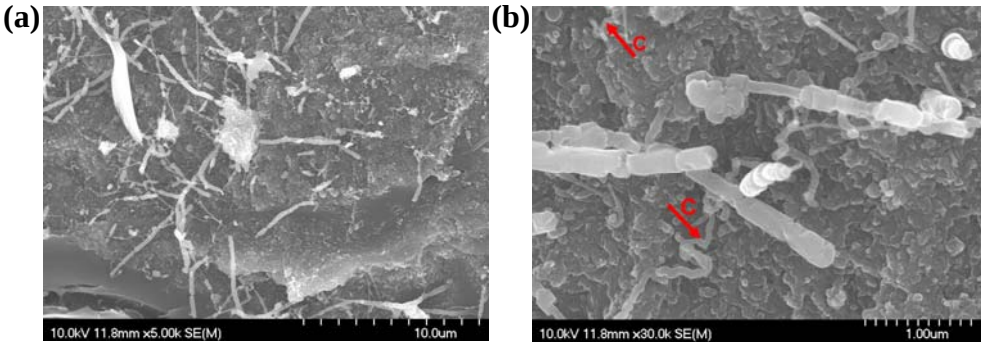

Figure 3. SEM images of fracture surfaces of CNF reinforced C-C composites: (a) low magnification and (b) high magnification.

3.2 Mechanical behavior

The results of flexural strength of CNT and CNF reinforced C-C composites are presented in Fig. 4. Although the average strength of CNT reinforced C-C composites is larger than that of C-C composites without CNTs, no significant reinforcement was obtained considering the standard deviation. However, CNF addition resulted in a significant increase in flexural strength. An increase of 16.7% was measured when compared with that of C-C composites without CNTs. The reason why the CNF showed better reinforcement than CNT may be related to the formation of the rod-like structure, which has a weaker bonding with the glassy carbon matrix.

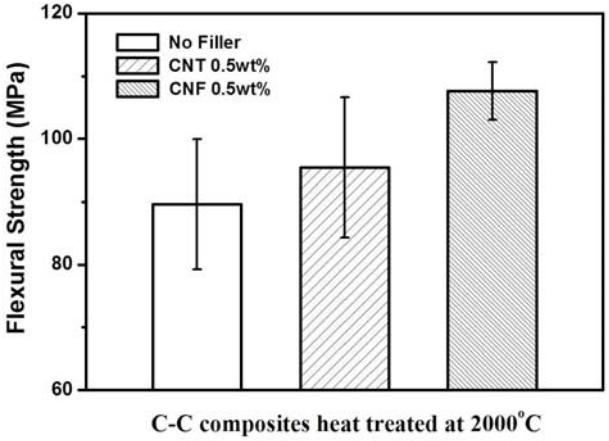

Figure 4. Flexural strength of CNT and CNF reinforced C-C composites heat treated at 2000℃.

4 Conclusions

CNTs or CNFs were mixed with phenolic resin, which was then used to fabricate the CNTs- or CNFs-reinforced phenolic resin based C-C composites. Formation of CNT-centered rod-like graphitic structure was found in CNTs-reinforced C-C composites. However, due to the crooked morphology of CNFs, the number of CNF-centered rod-like structure was much less. No significant reinforcement in flexural strength was obtained for CNTs-reinforced C-C composites. However, CNF addition resulted in a significant increase in flexural strength. An increase of 16.7% was measured when compared with that of C-C composites without CNTs. The reason why the CNF showed better reinforcement than CNT may be related to the formation of the rod-like structure.

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