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# Study of the mechanical properties of carbon nanofiber reinforced carbon/carbon composites

Jinsong Li, Ruiying Luo *

*College of Science, Beijing University of Aeronautics and Astronautics, Beijing 100083, China*

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ABSTRACT

The effects of carbon nanofibers (CNFs) on the flexural properties and interlaminar shear strength of CNF-reinforced C/C composites are discussed. The results show that the flexural strength, modulus and interlaminar shear strength of the composite containing 5 wt.% CNFs are increased by nearly 21.5%, 33.5% and 40.7%, respectively, compared to that of the composite containing no CNFs. When the additive content is increased to 20 wt.%, due to the holes and cavities in the CNF web and between carbon cloth and matrix, both the flexural properties and interlaminar shear strength decrease from the maximum value with the additive content at 5 wt.%.



## 1. Introduction

Carbon/carbon(C/C) composites made from woven- and braided-fabric reinforcements have found potential applications in the aerospace, automobile and marine industries. This is because they have better out-of-plane stiffness, strength and toughness properties, lower fabrication cost, and easier handling in production quality than tape laminates [1,2]. However, laminated carbon cloth C/C composites are rather susceptible to interlaminar failure between the layers. Such an interlaminar failure (or delamination) may lead to a loss in stiffness as well as in the reliability of structural components. CNFs as well as single and multiwall carbon nanotubes (CNTs) are deemed to be useful for the preparation of novel composite materials with enhanced mechanical properties [3–6]. Along with the efforts towards improvement of matrix pyrocarbon mechanical properties, research on the preparation of CNF/CNT-reinforced C/C composites has been carried out [7–9]. However, little is reported about the effect of CNF web structure on the mechanical properties of as-received C/C composites. In this study, effects of CNF content on the flexural properties and interlaminar shear strength of the C/C composites are investigated.

## 2. Experimental

### 2.1. Preform preparation

Plain carbon cloth of type HS of 3 K Polyacrylonitrile(PAN) based carbon fiber fabricated in Jilin Carbon Plant, China, was used as preform of C/C composites. The CNFs (PR-19-PS of Polygraf III) obtained from Applied Sciences Inc., of Cedarville, Ohio, were used as a secondary reinforcement. The CNFs have an average diameter of 200 nm and lengths from several microns to over 200 μm. Preforms were fabricated by spreading layers of carbon cloth containing 0, 5, 10, 15 and 20 wt.% CNFs, which has been described in Ref. [10]. As shown in Fig. 1, CNFs are attached on carbon fibers close to the surface of carbon layer, and the CNF web layer is uniformly dispersed on the surface of carbon layer. Twenty six layers of the carbon cloth have been necessary to build the given preforms, and two successive layers have been oriented at an angle of 90°. The outer and inner diameters of the preforms were 100 mm and 20 mm, respectively.

### 2.2. Densification of preforms

The preforms were densified by using the technique of isothermal chemical vapor infiltration (ICVI) with a flowing mixture of propane and nitrogen in the ICVI furnace at the temperature of 1100 °C under the pressure of propane/nitrogen 1 kPa. The ratio of propane to nitrogen was about 13:1, and the flow rate of mixture was 1.4 $m^3$/h. Every 50 h, the sample was machined for crust removal. After 580 h, the densities of the five composite samples prepared from different preforms were 1.70, 1.72, 1.67, 1.64, 1.63 g/$cm^3$, they were then treated at 2500 °C for 3 h.

### 2.3. Measurement of the bulk density of the samples

Specimens of 10 × 4 × 2 mm obtained from different parts of each composite were determined to evaluate the spatial uniformity of densification, and the number was not less than seven

* Corresponding author. Tel.: +86 10 8233 8267; fax: +86 10 5173 6729.
*E-mail address:* ryluo@buaa.edu.cn (R. Luo).

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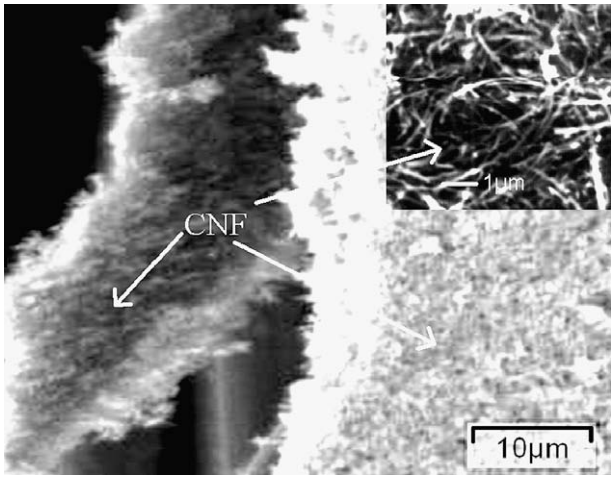


**Fig. 1.** SEM micrograph of 5 wt.% CNFs on the surface of carbon fibers.

for each test point. Then they were weighed in an analytical balance. The bulk density of the samples can be calculated. In each density measurement, we have not performed any surface machining for crust removal. To determine the open pore volume and size distribution of the preforms, Poremaster 33, a mercury porosimeter produced by Quantachrome Instruments Corporation, Florida, USA, was used.

### 2.4. Test of mechanical properties

Flexural strength and modulus were measured in plane direction using a universal testing machine model MTS880-50KN to perform comparisons between the composites. The test samples were cut off to be the nominal dimension of $60 \times 10 \times 8$ mm. The number of specimens used for the flexural property test was seven for each test point. The support span is 40 mm and the crosshead speed was 0.5 mm/min. In order to gain the true defection, a dial indicator was used to demarcate and correct the defection in the process of testing. The interlaminar shear strength test samples of 10 mm width were cut in the layer direction and tested in a three-point rig over a span of 12 mm between a 3-mm diameter supporting rollers and a 6-mm diameter loading, and the number was still not seven for each test point. The results are shown in Table 1.

### 2.5. Analytical methods

Scanning electron microscopy(SEM), JEOL JSM-5800, and Polarized light micrograph(PLM), NEOPHOT 21, were used in the investigations.

## 3. Results and discussion

### 3.1. Effect of CNFs on the bulk density and open porosity

In this test, open porosity is the ratio of the mercury volume occupied by the continuous mercury phase to the total volume of porous material. Figs. 2 and 3 show the variation of bulk density with open porosity in the CNF-reinforced C/C composites and the open pore in the CNF web after 20 h, the slope of bulk density versus open porosity curve reveals the deposition efficiency in the CNF-added preform. As shown in Fig. 2, when the CNF content of a preform remained at 5 wt.%, the slope of bulk density versus open porosity curve of the 5 wt.% CNF preform, as expected, were higher than that at 0 wt.%, indicating higher achievable degree of pore filling. However, as the CNF contents varied from 10 to 20 wt.%, an insignificant density increase is accompanied by an unexpected significant decrease in open porosity in the final stages of densification, i.e. infiltration was not complete (Fig. 3), as a result, the slope of bulk density versus open porosity curve decreases with the CNF content increasing. These results can be attributed to an effect of CNFs on the competition between diffusion and reaction. Ref. [10] has proven that CNFs has a strong influence on the initial rates of in-pore deposition due to the higher aspect ratio of the CNFs, the initial infiltration rates of the CNF-added preforms are higher than that of the no CNF preform. After finite infiltration time, diffusion coefficients decreased due to the pore diameter becoming small, an overgrowing of the pore entrances was accelerated and an incomplete filling of the pores was possible with the additive content increasing. When more CNFs were added in, the pore diameter reduced more quickly and the pore entrances were sealed more rapidly, resulting in decrease of the open porosity, which lead to lower pore deposition efficiency.

### 3.2. Effect of CNFs on the flexure properties

The load–displacement curves and fractography are shown in Figs. 4 and 5, respectively. As seen from Fig. 4, all the composites exhibit some pseudo-plastic fracture characteristic. From Table 1, when the CNF content remains at 5 wt.%, the flexural strength and flexural modulus are increased by nearly 21.5% and 33.5%, respectively, compared to the composite containing no CNFs, indicating the effect of CNFs on flexural properties at 5 wt.%. However, in the additive range of 10–20 wt.%, both the flexural strength and flexural modulus decrease from the maximum value with the additive content at 5 wt.%, this may due to the higher open and closed porosity at the interface and matrix in the final carbon material which have an adverse effect on the mechanical properties not only by reducing the area under load but also by acting as critical flaws [11]. The polished transverse sections of the CNF-reinforced composites viewed by polarized-light microscopy are shown in Fig. 6. The aspects of the composite prepared with 5 wt.% CNFs, have a less developed porous structure(i.e., a more densified CNF web) and a little crack between integrated CNF/pyrocarbon in the CNF web and in the carbon fiber bundles (Fig. 6b) because of the achievable degree of pore filling in the CNF web [10]. As a result, the matrix bears greater loads without cracking in the more densified composite with 5 wt.% CNFs, this together with a better interface allows the fiber to play a major role in the mechanical test, causing an increase in the initial slope (Fig. 4). Magnified image of the composite with 5 wt.% CNFs shows no pulled-out CNFs on the fracture surface (Fig. 5), which implies strong interfacial bonding between CNFs and the matrix pyrocarbon. A network formation is observed in the SEM (Fig. 7a), which has effects on matrix chain motion, and plays a role of physical cross-linking, thus causing

**Table 1**
Illustration of CNF-reinforced composite with different CNF contents and mechanical properties of carbon/carbon composites(average ± standard deviation, $N = 7$)

| CNF content (wt.%) | 0 | 5 | 10 | 15 | 20 |
|---|---|---|---|---|---|
| CNF web thickness (μm) | 0 | 75–90 | 155–190 | 215–260 | 285–350 |
| Flexural strength (MPa) | 129.6 ± 5.8 | 157.4 ± 3.4 | 137.4 ± 6.1 | 118.6 ± 6.6 | 104.9 ± 7.3 |
| Flexural modulus (GPa) | 30.1 ± 4.3 | 40.0 ± 2.2 | 34.4 ± 5.6 | 25.0 ± 6.8 | 23.4 ± 7.2 |
| Interlaminar shear strength (MPa) | 10.28 ± 3.1 | 14.46 ± 2.6 | 12.15 ± 4.5 | 9.34 ± 4.9 | 8.51 ± 4.6 |