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Compressive properties of carbon/carbon composites reinforced by carbon nanotubes with different orientations and lengths

Hai-yan Yu, Jin-hua Lu*, Qiang Song, Ke-zhi Li, He-jun Li, Qian-gang Fu, Lei-lei Zhang

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

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Carbon nanotubes (CNTs) with different orientation and lengths were grafted onto carbon fibers by catalytic chemical vapor deposition to produce hybrid preforms that were used to reinforce carbon/carbon (C/C) composites. Compressive property tests indicated that these C/C composites have obvious improvements in out-of-plane compressive strength, compared with pure C/C composites. Furthermore, the improvement has strongly influenced by the orientation and length of CNTs. Compared with entangled CNTs and radially-grown straight CNTs with smaller length, CNTs with a radial grafting morphology and longer length can reinforce the F/M interface and the whole matrix more efficiently and then increase the compressive strength better.

A lot of challenges still exist in reinforcing carbon/carbon (C/C) composites though so many efforts have focused on this issue over the past few decades [1,2]. The greatest one is how to provide more substantial reinforcements than traditional methods through improving fiber/matrix (F/M) interfacial bonding only via treating carbon fiber surface. Recently, some researches [3] have proved an effective method of reinforcing the F/M interface of fiber/polymer composites by grafting carbon nanotubes (CNTs) onto fibers. Theoretically, the transfer of this technique should also generate some exciting results in reinforcing C/C composites. Although the researches of Gong et al. [4] have implied the clear improvement of F/M interface of C/C composite after grafting CNTs on carbon fiber, the corresponding mechanical properties of CNTs reinforced C/Cs are very rare [5], let along excellent reinforcements. Possible reasons for these problems are various, which has been involved in the issues such as efficient grafting on carbon fiber surface and dispersion of CNTs, and so on. On the other hand, to maximize the performance of CNT reinforced C/C (CNT-C/C) composites, a big part of energies should be divided and paid on the work of CNT-morphology optimized tailoring, which could allow CNTs to reinforce the mutual interaction between fiber and matrix availably and meanwhile offer further benefits i.e. providing increased lateral support of the load-bearing fibers and influencing and stiffening the surrounding matrix at greater depth (Table 1).

In this work, CNTs, with different orientations and lengths, were grafted onto carbon fibers by a simple catalytic chemical vapor deposition (CCVD) respectively. And then they were used to reinforce C/C composites. Our aim is to evaluate the role of CNTs with different grafting morphologies in enhancing C/C composites. It is believed that this work can pave a meaningful way to maximize the excellent performance of CNT-C/C composites.

Carbon felts (bulk density: 0.2 g/cm^3) were used as preform materials. They were firstly coated with a layer of pyrolytic carbon (PyC, several dozens nanometers) by CVD to prevent the dissolution of metal catalyst into carbon fibers and to improve the surface morphology. The graft of CNTs on carbon fibers was accomplished by CCVD using $Ni(NO_3)_2 \cdot 6H_2O$ as catalyst precursor. Incipient wetness technique was adopted to introduce catalyst onto carbon fibbers using acetone as solvent. For growing entangled CNTs, the concentration was 0.5 wt.%, the reaction gas system was C_3H_6/H_2 (flow ratio: 1/10) and the reaction temperature was 700 °C. For growing straight CNTs with radial orientation, the concentration was 1.5 wt.%, the reaction gas system was CH_4/N_2 (flow ratio: 1/10) and the reaction temperature was 1020 °C. The straight CNT length can be controlled by adjusting the growth time.

The CNT hybridized preforms were densified by medium-textured (MT) pyrocarbon in a self-made chemical vapor infiltration (CVI) reactor [6] at about 1080 °C with CH_4 as carbon source. For comparison, C/C composites with the same preforms were prepared under the same conditions. The density of CNT-C/C and C/C composites is 1.65/cm^3. Finally, all the composites were

* Corresponding author.
E-mail address: lujinhua@nwpu.edu.cn (J.-h. Lu).

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Table 1
Compressive properties of the four composites.

Composites	Orientation	Length/μm	Compressive modulus/GPa	Compressive strength/MPa
1	/	/	1.1 ± 0.2	61 ± 8
2	Entangled	>4	1.7 ± 0.2	100 ± 7
3	radial	2–3	1.6 ± 0.3	97 ± 5
4	radial	8–20	2.7 ± 0.3	230 ± 10

graphitized at 2500 °C for 2 h. Out-of-plane compression strength testing was to evaluate the role of CNTs with different grafting morphologies in enhancing C/C composites. Pure C/C composites, C/C composites reinforced by entangled CNTs, C/C composites reinforced by straight CNTs with smaller length and larger length are respectively named by composite 1, 2, 3 and 4.

Fig. 1 shows SEM images of carbon fibers before (a) and after grafting CNTs with different orientations and lengths (b, c, d). For entangled CNTs, CNT bodies are greatly curve and the growth directions of all CNTs are random (Fig. 1b). The thickness of CNT coating on fibers is about 3 μm and the length of single CNT is over 4 μm. For straight CNTs, their growth shows a radial pattern (Fig. 1c and d). In Fig. 1c, the CNT length ranges from 2 μm to 3 μm and the corresponding time is 0.5 h. In Fig. 1d, the CNT length ranges from 8 μm to 20 μm and the corresponding time is 2 h. The contents of entangled CNTs and two types of radially-grown straight CNTs in the hybrid felt are 5.1 wt.%, 4 wt.% and 9.5 wt.%, respectively.

After grafting entangled CNTs, straight CNTs with 2–3 μm length and with 8–20 μm length, out-of-plane compressive strength and modulus of C/C composites have improvements of 56% and 50%, 59% and 33% and 277% and 125%, respectively. However, although the content of entangled CNTs is larger than that of straight CNTs with 2–3 μm length, the corresponding composite has no obvious superiority in mechanical performance. On the other hand, when the length of radially-grown straight CNTs is over 10 μm, the CNT role in reinforcing mechanical properties of C/C composites becomes very striking. Thus, we can say that grafting CNTs on carbon fibers can improve the mechanical properties of C/C composites; however, such improvements are strongly influenced by the CNT grafting morphology. Compared to entangled CNTs, radially-grown straight CNTs can reinforce C/C composites better; while, compared to straight CNTs with smaller length, longer straight CNTs are more conducive to improve the compressive properties of C/C composites.

SEM investigations into the fracture surfaces of the four composites were used to obtain CNT reinforcing mechanisms. C/C composite shows a rough fracture surface with clear sliding steps in the direction vertical to the compressive force (Fig. 2a). The formation of sliding steps strongly depends on the long-distance propagation of destructive cracks through F/M interfaces and pyrocarbon (PyC) matrices. Existing annular matrix cracks (Fig. 2a) provide main channels for destructive crack growth. Two typical ways are longitudinal breakthrough and lateral link-up of adjacent annular cracks as labeled by solid arrows in Fig. 2a, leaving lots of delaminated PyC panels (Fig. 2a). In contrast, CNT-C/C composites (especially composite 4, Fig. 2d) have a relatively smooth fracture surface. No obvious fracture step has been found and the damage tends to be a falling fracture rather than a sliding one. The change of fracture behavior means the increase of the cohesion of C/C composites after adding CNTs (Fig. 3).

Concretely, the increased compressive strength and modulus of composite 2 and 3 can be attributed to the enhanced F/M interface, which can exert the force-bearing role of carbon fibers to a greater extent (more detailed explanations can be found elsewhere [7]); while, the largely-increased compressive strength and modulus of composite 4 have been caused by the reinforcements of radially-grown straight CNTs with long length to PyC matrix in the direction of thickness. This is because out-of plane compressive performance of C/C composites is dominated by carbon matrix [3], especially when

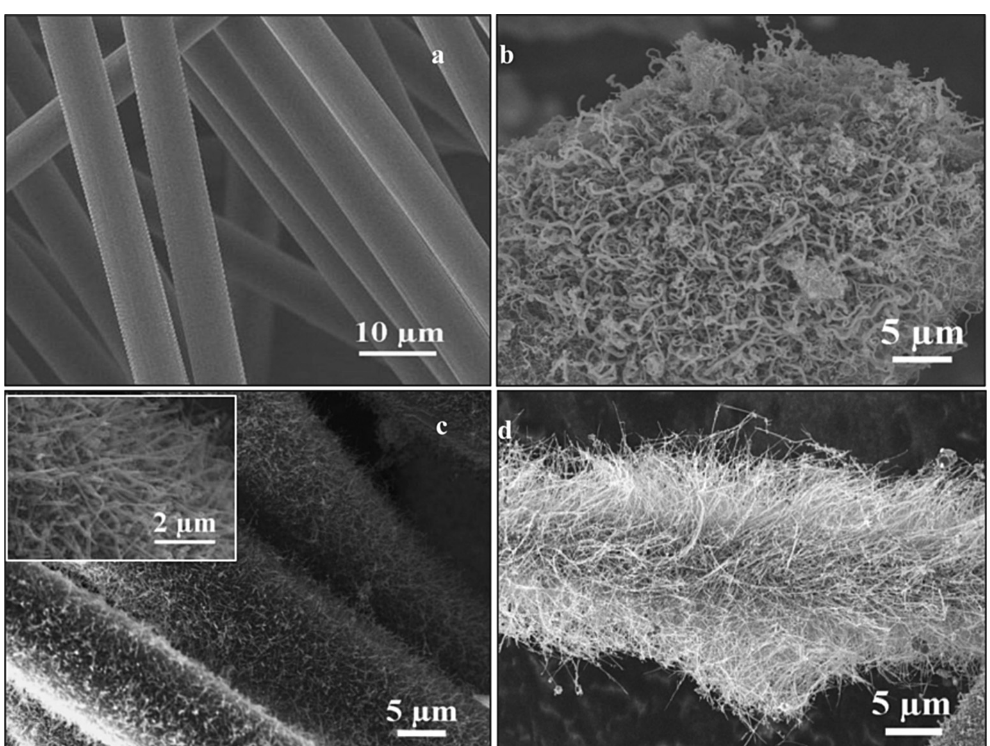

Fig. 1. SEM images of carbon fibers before (a) and after grafting CNTs with different orientations and lengths (b, c, d).