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ScienceDirect

Ceramics International 41 (2015) 1943–1949

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Simultaneous improvements in flexural strength and ductility of carbon nanotube-doped carbon/carbon composites by depositing a pyrocarbon layer on carbon fibers

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Received 12 March 2014; received in revised form 5 July 2014; accepted 26 July 2014
Available online 2 August 2014

Abstract

Introducing carbon nanotubes (CNTs) on carbon fibers (CFs) can significantly improve the matrix-dominated mechanical strength of carbon/carbon composites (C/Cs). As for the CF-dominated mechanical properties such as flexural property, however, the direct introduction of CNTs on CFs always leads to a humble improvement of flexural strength and a brittle fracture mode of the composites. To overcome this limitation, in this work, a thin medium-textured pyrocarbon (PyC) coating, as an interphase layer, was deposited on CFs by isothermal chemical vapor infiltration (ICVI) and its effects on flexural property of CNT-doped C/Cs (CNT-C/Cs) were investigated. Results show that CNT-C/Cs with ICVI PyC layer (PCCT) have a 1100% improvement in flexural ductility and a 44.3% improvement in flexural strength, compared with CNT-C/Cs without ICVI PyC layer (CCT), which are attributed to the toughening role of CFs through their pullouts and the strengthening role of CNTs on the composites. This work could pave a meaningful way for the development of CNT-C/Cs with high mechanical strength and good toughness.

Keywords: Carbon nanotubes; Carbon–carbon composites; C. Mechanical properties; Chemical vapor deposition (CVD)

1. Introduction

Carbon/carbon composites (C/Cs), as high-temperature materials, are widely used in the aerospace industry [1]. During the fabrication of C/Cs, microdefects, including matrix annular crack and fiber/matrix (F/M) interface relaxation, are unavoidable, which have a negative effect on their properties [2,3]. To alleviate this limitation, it is efficient to apply carbon nanotubes (CNTs) with excellent mechanical properties [4–6] to strengthen the F/M interface and to stitch the cracked carbon matrix as the secondary reinforcements, resulting in the formation of multiscale hybrid composites, i.e. CNT-C/Cs that have attracted wide attention recently [7–10].

According to the previous reports, CNT-C/Cs show some excellent matrix-dominated mechanical properties due to the CNT reinforcing role to the F/M interface and carbon matrix of C/Cs and the resulted microstructure improvements of the composites by the introduced CNTs. For example, radially-grown straight CNTs on carbon fibers endowed C/Cs with improvements in out-of-plane compressive strengths and interlaminar shear strength of 275% and 206% [8]. As for the carbon fiber (CF)-dominated mechanical properties such as flexural property, however, the direct introduction of CNTs on carbon fibers contributed only ~30% improvements to flexural strength, which was always accompanied by a sharply deteriorated fracture ductility [9,10]. The unsatisfied reinforcing effect of CNTs on the flexural property of C/Cs results from their F/M interface with isotropic and intertwisted microstructures inductively formed by CNTs coated on CFs with random layouts [11]. Specifically, such a F/M interface obstructs the crack deflection along the axis of CF which results in the stress concentration in the direction perpendicular to fiber surface and induces the early failure of the fibers by a notch effect that further inhibits the CF pullout as an effective strengthening and toughening mechanism and then generates

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http://dx.doi.org/10.1016/j.ceramint.2014.07.134
0272-8842/

the low flexural strength and the poor fracture ductility [12–14]. Therefore, to improve the flexural property of CNT-C/Cs, the interface must be improved. In this work, a thin medium-textured pyrocarbon (PyC) coating, as an interphase layer, was deposited on CFs by isothermal chemical vapor infiltration (ICVI) and its effects on flexural property of CNT-C/Cs were investigated based on the strength and fracture ductility measurement.

2. Experimental

2.1. Materials preparation

The effects of the PyC layer on flexural property of CNT-C/Cs were investigated based on the flexural properties of four types of C/Cs,which were pure C/Cs (labeled by "CC"), CNT-C/Cs ("CCT"), C/Cs with ICVI PyC layer ("PCC") and CNT-C/Cs with ICVI PyC layer ("PCCT"). During the preparation of the four composites, laminated CF felts (T300, 7–9 μm, Tianniao High Technology Co. Ltd., China) with a bulk density of 0.2 g/cm^3 and multi-walled CNTs (97% purity, Timesnano, China) with the outer diameter of 20–40 nm and the length of ~30 μm were used as the starting materials. Electrophoretic deposition (EPD) was used to introduce CNTs into CF felts due to its low cost and high efficiency [15]. The detailed process was described as follows: CNTs were first dispersed in isopropyl alcohol by 3 h ultrasonic to obtain dispersions of 1.6 g/L. And then, the felt connected with a copper wire as a cathode was fixed in a plastic frame, and was immersed in an EPD cell containing stable CNTs suspension. A stainless steel plate was placed on the opposite side as an anode. The experiment with a PowerPac Basic (Bio-Rad Laboratories, Inc., USA) was performed at a constant voltage of 40 V and an electrode distance of 25 mm. EPD time was 60 s. ICVI was used to deposit medium-textured PyC on CFs, which was carried out at 1 atm and 1080 °C with the CH_4/N_2 flow rate of 36/144 ml/min for 1 h. Thermal gradient chemical vapor infiltration (TCVI) was used to densify the felt to prepare C/Cs and CNT-C/Cs, which was carried out at 1 atm and 1000 °C with the CH_4 flow rate of 3 m^3/h for 80 h. Finally, the bulk density of each composite was not less than 1.74 g/cm^3 (details are shown in Table 1) and CNT contents in PCCT and CCT were 0.19 wt% and 0.18 wt%, respectively. The detailed preparation processes of the four composites were summarized in Fig. 1.

2.2. Test and characterization

Three-point bending tests were carried out to evaluate the flexural performance of the composites using a SANS universal testing machine (CMT5304-30 kN) at room temperature, conducted at a loading speed of 0.5 mm/min and a support span of 40 mm according to the Chinese aerospace industry standard (Q/GB95-92). The size of samples was 55 mm × 10 mm × 4 mm and loading direction was perpendicular to CF plies (*Z* direction). The number of testing samples was no less than seven for each test. The flexural strength and strain were calculated from the following equations:

$$\sigma_f = \frac{3FL}{2bh^2} \tag{1}$$

$$\varepsilon = \frac{6sh}{L^2} \times 100\% \tag{2}$$

where F is the load (N), L is the span (mm), b is the sample width (mm), h is the sample depth (mm), and s is the displacement of the pressure head. In order to compare the quasi-ductile fracture behavior of the samples, a ductility factor F_D is introduced [16]. It is calculated from the ratio of the secant modulus (the slope of the line from the origin to the stress at failure in the stress–strain curve) to the elastic modulus, as shown in Fig. 4a.

Distribution morphologies of CNTs on CF and PyC interlayer and the fracture surface of the four composites after mechanical tests were observed using a MIRA3 TESCAN field emission scanning electron microscope (SEM). The texture of PyC was investigated by polarized light microscopy (PLM, Leica DMLP optical microscopy).

3. Results and discussion

3.1. Morphology and microstructure

Fig. 2a shows the PyC-coated CFs and the PyC thickness is about 150 nm according to the cross-section high resolution SEM observation (as shown in Fig. 2b). Fig. 2c and d shows the SEM images of CNT added on PyC-coated CFs and pristine CFs by EPD. CNTs deposited uniformly on PyC and CF have a uniform distribution with no distinct agglomeration or acutely curly body. The directions of all CNTs are in the plane parallel to the CF axis, forming a three dimensional (3D) network structure.

Table 1
Bulk densities, open porosities and flexural properties of the four composites.

Samples	Bulk density (g/cm^3)	Open porosity (%)	Flexural strength (MPa)	Flexural F_D
CC	1.77 ± 0.02	12 ± 3	94.2 ± 6	0.08 ± 0.02
CCT	1.75 ± 0.02	13 ± 5	111.4 ± 8	0.02 ± 0.01
PCC	1.78 ± 0.03	10 ± 2	109.3 ± 9	0.18 ± 0.04
PCCT	1.74 ± 0.03	13 ± 4	160.8 ± 11	0.24 ± 0.06