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Optimizing matrix and fiber/matrix interface to achieve combination of strength, ductility and toughness in carbon nanotube-reinforced carbon/carbon composites

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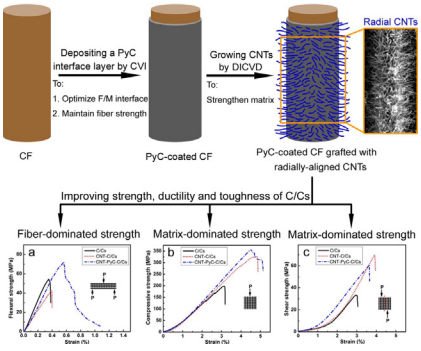
HIGHLIGHTS

- Both matrix and fiber/matrix interface of carbon/carbon composites were optimized.
- Radial carbon nanotube (CNT) was grown on carbon fibers (CF) to strengthen matrix.
- Pyrocarbon layer was introduced between CF and CNT/matrix to optimize interface.
- Optimal designs endowed composite with improved strength, ductility and toughness.

GRAPHICAL ABSTRACT



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ABSTRACT

The direct attachment of carbon nanotubes (CNTs) on carbon fibers (CFs) always leads to a decrease of fiber-dominated properties (e.g., flexural strength) and a brittle fracture behavior of C/Cs, although the matrix-dominated properties (e.g., compressive strength and interlaminar shear strength (ILSS)) exhibit an obvious enhancement. To achieve the combination of mechanical strength, ductility and toughness in C/Cs, in this work, efforts were spent on simultaneously optimizing the matrix and fiber/matrix (F/M) interface. CNTs with radial orientation were grown onto the CFs by double-injection chemical vapor deposition to modify the microstructure of matrix. Pyrocarbon was deposited on the surface of CFs before CNT growth to protect CFs and to weaken interfacial strength between CFs and CNT/matrix. These optimal designs create strengthening and toughness mechanisms such as crack deflection and long pullout of CFs in the failure process of composites, which endow C/Cs with improved flexural strength of 31.5%, flexural ductility of 118%, compressive strength of 81.5% and ILSS of 82%, accompanied by a clear change from brittle fracture to pseudo-plastic fracture during flexural test. This work may provide a meaningful way to not only enhance both the fiber- and matrix-dominated strength but to substantially improve the ductility and toughness of C/Cs.

1. Introduction

Design of high-performance structural engineering carbon/carbon composites (C/Cs) is driven by optimizing combinations of mechanical

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properties such as strength, ductility, toughness and requirements for stability and non-catastrophic failure during service [1,2]. C/Cs exhibits high specific strength and modulus, however, they have weak compression and interlaminar properties, lack ductility and toughness, and always fail in an apparently brittle manner in unconstrained loading geometries [3–5].

Recently, the huge interest in incorporating carbon nanotubes (CNTs) into structural composites have been stimulated by virtue of their extraordinary intrinsic properties, such as ultrahigh strength, excellent electrical and thermal conductivities [6,7]. These outstanding mechanical and physical properties, in combination with their unique 1D nanostructures with high specific surface areas, allow for efficient tailoring of both matrix microstructure and fiber/matrix (F/M) interface state [8,9]. For the incorporation of CNTs into composite structures, the general trend has been focused on in situ-growth of CNTs [10–12] or attaching CNTs to the carbon fibers (CFs) [13–15]. Unlike attracting CNTs which trend to lie in the plane of fiber surface and thus only provide one-side reinforcement to the C/Cs (just at F/M interface area), growing CNTs on the surface of CFs by catalytic chemical vapor deposition (CVD) has many advantages in terms of controllability of size and orientation of CNTs, particularly a radial orientation that allows for simultaneous reinforcements to the matrix and F/M interface [16]. Exciting increases in matrix-dominated properties (e.g., compressive strength and interlaminar shear strength) of C/Cs have been observed by growing CNTs onto carbon fibers [17–19]. Nevertheless, there still exit some critical issues regarding the C/Cs reinforced with CVD-grown CNTs. Firstly, due to the potential damage (dissolution of metal catalysts into carbon, local oxidation and gasification) of the CFs during the growth reaction [20,21], and the difficulty of controlling the orientation and uniformity of the grafted CNTs on CFs [16,22,23], the studies on the enhancements both in fiber- and matrix-dominated strengths of C/Cs have rarely been reported. Secondly and more importantly, the direct attachment of CNTs onto CF surface always result in strong F/M interfacial bonding and thus obstructs the crack deflection along the axis of CFs [17,23–25], which leads to the failure of fiber pullout as an effective strengthening and toughening mechanism. There will be little or no property enhancement in the ductility and toughness expected in such a mode of composite failure [26,27]. If CNT-reinforced C/Cs is to replace C/Cs in industries, it is necessary to achieve the combination of global strength, ductility and toughness in C/Cs. Over the past few decades, however, few efforts have been spent on this issue.

To improve the comprehensive mechanical performance of CNT-reinforced C/Cs, the substantial problem and great challenge are how to moderate the F/M interfacial bonding so that it is neither too strong nor too weak and how to supply effective reinforcements to the carbon matrix without degrading the fiber strength. In this work, a thin pyrocarbon (PyC) interface layer was deposited on the surface of CFs by chemical vapor infiltration (CVI) technique to optimize the F/M interfacial bonding, whilst preventing the dissolution of metal catalysts into CFs occurred during the subsequent growth of CNTs. Afterwards, double-injection CVD (DICVD) technique was developed to grow radially-aligned CNTs on PyC-coated CFs. The schematic of this manufacturing process is depicted in Fig. 1. The hybrid fiber preforms were then desified by CVI technique to obtain the final CNT-reinforced C/Cs. Three-point bending, compression and interlaminar shearing tests were applied to examine the effect of these optimal designs on the mechanical properties of C/Cs.

2. Experimental

2.1. Raw materials

Carbon felts (bulk density 0.2 g/cm^3, fiber diameters 6–8 μm, Yixing Tianniao Co. Ltd., China) used in this work were fabricated by alternatively overlapping layers of randomly oriented short fiber bundles with needle-punching step-by-step.

2.2. Deposition of PyC interface layer on CFs and the growth of CNTs

Carbon felts were firstly deposited with an interface layer of PyC by isothermal CVI technology, which was carried out at 1080 °C using flowing mixture of CH_4 (40 L/h) and N_2 (160 L/h) under the ambient pressure. The growth of CNTs in carbon felts was conducted by DICVD technique using $FeSO_4 \cdot 6H_2O$ as catalyst precursor. Incipient wetness technique was applied to introduce catalysts into felts using distilled water as solvent. Afterwards, they were placed in a CVD reactor and heated to 750 °C under Ar flowing. At the growth temperature, xylene as the hydrocarbon source was injected into the reactor through a thin tube via a syringe. Ethylenediamine as the growth promoter was filled in another syringe and was injected separately from the same side for the xylene injection. The ratio of injection rates of xylene and ethylenediamine was 8:1. The Ar/H_2 (2/1) gas mixture was used as the carrier gas with a flow rate of 600 sccm. The growth time was 2 h. The direct growth of CNTs in carbon felts without PyC interface layer was also performed by DICVD technique under identical growth conditions. The volume fractions of CNTs in carbon felts with and without PyC interface layer were approximately 1.3%.

2.3. Composite preparation and mechanical property tests

The densification was carried out by isothermal CVI technique for 150 h under the conditions described in section 2.2. The C/Cs containing both the PyC interface layer and CNTs were denoted as CNT-PyC-C/Cs, while the C/Cs containing only CNTs were denoted as CNT-C/Cs. The

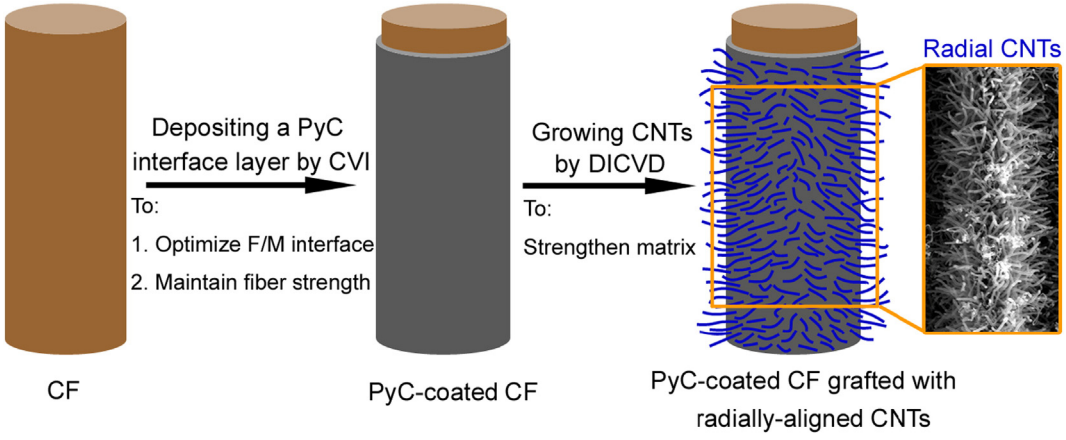

Fig. 1. Schematic of depositing PyC interface layer on CFs and followed by growth of radial CNTs by DICVD to maintain fiber strength, optimize F/M interface and strengthen matrix of C/Cs.