Composites: Part A 90 (2016) 480–488

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Surface structures of PAN-based carbon fibers and their influences on the interface formation and mechanical properties of carbon-carbon composites

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ARTICLE INFO

Article history:
Received 6 May 2016
Received in revised form 25 June 2016
Accepted 19 August 2016
Available online 21 August 2016

Keywords:
A. Carbon fibers
A. Carbon-carbon composites (CCCs)
B. Interface/interphase
B. Mechanical properties

ABSTRACT

Defects and microvoids in the surface region not only influenced the tensile strength and strain of carbon fibers but also affected the interface formation with pyrocarbon. The interface formation in carbon-carbon composites was closely correlated to rearrangement of carbon atoms and the evolution of surface structure of carbon fiber. Half-open elliptic microvoids or edge planes at the fiber surface were beneficial to the mechanical interlocking as well as chemical bonding with pyrocarbon, contributing to a compatible interface with high interlaminar shear strength of the composites. The closed microvoids in the surface region of carbon fiber would hardly open up to bond with pyrocarbon, which brought negative effects to the mechanical properties of composites. Carbon fiber without obvious microvoids or surface defects tended to have better tensile strain but form weak interface with pyrocarbon, leading to a better pseudo-ductility and ability to absorb more fracture energy under load.

1. Introduction

Carbon fiber is widely used as structural reinforcement in composites used in applications requiring excellent mechanical properties and light weight [1–3]. The most commercially available carbon fiber currently is produced from the polyacrylonitrile (PAN) precursor using wet spinning technique. In the stabilization and carbonization processes of the precursor, several kinds of decomposition gases like HCN and H_2O are released, which is totally unavoidable [4]. A number of voids were developed mainly in the external zones of the PAN-based carbon fibers, which was proved through small angle X-ray scattering studies [5–7]. Due to the different process of manufacturing, commercially available carbon fiber varies according to the precursors, strength, stiffness and surface characteristics [8,9]. It was known that the tensile strength of carbon fibers was influenced both by internal structure and surface defects [10]. Therefore, both the voids and surface defects were obviously obstacles to improve the tensile strength of PAN-based carbon fibers.

In carbon fiber reinforced composites, fiber/matrix bonding influenced the crack propagation during failure and good fiber strength utilization depended on the control of fiber/matrix interface structure [11–13]. It was obvious that the surface structure of carbon fiber played a key role in the interface formation with matrix. Rough surface of carbon fiber was reported to be beneficial for interface bonding in fiber reinforced composites, which was mainly due to the enhanced mechanical interlocking between fiber and matrix [14,15]. As for the carbon-carbon (C/C) composites with pyrocarbon (PyC) by chemical vapor infiltration (CVI) after graphitization, the formed interface region between carbon fiber and pyrocarbon showed differently textured region and the first 10 nm of the deposited pyrocarbon were deeply influenced by the fiber topography [16]. It was considered that proper defects or functional groups of fiber surface would also be beneficial to inducing the well deposition of pyrocarbon [17]. However, how the surface structure in carbon fibers evolved and influenced the interface formation in composites was still unclear. The interfacial structure of the C/C composites was closely related with their mechanical properties and fracture behavior under load [18].

In this paper, four types of PAN-based carbon fibers were used to prepare preform of the same architecture and density. The pyrocarbon matrix was deposited by CVI process under the same infiltration parameters. Surface structures, including microvoids and surface defects, and mechanical properties of the four types of PAN-based carbon fibers were studied. Furthermore, the microstructure and mechanical properties of their fiber-matrix interfaces developed in the C/C composites were compared. The

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http://dx.doi.org/10.1016/j.compositesa.2016.08.023
1359-835X/

interface formation process of the samples was modeled and the structure-property relationships in C/C composites were discussed.

2. Experimental

2.1. Materials

The PAN-based carbon fibers used in this study were commercially available 12 K carbon fiber CF-I (as received, GQ3522-12K from Weihai Tuozhan Fiber Co. China), CF-II (as received, GQ4922-12K from Weihai Tuozhan Fiber Co. China) and CF-III (as received, T300-12K from Toray Industries, Inc.). The surface of CF-II was modified by nitric acid (65%) for 60 min under 55 °C and the obtained carbon fiber was labeled as CF-IV.

Four preforms made of CF-I, CF-II, CF-III and CF-IV respectively were fabricated by alternatively stacked non-woven layers and carbon fiber webs through a needle-punching technique to a density around 0.50 g/cm^3. Pyrocarbon was deposited by the CVI process using natural gas as carbon source to obtain C/C composites. The final bulk density of the C/C samples was controlled at about 1.20 g/cm^{3}after CVI process without any other treatment and the prepared C/C composites were correspondingly labeled as C/C-I, C/C-II, C/C-III and C/C-IV according to their carbon fiber types.

2.2. Characterization of surface structure of PAN-based carbon fibers

2.2.1. Microstructural analyses of carbon fiber surface

Surface morphologies of the studied PAN-based carbon fibers were obtained by scanning electron microscopy (SEM, Nova Nano SEM230). Atomic force microscopy (AFM) imaging of carbon fibers was performed using a Veeco NanoManTM VS + MultimodeV atomic force microscope in tapping mode. Single fibers were fixed on the sample holder using double-side adhesive tape. The surface roughness (R_a) of the micro-domains was obtained through the installed software. At least five filaments were tested for each kind of carbon fibers.

Focused ion beam machining (FIB, FEI Helios Nanolab 600i) was applied to get cross-sectional slices of the carbon fibers for transmission electron microscopy (TEM, Titan G2 60-300 with image corrector). A deposition of a thin Platinum (Pt) layer was firstly conducted to protect the exposed surfaces and avoid damage of the surface regions during the FIB milling.

2.2.2. Investigation of the surface structure of the carbon fibers by Raman spectroscopy

Raman analysis was conducted with an XY Raman microspectrometer (LabRAM Aramis, Jobin Yvon) using a laser wavelength of 532 nm and fixed power at 2.1 mW since carbon fibers could be very sensitive to the heat generated by the laser. The laser was focused with a 50× magnification objective and the spot diameter was 1 μm. For each spectrum, the accumulation time was 50 s. Spectra were measured in the 1000–1800 cm^{-1} range. Carbon fiber samples were placed directly at the microscope stage and the surface zone was selected optically. The characterization of each sample involved 20 different single fibers.

2.2.3. Tensile strength of single-filament carbon fiber

The tensile strength of the carbon fibers was measured using a single-filament fiber tensile test according to the method described in ASTM Standard D3379-75. Over 60 filaments were tested to obtain the average value.

2.3. Characterization of the C/C composites

2.3.1. Microstructure characterization

Slices with a thickness of 200 μm were cut from the composites and further reduced in thickness by mechanical grinding and polishing to 80 μm before the Ar$^+$-ion milling. TEM studies were performed to observe the interface structure between carbon fiber and pyrocarbon matrix.

2.3.2. The mechanical properties of the C/C composites

Rectangular bars of 36 × 10 × 6 mm^3 with the plane of maximum area parallel to the non-woven cloth layer were cut from C/C samples for the interlaminar shear strength (ILSS) test [19] to determine the quality of matrix and fiber bonding in the four types of composites. The tests were carried out in a three-point bending rig over a span of 24 mm with a ϕ4 mm supporting roller and a ϕ 6 mm loading roller on a testing machine CSS-44100. The tests were carried with a constant crosshead speed of 1.5 mm/min and the loading direction was perpendicular to the non-woven cloth layer. Impact toughness tests were performed on bar specimens (10 × 10 × 55 mm^3) with the load in the direction perpendicular (⊥) and parallel (//) to the non-woven cloth using the Charpy method [20]. The dimension of the samples for ILSS and impact toughness tests were shown in Fig. 1.

3. Results and discussion

3.1. Surface structure of carbon fibers

Fig. 2 showed the surface topographies of CF-I, CF-II, CF-III and CF-IV observed by SEM and AFM. All the four types of carbon fibers had grooves which distributed parallel along the longitudinal direction of carbon fibers. It was remarkable that the surface of CF-III (Fig. 2(e) and (f)) was relatively smooth with grooves almost evenly distributed both in width and depth, while the grooves of CF-I (Fig. 2(a) and (b)) and CF-II (Fig. 2(c) and (d)) were wider and deeper at some extent. CF-II had the highest surface roughness (R_a) among the three carbon fibers in as-received state.

However, after the oxidation treatment by nitric acid for 60 min at 55 °C, the R_a value of CF-II decreased from 43.6 to 28.4 nm,

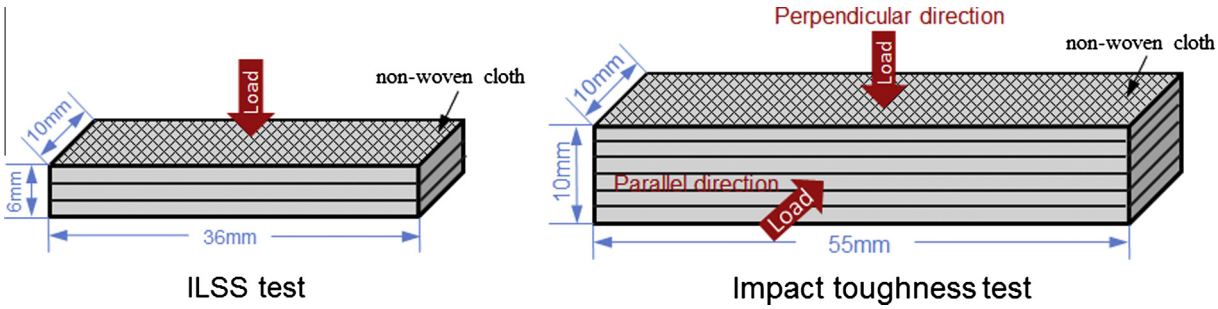

Fig. 1. The dimension of the samples for ILSS and impact toughness tests.