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The effects of phenolic resin-derived PyC interlayers on microstructure and mechanical properties of Cf/SiC composites

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ABSTRACT

A novel, easy and cost-effective way, infiltration and pyrolysis of phenolic resin solution, was exploited to prepare pyrolytic carbon (PyC) interlayers for carbon fiber/silicon carbide (Cf/SiC) mini-composites. X-ray photoelectron spectroscopy, dynamic contact angle measurement and scanning electron microscope were carried out to characterize chemical structure of carbon fibers (CFs), wetting properties between CFs and phenolic resin solution and microstructure of CFs and their composites, respectively. Remarkably, SEM results showed regulation of uniformity and thicknesses of PyC interlayer could be achieved through controlling the concentration of phenolic resin solution and oxidation condition of CFs. When CFs were treated by 10 min' oxidation with 40 mg/L ozone followed by dip-coating with 4 wt% phenolic solution, uniform PyC interlayer with approximately 120 nm were prepared on CFs. The corresponding Cf/SiC specimens had the largest increase in tensile strength and work of fracture with the improvement of 26.2% and 71.6% from the PyC-free case.

1. Introduction

Carbon fiber/silicon carbide (Cf/SiC) composites have considerable potential to be used in aerospace field as thermostructural materials partially in place of superalloys due to higher strength to density ratio, higher temperature-resistance, better thermal shock resistance [1–4]. For Cf/SiC composites, improvement in their fracture toughness is one of important research issues [5–7]. In order to achieve good toughness of SiC composites, weak interlayers like pyrolytic carbon (PyC) and boron nitride (BN) have been extensively investigated to be introduced in composites [8–11].

PyC layer is always introduced on carbon fibers (CFs) fully through chemical vapor infiltration (CVI). The obtained PyC layers could be textured and has low shear strength [12,13], which are beneficial for pull-out of CFs from composites and improvement of fracture toughness of composites. However, CVI process takes long processing time and costs high expenses. Phenolic resin is available to form PyC by curing and pyrolysis [14–18] and the processes are time-saving and cost-effective, but it has rarely been exploited to prepare PyC interlayer of Cf/SiC composites [19]. Precursor infiltration and pyrolysis (PIP) process, an efficient method to prepare Cf/SiC composites [20,21], is probably an effective way to prepare PyC interlayer for composites with phenolic resin.

Furthermore, to fabricate full and uniform PyC interlayers for Cf/SiC composites is really very important to composites' mechanical properties because roughness of CFs has significant impact on thermal stress of composites tightly related to composites' mechanical properties [22,23]. Considering CFs' inertness, it will be a very difficult task to obtain full and thin PyC coating prepared from phenolic resin by PIP process on CFs, let alone obtain uniform PyC coating. Thus, prior to manufacturing uniform PyC coating, it is necessary to ensure good wetting property between CFs and phenolic resin solution. It has been reported that oxidation treatment for CFs could improve its surface energy [24] and enhanced wetting property between CFs and PA-12 resin [25]. Taking hydroxyl groups on phenolic resin into consideration, if CFs could have many oxygen-containing functional groups, the above goal is possible to be achieved based on good compatibility between them. Ozone was used to oxidize CFs in this work, which was a very effective way to increase oxygen-containing functional groups of CFs [26] and won't clutter CFs. After oxidized CFs are treated by phenolic resin solution through the PIP process, it is expected to obtain uniform PyC coatings on CFs.

In this paper, the effects of concentration of phenolic resin solution and oxidation condition of CFs on uniformity and thicknesses of phenolic resin-derived PyC interlayers in Cf/SiC mini-composites were studied. PyC interlayers with different uniformity and thicknesses on

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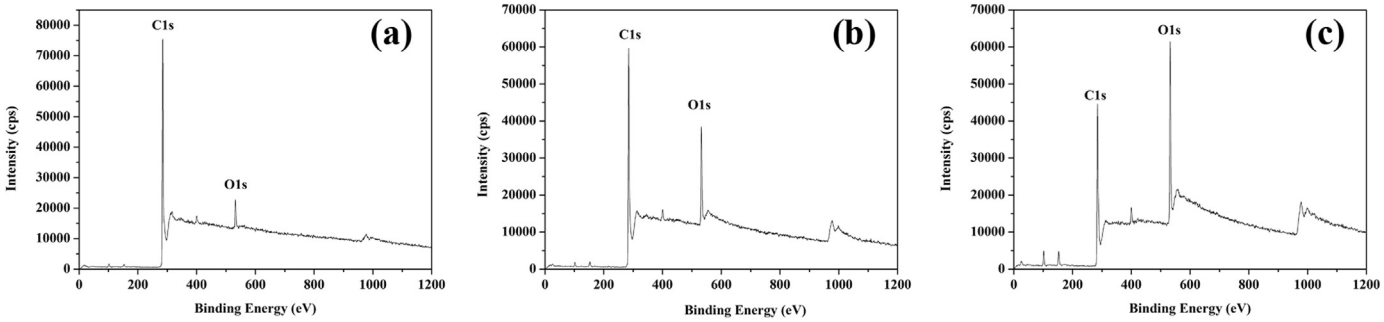

Fig. 1. The overall XPS spectra for CFs: (a) desized CF; (b) CF with 10 min' oxidation; (c) CF with 20 min' oxidation.

tensile strength, work of fracture (WOF) and microstructure of Cf/SiC mini-composites were also studied.

2. Experimental procedure

2.1. Raw materials

Carbon fiber tow (12k, T700) was obtained from Zhongfushenying Co. Ltd (Suzhou, China). PFNH-200 phenolic resin and hexamethylenetetramine were provided by Bomafenfang Co. Ltd (Xinxiang, China). Polycarbosilane (PCS) with number average molecular weight of 1742 and soften point of 175 °C was obtained from Sailifei Ceramic Fiber Co., Ltd. (Shuzhou, China). All other chemical reagents (analytical grade) were purchased from Aladdin (Shanghai, China).

2.2. Preparation of PyC interlayers and Cf/SiC composites

Prior to oxidation of CFs, CFs were firstly desized with heat treatment at 500 °C for 1 h in an N_2 atmosphere. Desized CFs were oxidized in tube furnace using 40 mg/L ozone at 140 °C for different time (5 min, 10 min, 15 min and 20 min, respectively). Phenolic resin and hexamine (with weight ratio of 10:1) were mixed in methanol to prepare phenolic solutions with different concentrations. CFs were dipped in the 4 wt% phenolic solution for half hour followed by curing (80 °C, 12 h; 145 °C, 2 h; 210 °C, 2 h.) and pyrolysis (keeping at 700 °C for 1 h with a heating rate of 10 °C/min in an N_2 atmosphere) to obtain PyC interlayer.

The Cf/SiC mini-composites were prepared using 9 cycles of PIP with 50 wt% PCS–xylene solutions, and the pyrolysis of PCS was conducted at 1100 °C for one hour with heating rate of 10 °C/min in N_2 atmosphere. During the Cf/SiC mini-composites preparation, CF tow was tightly fixed on graphite frame (the length of 10 mm) until the second PIP process of PCS. Each final composite sample had length of 100 mm and cross-section area of around 0.9 mm^2. The detailed procedures have been described elsewhere [27,28].

2.3. Samples characterization

The chemical structures of CFs were characterized by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA, Kratos, England). The C 1s region was fitted to component peaks by CasaXPS, with C 1s binding energy of the graphitic peak fixed at 284.6 eV for calibration purposes. The wetting performance between CFs and phenolic resin sizing was characterized by dynamic contact angle measurement with DCAT 21 system (Dataphysics, Germany). Wilhelm plate technique was taken with insert depth of 4 mm and insert speed of 0.01 mm/s in solution. The work standard about preparing the sample and testing have been detailed elsewhere [29]. Single filament strength testing was performed according to the ASTM standard of D3379-75 using Instron tensile testing device (Instron 4411, Norwood) with a 0.05 cN/dtex pre-tension. The tested gauge length was 25 mm, and the strain rate was 5 mm/min. In total, 40 samples of each fiber were tested, and the preparation of samples could be found elsewhere [30].

Based on a schematic of one-dimensional composite tensile test proposed by Li et al. [31], tensile strength of Cf/SiC composites were tested at room temperature by a single column servohydraulic tester (Instron3345, Norwood, MA, USA) under crosshead displacement control at a rate of 0.2 mm/min and a span of 50 mm. Specimens of tension tests were prepared as follows. The two ends of Cf/SiC composites were bonded on certain sized kraft papers as protection plates with epoxy adhesive, the protection plates were finally cured. Tensile strength of each composite was counted dividing the max tensile stress by the composite fracture cross-section area, which could be measured by Photoshop software based on scanning electron microscope (SEM) image of composite fracture cross-section. Fracture toughness of each composite was estimated with work of fracture counted by integration of the tensile stress–strain curve. To ensure the valid data, ten specimens for each composite were tested. SEM (Hitachi S-4800, Japan) was applied to observe surface or cross-section morphologies of CFs and composites. In addition, the samples of CFs with PyC coating for SEM observation were prepared by cutting down the CFs in liquid nitrogen environment.

3. Results and discussion

3.1. Characterizations of modification of CFs

The overall X-ray photoelectron spectroscopic (XPS) spectra for CFs are exhibited in Fig. 1. Fig. 1a shows the desized CFs have a dominant C 1s line and slight O 1s line. Fig. 1b displays the CFs with 10 min' oxidation have obvious O 1s line, and Fig. 1c exhibits the CFs with 20 min' oxidation have in the strongest O 1s peak. The C 1s region was then fitted to component peaks to give the fitted spectra seen in Fig. 2. Similar type and position of peaks in curve fitting of the C 1s region could be found in literatures [32,33]. The C=O peak and O=C-O peak are very weak for desized CFs in Fig. 2a, while both of the two peaks are obvious for CFs with 10 min' oxidation in Fig. 2b. Especially for CFs with 20 min' oxidation in Fig. 2c, the two peaks become very strong. The binding energies of different peaks and the relative amount of corresponding functionalities are shown in Table 1. It was very clear that the amount of oxygen-containing functional groups on CFs increased gradually with the increase of oxidation time.

For as-received CFs, its tensile strength is 3.67 ± 0.51 GPa, and the dynamic contact angle between CFs and 4 wt% phenolic solution is 79.41°. Properties of single CFs with different oxidation time are presented in Table 2. For desized CFs without oxidation, the tensile strength decreased slightly from that of as-received single CFs, and the dynamic contact angle between desized CFs with 4 wt% phenolic solution fell a little from that for as-received CFs. With the increase of oxidation time, both the tensile strength of single CFs and the dynamic contact angle between CFs and 4 wt% phenolic solution declined gradually. The tensile strength of single CFs with 20 min' oxidation reduced by approximately 6.8% from that of as-received CFs. The