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Preparation of vertically aligned carbon nanotube arrays grown onto carbon fiber fabric and evaluating its wettability on effect of composite

Feng An[a,b], Chunxiang Lu[a,*], Jinhai Guo[a,b], Shuqing He[a,b], Huibin Lu[a,b], Yu Yang[a]

[a] National Engineering Laboratory for Carbon Fiber Technology, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Vertically aligned carbon nanotube (CNT) arrays have been grown onto the carbon fiber fabric using a catalytic chemical vapor deposition (CCVD) method. The as-synthesized CNT arrays are about 20 μm in height, and the nanotube has a mean inner and outer diameter of 2.6 nm, 5.5 nm, respectively. The CNT-grafted carbon fabric shows a hydrophobic property with a contact angle over 145°, and the single CNT-grafted carbon fiber shows a sharp increase of dynamic contact angle in de-ionized water from original 71.70° to about 103°, but a little increase does in diiodomethane or E-51 epoxy resin. However, the total surface energy of carbon nanotube-grafted carbon fiber is almost as same as that of as-received carbon fiber. After CNTs growth, single fiber tensile tests indicated a slight tensile strength degradation within 10% for all different lengths of fibers, while the fiber modulus has not been significantly damaged. Compared with the as-received carbon fibers, a nearly 110% increase of interfacial shear strength (IFSS) from 65 to 135 MPa has been identified by single fiber pull-out tests for the micro-droplet composite, which is reinforced by as-received carbon fiber or CNT-grafted carbon fiber.

1. Introduction

Composite materials reinforced by carbon fibers are widely used in aerospace, sports goods and automobile industries due to their outstanding properties, such as high specific strength and stiffness, lower density and flexible tailoring, etc. [1]. Different from the excellent in-plane tensile properties of the carbon fiber reinforced polymer composites (CFRPs), the relatively weak out-of-plane properties which control compression and delamination performance still remain major obstacles. As is known, the principles indicate that the ultimate performance of CFRPs is strongly dependent on the interfacial adhesion of matrix and fiber, which relates to the wettability of fibers by the matrix [2]. Recently the research of hierarchical (or multiscale) CNT-grafted fiber reinforced polymer composites, in which a nanoscale reinforcement of carbon nanotube (CNT) or carbon nanofiber (CNF) is jointly applied with traditional microscale fibers to enhance out-of-plane properties of composite, has attracted a significant interest [3–5]. However, floating and agglomeration are two troublesome problems when the CNT is directly dispersed in the resin-matrix fiber composites [6,7]. By grafting CNTs onto the surface of carbon fiber (CNT-grafted carbon fiber), it shows a great potential to solve above problems and expects to stiffen the matrix surrounded the fiber for inhibiting fiber microbuckling during fracture, finally leads to an effective load transfer from matrix to fiber [8].

The ways of fabricating CNT-grafted carbon fiber mainly include chemical reactions between modified carbon fibers and CNTs [9,10], electrophoretic deposition [11,12] and growth of CNTs onto fibers via catalytic chemical vapor deposition (CCVD) [13,14]. Amongst them, CCVD appears to be a most frequently used way for its controllable diameter size [15] and orientation [16,17]. However, owing to the catalyst particles, such as iron (Fe), may be easily diffused into the carbon substrate at high temperature (over 850 °C) to lose activity [18], direct growth of CNTs onto carbon fiber commonly results in low density and inhomogeneity of CNTs with no orientation on the carbon fibers using CCVD [14]. An alumina [19], silicon [20] or silica [21] buffer layer may prevent the Fe catalyst diffusing into the carbon substrate and obtain vertically aligned CNT arrays grown onto the carbon fiber surface. Due to the hydrophobicity of CNT grafting, some scholars may deduce that a poor interfacial adhesion probably appears if preparing CFRPs using CNT-grafted carbon fiber as reinforcement [22,23]. However, some positive results have proved the increase of composite properties using this CNT-grafted carbon fiber as reinforcements, such as a 30% improvement of interlaminar shear strength (ILSS) [12], about 50% enhancement of fracture toughness [24] and a 69% increase of tensile strength [25].

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* Corresponding author. Tel.: +86 351 4166215; fax: +86 351 4166215.
E-mail address: chunxl@sxicc.ac.cn (C. Lu).

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Table 1
Physical properties of PAN-based carbon fiber substrate.

Carbon fiber (PAN-based)	Tensile strength σ_f (GPa)	Tensile modulus E_f (GPa)	Density (g/cm^3)	Failure strain (%)	Diameter d_f (μm)
T300-3K	3.90 (0.10)	230(2)	1.76 (0.01)	≥1.5	7.0 (0.1)

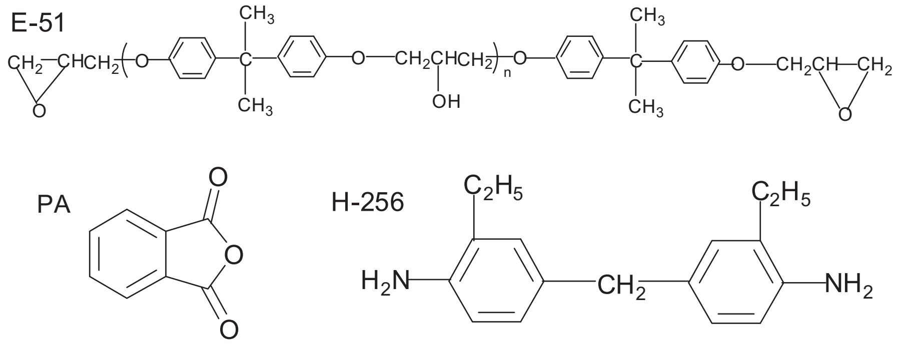

Fig. 1. The chemical structures of E-51 epoxy resin and curing agents.

Inspired by Hart et al. [26], high-yield growth and morphology control of aligned CNTs could be grown onto ceramic (Al_2O_3) fibers. In this study, vertically aligned CNT arrays were densely grown onto the carbon fiber fabric by introducing an alumina (Al_2O_3) buffer layer on the fabric prior to CNT growth. The aims of this research work are to investigate the influence of Al_2O_3 buffer on CNT morphology and tensile strength of single carbon fibers after CNT growth, then the property of CNT-grafted carbon fiber and its effect on interfacial shear strength (IFSS) of micro-droplet epoxy composite has also been investigated.

2. Experimental procedure

2.1. Materials

The polyacrylonitrile (PAN)-based carbon fiber fabric (or carbon cloth with 8 cm × 12 cm cm size) possessing special properties in Table 1 (Yixing Hengtong Carbon Fiber Weaving Co., Ltd.) was thermally treated at 400 °C in pure nitrogen (N_2) for 1 h to remove sizing.

Analytical grade reagents of $Fe(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, acetone and ethanol were all supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The chemical structure of commercially available thermoset epoxy resin diglycidyl ether of bisphenol-A (DGEBA, trade name: E-51) with an epoxy equivalent weight 0.54/100 g and curing agents: phthalic anhydride (PA) and benzyl dimethylamine (H-256) is all shown in Fig. 1, all which are supplied from Shanghai Research Institute of Synthetic Resins (China).

2.2. Growth of carbon nanotubes onto carbon fiber fabric

Before growth of CNTs onto carbon fiber fabric, the de-sized woven cloth (above) was firstly soaked into a 0.1 M ethanol solution of aluminium nitrate, then a thin film of Al_2O_3 buffer layer was coated onto the fiber surface by decomposing the aluminium salt at a heating rate of 2 °C/min to 250 °C. An incipient impregnation method was employed to introduce iron catalyst precursor (50 mM, 2.02 g $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in 100 ml acetone) onto the carbon fiber fabric using a syringe prior to the CCVD synthesis of CNT. The growth of CNT was carried out in a horizontal tubular quartz furnace (OTF-1200X, Hefei Kejing Materials Technology Co., Ltd.) by using acetylene (C_2H_2) as carbon source. Before reaction, the tube was evacuated with a vacuum pump and flushed with pure N_2 three times to remove moisture and atmosphere in it. After 10 min reduction by hydrogen (H_2) at 700 °C, the CNT growth started as we fed a constant flow of 20 sccm C_2H_2 together with a total 400 sccm flow of 10% H_2/N_2 carrier gas into the reactor when the tube reached 750 °C. After 30 min reaction, the carbon source and power were turned off to let furnace cool down. The amount of as-synthesized products on the carbon fiber fabric can be calculated from Eqs. (1) and (2).

$$W = W_T - W_{Al} - W_0 \tag{1}$$

$$W_\eta \ (\%) = \frac{W}{W_0} \times 100\% \tag{2}$$

where W is the amount of as-synthesized products after CCVD process, W_η is the percentage of as-synthesized products to de-sized carbon fabric, W_0 is the weight of de-sized carbon fiber fabric, W_{Al} is the weight of Al_2O_3 buffer layer after 250 °C treatment, W_T is the total weight after reaction, including de-sized carbon fabric, Al_2O_3 coating and as-synthesized products. The whole fabrication process is depicted in Fig. 2.

2.3. Preparation of micro-droplet composite specimens

A single filament of as-received carbon fiber or CNT-grafted carbon fiber detached from the fabric was fastened to a thin concave metal holder (20 × 100 mm) with double sided adhesive tape (detailed description in the previous report [27]). Some epoxy micro-droplet specimen made by applying epoxy resin/phthalic anhydride/benzyl dimethylamine at a weight ratio of 100:70:1 were adhered on a single filament with an embedded length of 50–90 mm using a fine-point applicator. Then the specimens were cured in an air dry oven (101A-1, Shanghai Laboratory Instrument Works Co., Ltd.) under the normal pressure at 90 °C for 1.5 h, then at 120 °C for 2 h and finally at 150 °C for 3 h.

2.4. Characterizations

2.4.1. Morphology and microstructure of carbon fabric

The morphology and microstructure of carbon fabric or monofilament were characterized by scanning electron microscopy (JSM-6360LV, SEM JEOL, Japan) and high resolution transmission electron microscopy (JEM-2010, HRTEM JEOL, Japan). The inner and outer diameters of as-synthesized CNTs were