NON-DAMAGING AND SCALABLE CARBON NANOTUBE SYNTHESIS ON CARBON FIBRES

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Abstract

The growth of carbon nanotubes (CNTs) on carbon fibres (CFs) to produce a hierarchical fibre with two differing reinforcement length scales, in this instance nanometre and micrometre respectively, is considered a route to improve current state-of-the-art fibre reinforced composites [1]. The scalable production of carbon nanotube-grafted-carbon fibres (CNT-g-CFs) has been limited due to high temperatures, the use of flammable gases and the requirement of inert conditions for CNT synthesis, whist (ideally) maintaining underlying original substrate mechanical properties. Here, the continuous production of CNT-g-CF is demonstrated in an open chemical vapour deposition (CVD) reactor, crucially, whilst retaining the tensile properties of the carbon fibres. As synthesised CNTs have a diameter of sub 20 nm and length ca. 120 nm, which are predicted to provide ideal fibre reinforcement in composites by retaining optimal composite fibre volume fraction (60%), whilst improving interfacial bonding of the matrix and reinforcement [1, 2]. Mild processing techniques enable this modified CVD process to be fully compatible with industrial practices, and have the potential to generate large volumes of hierarchical CNT-g-CF material.

1. Introduction

Carbon nanotubes (CNTs) have received considerable attention over the past decades due to their outstanding mechanical, thermal and electrical properties [3]. Recently, the use of CNTs as secondary reinforcement in conventional fibre-reinforced matrices have provided the opportunity to enhance the efficiency and quality of composite interfaces (i.e. interfacial shear strength, interlaminar delamination toughness) [4, 5]. The two main approaches to incorporate CNTs into conventional fibre-reinforced matrices consist in dispersing CNTs throughout the matrix [6] or attaching CNTs directly onto the primary reinforcing fibres. The first approach is restricted in terms of CNT loading due to increase in matrix viscosity and self-filtration. The second approach, on the other hand, alleviates this CNT loading issues and provides reinforcement of the fibre-matrix interface [7, 8]. CNT-grafting has been reported on a variety of substrates i.e. alumina, silica, carbon fibres. The latter, carbon fibres, out-perform silica and alumina fibres in terms of stiffness, strength and exhibit lower density which make them ideal for advanced structural composites. However, issues arise when carbon fibre is used as a substrate for CNT-synthesis given that common metallic catalysts dissociate in the carbon substrate leading to severe degradation of the initial substrate mechanical properties. Recently, De Greef *et al.*[9] produced carbon nanotube-grafted-carbon fibres (CNT-g-CFs) with reduced damage to the carbon fibres by extensive control of the chemical vapour deposition (CVD) parameters such as the use of low temperature (i.e. 500 °C). In this work, multi-walled carbon nanotubes are grafted onto high strength carbon fibres in a continuous fashion through the use of an open CVD reactor with and without promotion [10]. Initial experiments were carried out within the group on a batch system [11] and subsequently scaled up to continuous processing. An alternative method to promote CNT-grafting on carbon fibre substrates without damaging the underlying original substrate mechanical properties via a slight alteration of the CVD reaction conditions is presented. The morphology and mechanical

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properties of the modified carbon fibres were assessed using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and the single-fibre tensile test.

2. Experimental

2.1. Materials

- Continuous tow of sized, PAN-based carbon fibres, 7.1 µm diameter, AS4C-GP-12K, Hexcel Composites, UK.
- The bi-catalyst solution consist of iron(III) nitrate (≥98% ACS reagent, Sigma-Aldrich, UK) and nickel(II) acetylacetonate (≥98%, VWR, UK) in ethanol (>99.7% BDH Prolabo, VWR, UK).
- Acetylene in nitrogen (N_2 98.7 vol% and C_2H_2 1.3 vol%, C certificate), hydrogen in nitrogen (N_2 97.6 vol% and H_2 2.4 vol%, C certificate) and nitrogen (99.998 vol% minimum) were respectively used as the carbon source, reduction and carrier gases. All gases were purchased from BOC gases, UK.

Table 1. *Properties of the AS4C fibres, as described by manufacturer [12]*

Fiber type	Tensile strength [MPa]	Tensile modulus [GPa]	Strain to failure [%]	Density $[g.cm^{-3}]$
AS4C	4385	231	1.8	1.78

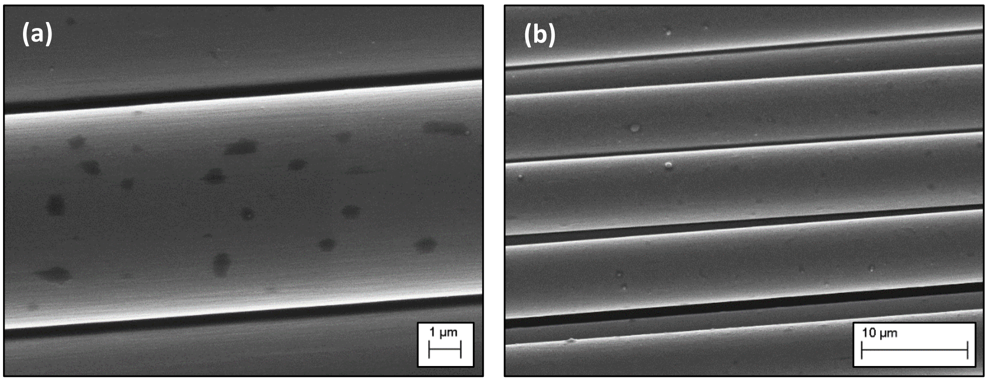

Figure 1. (a) and (b) SEM images of as-received carbon fibre surfaces.

2.2. Catalyst precursor deposition on carbon fibres

The bi-catalyst precursor solution was prepared by introducing 2 wt.% iron(III) nitrate and 2 wt.% nickel acetylacetonate in ethanol. The solution was stirred for one hour to ensure homogenisation prior to the deposition. Fifty metres of carbon fibres tow were wound onto a PTFE frame and submerged in the precursor solution for 2 min. The carbon fibres were then dip washed in deionised water for 1 min and dried at standard ambient atmospheric temperature and pressure.

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Figure 2. Photographs of (a) as-received fibres winding, (b) as-received fibres wound with scale and (c) bi catalyst precursor deposited carbon fibres.

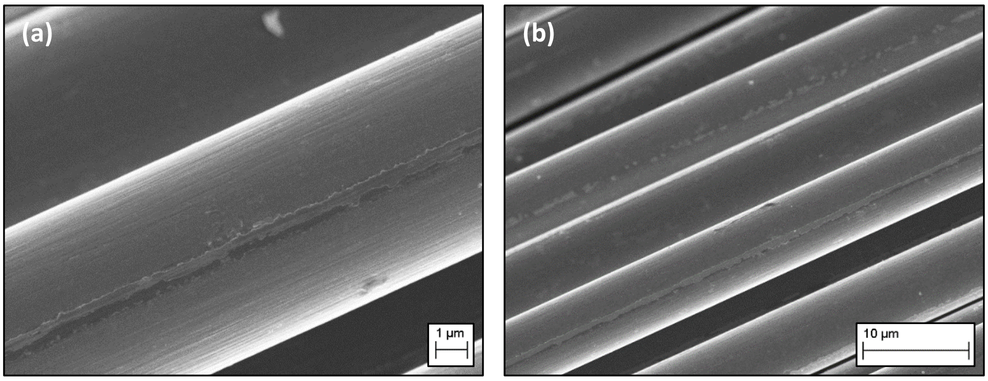

Figure 3. (a) and (b) SEM of bi-catalyst precursor deposited carbon fibres.

2.3. Continuous synthesis of carbon nanotube-grafted-carbon fibres

Using a hot-walled CVD synthesis technique, CNTs were continuously grown on the surface of carbon fibres, previously coated with bi-catalyst precursor. The bi-catalyst precursor deposited carbon fibres were loaded on to a spool and then pulled through the tubular furnace (PTF15//610, Lenton, UK) using a motor (D.C. geared motor with brushes, 0.5 Nm, 3.9 watts, Crouzet Motors) at a speed of 1.2 m.h^{-1}. The modified fibres which passed through the reactor were then wound on a collection spool. The chamber was purged with nitrogen for at least 40 min (7500 sccm) prior to heating to 760 °C at 10 °C min^{-1} under the same inert conditions (N_2, 7500 sccm). The carbon fibres was continuously pulled through the system and exposed to different gas conditions via an alterable arrangement of internal quartz tubing. As the fibre tow entered the furnace, it was first exposed to nitrogen (7500 sccm), then in the hot-zone hydrogen in nitrogen (3400 sccm) for catalyst reduction. After reduction, the tow was then subjected to acetylene in nitrogen (325 sccm) which acted as the carbon source for CNT synthesis for duration of ca. 25 min. The fibre was then passed through another nitrogen region (7500 sccm) to exit the reactor unimpeded. Once the reaction was complete, the acetylene source was turned off and the furnace was cooled under a nitrogen flow of 7500 sccm. A schematic of the CVD set-up is shown in (Figure 4).

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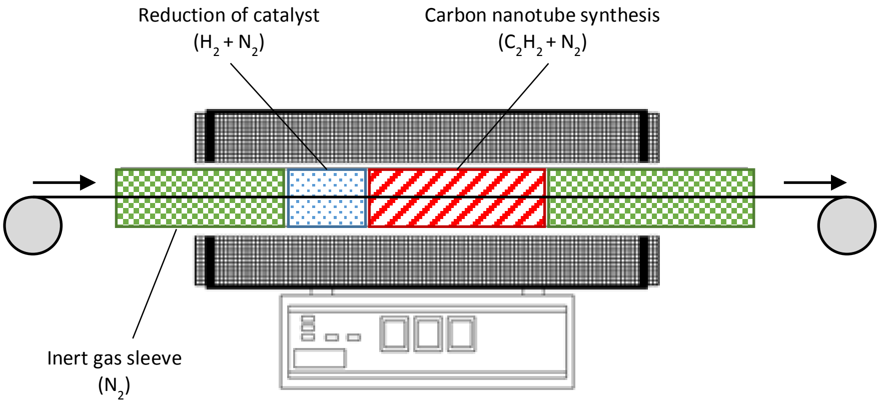

Figure 4. Continuous CVD line set-up zones with carbon fibre tow and direction indicated.

2.4. Fibre morphology characterisation

The morphology of the fibres were investigated to confirm the formation of CNTs using a high resolution field emission gun scanning electron microscope (SEM) (Leo Gemini 1525 using SmartSEM software interface V05.05.03.00, Carl Zeiss NTS Ltd., UK). SEM samples were prepared on Al stubs using silver dag (Agar Scientific, UK). Transmission electron microscopy (TEM) JEOL-2010F Electron Microscope (100 kV, JEOL (UK) Ltd., UK) was used to determine CNT length, with samples set in a folding butterfly grid (Cu mesh, Agar Scientific Ltd., UK). Open-source Java software ImageJ (V. 1.45s, U. S. National Institutes of Health, USA [13]) was used to post-process images and determine carbon fibre and CNT dimensions.

2.5. Single fibre tensile test

The tensile strength and modulus of as-received fibres, CNT-g-CF without/with promotion were tested using a TST350 tensile stress tester (Linkam Scientific Instruments Ltd., UK) with a 20N load cell and a cross-speed of 15 $\mu m\ s^{-1}$. The British standard (BS EN ISO 11566, 1996)[14] was followed (Method B, compliance value (K) 16.6 $mm.N^{-1}$). A minimum of 30 specimens were tested for each fibres. CNT-g-CF were assumed to have the same diameter as unmodified fibres given that CNTs carry insignificant axial load in comparison to carbon fibres. Single fibre were isolated from the bundle and glued to a card mount (25 mm gauge length) using a two component fast cure epoxy adhesive (Araldite Rapid Adhesive, Bostik Findley Ltd., UK).

3. Results and discussions

3.1. Morphology of the fibres

Bi-catalyst precursor deposition on carbon fibres was inspected via SEM and subtle differences in the surfaces (Figure 3) when compared to the as-received fibres (Figure 1), indicated a predominately thin coating on the surface; furthermore in this instance a line of collected catalyst precursor can be seen due to fibres drying next to each other. CNT-g-CF without and with promotion are depicted in Figure 5 (a) and (b) respectively, with the former only partial CNT growth and pitting is observed, whist in the latter, a short dense forest-like CNT morphology on the fibre surface is observed. To confirm CNT length on the CNT-g-CF with promotion sample TEM analysis was conducted (Figure 6) and indicated length on the order of 120 nm.

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3.2. Single fibre tensile tests

Single fibre tensile tests were carried out to examine the effect of the CNT-synthesis CVD conditions on the carbon fibres mechanical properties. The results of single fibre tensile testing for as-received carbon fibres, bi-catalyst precursor deposited carbon fibres and CNT-g-CF without/with promotion are shown in Table 2. CNT-g-CF without promotion exhibited a slight mechanical degradation (8%) compared to as-received carbon fibres yet minimal CNT growth. This decrease in tensile strength is mainly attributed to the dissolution of catalyst into the carbon fibres during the CVD conditions. On the other hand, CNT-g-CF with promotion showed the retention of the tensile properties comparable to the as-received/bi-catalyst precursor deposited carbon fibre controls and a significant, even coverage of CNTs.

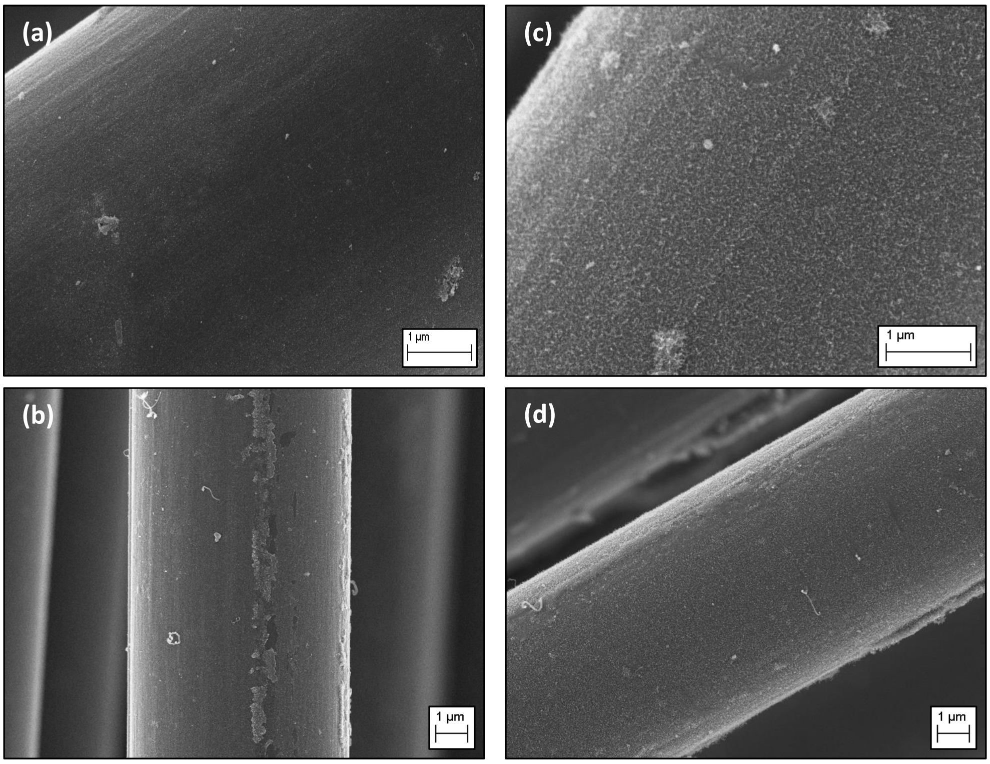

Figure 5. SEM of (a, b) CNT-g-CF without promotion and (c, d) CNT-g-CF with promotion.

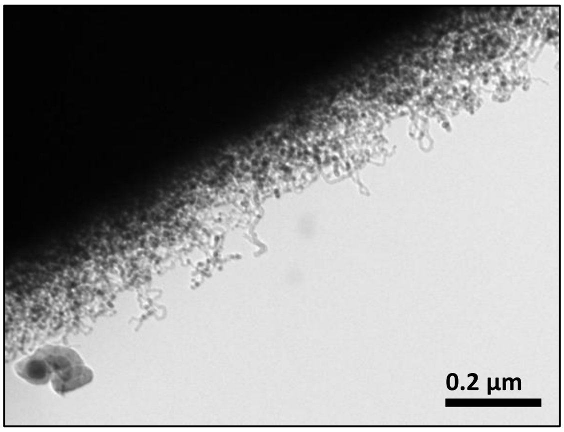

Figure 6. TEM of CNT-g-CF with promotion

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Table 2. Single-fibre tensile test results (25 mm gauge length)

Fibres	Tensile Strength (σ_t) [MPa]	Tensile Modulus (E_t) [GPa]	Number of samples
As-received	2833 ± 118	216 ± 2	24
Bi-catalyst precursor deposited	3049 ± 120	212 ± 3	25
Continuous CNT-g-CF (*)	2600 ± 60	209 ± 3	29
Continuous CNT-g-CF (**)	2937 ± 58	213 ± 3	27

** without promotion, ** with promotion*

4. Summary

In summary, CNTs were grown directly on the surface of carbon fibres in a continuous fashion using a thermal CVD synthesis technique. Original mechanical properties of the substrate were retained through a slight alteration of the CVD set-up. This CNT-grafting process should allow the manufacture of large composites parts for mechanical tests (compression, toughness, delamination, etc.).

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