CARBON NANOTUBE-GRAFTED QUARTZ FIBERS AS PIEZORESISTIVE REINFORCEMENT ELEMENTS

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ABSTRACT

The mechanical properties of fiber-reinforced composites depend on the properties of the fiber/matrix interface where stress concentrations dominate. Grafting of carbon nanotubes to produce a “hairy” or “fuzzy” carbon fiber creates hierarchical reinforcements, combining two different reinforcement length scales, in this instance micrometer and nanometer. This approach improves the interaction between fibers and polymer matrices, and can enhance thermal and electrical functionality of the final composite. Generally, hairy fiber production is limited to batch processes due to harsh synthesis conditions (e.g. high temperature, inert environment) inherent to chemical vapor deposition, and have only recently been scaled-up to continuous production. The development of hierarchical assemblies, which are the combination of reinforcements at different length scales for instance nanoscale and microscale, have shown promise as multifunctional and structural state-of-the-art materials. The concept of using carbon nano-reinforcements with macroscopic fibers (quartz in this occasion) can directly address the limitations of current composites architectures, e.g. catastrophic failure, limited fire retardancy properties, and poor electro-thermal performances.

Continuous production of such hierarchical materials, as a result of research carried out at Imperial College London and the University of Vienna, allows nano-engineered composites to finally meet industry implementation prerequisites. These methods are also compatible with commercial fiber production lines, which is a significant step forward towards the creation of a new class of high performance composite materials. Carbon nanotube-grafted-quartz fibers with uniform 200 nm long carbon nanotubes improved interfacial shear strength of 12% over a commercially sized counterpart (pull-out tests) in an epoxy matrix. Quartz fiber reinforced composites are normally electrically insulating, yet the carbon nanotube-grafted reinforcement allows a conductive pathway to prevail directionally (primarily parallel to the fiber’s axis). This imbued electroconductivity was exploited for structural health monitoring, demonstrating a linear piezoresistive response and strain gauge sensitivity of 3.64.

1 INTRODUCTION

The introduction of nanomaterials into the interphase region of fiber-reinforced composites is a popular method to reinforce the fiber-matrix interface [1]. Carbon nanotubes (CNTs) have high intrinsic mechanical properties as well as high electrical conductivity and are the most studied nanoreinforcing additive. Grafting, or growing carbon nanotubes from a macroscopic fiber surface, is a convenient and scalable method to locate these nanoscale reinforcers at this critical interface. The focus of carbon nanotubes growth from a fiber surface to create a hierarchical or "fuzzy" fiber, tends to be on carbon fibers [2], but other substrates, for example quartz [3], glass [4], and alumina [5] have also been reported. Here we present the characterization of carbon nanotube-grafted quartz fibers (CNT-g-QFs) made using a continuous chemical vapor deposition reactor at the tow scale [6].

2 MATERIALS AND METHODS

- A continuous roving of 6000 filaments, 13.0 ± 0.2 μm diameter sized quartz fibers (QFs), Quartzel® C14 1600 QS1318, was kindly provided by Saint-Gobain, FR.

- The precursor bi-catalyst solution for carbon nanotube synthesis consisted of nickel (II) acetylacetonate (⩾98%, VWR, GB) and iron (III) acetylacetonate (⩾99% ACS reagent, Merck, DE) in ethanol (96%, Brenntag, AT) in a 2:1 mol, respectively.

- The carbon source, reduction, and carrier gases for the reactions was acetylene in nitrogen (1.3 vol.% in 98.7 vol.%, respectively), hydrogen in nitrogen (2.4 vol.% in 97.6 vol.%, respectively), and nitrogen (99.998 vol.%), respectively. All gases were purchased from BOC gases, GB.

- For the preparation of single fiber (pull-out) composites Epon 828 (Netmro, US) with Jeffamine T-403 (Huntsman, US) were used as resin epoxy and hardener (100:42 by weight), respectively.

- For the preparation of the unidirectional bundle composites PRIME 20LV (Gurit, GB) with a slow hardener (ULV), were used as resin epoxy and hardener (100:19 by weight), respectively (as per manufacturer recommendations).

Carbon nanotube synthesis on quartz fibers is detailed elsewhere [6]. In short, sized QFs were used as received, and then pre-deposited at a rate of 10 m/h with a bi-catalyst with a residence time 2 min and dried at 40 °C and 70 °C, producing approx. 100 m of treated roving. The collected and spooled bi-catalyst deposited QFs were then passed, in inert conditions, through an open chemical vapor deposition reactor at 760 °C at 1.2 m/h and 2.4 m/h and subjected to reaction gases. After an initial inert gas sleeve, sequential regions of reaction gases for reduction (to activate the bi-catalyst), and a carbon rich gas (to grow the carbon nanotubes), and finally a second inert gas sleeve where the modified fibers were collected on a motorized spool. Heat-treated QFs were also prepared using this reactor with similar conditions on as-received QF but in the absence of reactive gases.

Fibers morphology was characterized through scanning electron microscopy (SEM), using a Zeiss LEO Gemini 1525 (DE) at an operating voltage between 2 keV to 5 keV. Single fiber pull-out tests were carried out on bespoke equipment [6] using a load cell with force resolution of 0.1 mN and a piezo-translator with resolution of 1.8 nm, operated at 0.2 μm/s. Unidirectional bundle composites were tested in accordance to ASTM D4018-17 [7], ensuring the fibers mass fraction is between 40 wt.% and 65 wt.%. Tensile tests were carried out using a Universal Testing Machine (Instron 5980, 250 kN load cell, US) at a cross-head displacement of 1 mm/min. During the tensile tests in-situ video gauge, acoustic emission, and in-plane electrical conductivity were recorded, for a complete description of experimental details please refer to H. De Luca et al. [6].

3 RESULTS

The length of carbon nanotubes produced on the fiber surfaces was proportional to the dwell time in the reactor with CNT-g-QF produced at 1.2 m/h (12 min dwell in carbon rich region) exhibiting carbon nanotubes lengths of 200 nm, and 2.4 m/h (24 min dwell) producing 30 µm length arrays (Figure 1). These sample morphologies are designated throughout as S (short) and L (long).

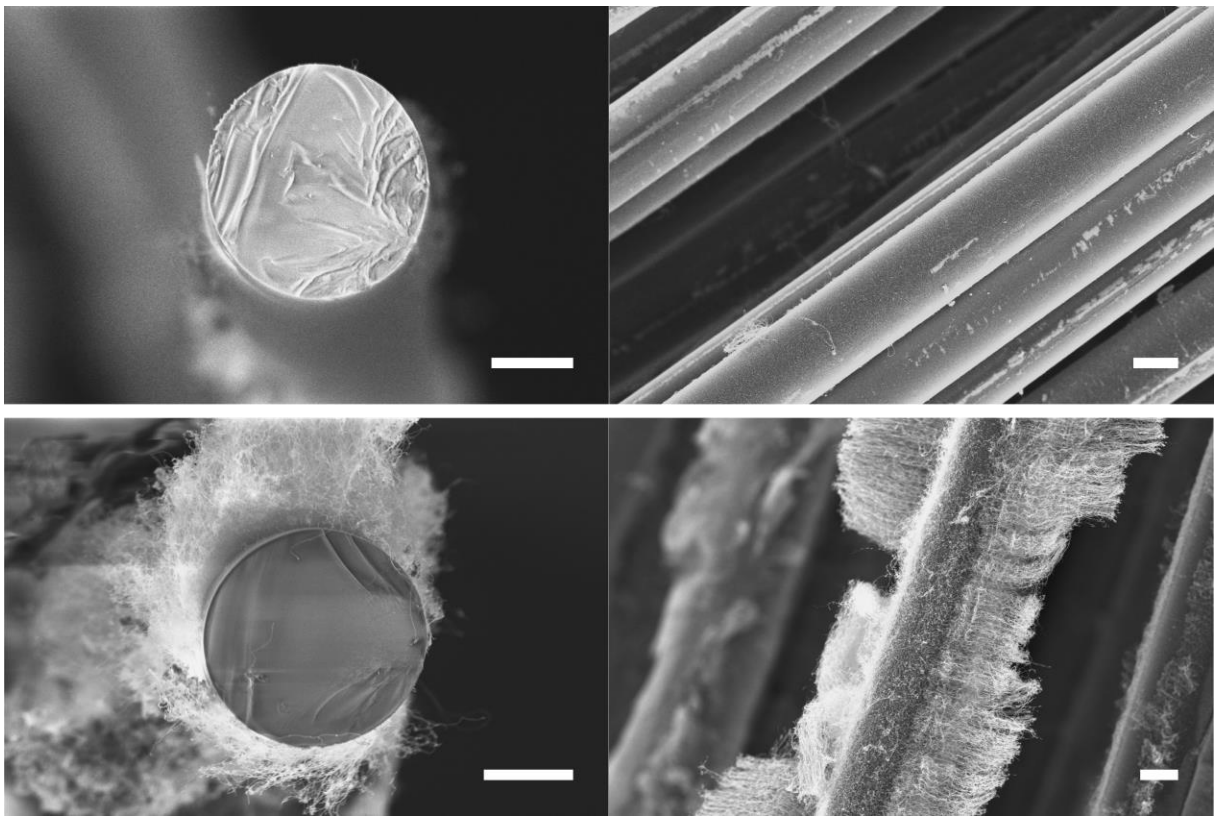

Figure 1: SEM micrographs of the modified QFs (Top) CNT-g-QF (S) with a uniform and short array of nanotubes, and (Bottom) CNT-g-QF (L) with long array of nanotubes exhibiting the characteristic "mohawk" motif. Scale bar is 5 µm for all panes.

Single CNT-g-QF (S) when embedded and pulled-out of in an epoxy matrix, demonstrated an improvement in apparent interfacial shear strength over the sized and heat-treated (desized) QF controls of 12% and 28%, respectively. The long length of the nanotubes in CNT-g-QF's (L) lead to non-uniform stress states due to the "mohawk" [8] motif, common for growth of carbon nanotubes from silica fiber surfaces. This resulted in no additional benefit for apparent interfacial shear strength for the addition of long nanotubes to the fiber surface when compared to the sized counterpart, but an increase of 13% over the heat-treated QF control. Bi-catalyst deposited QFs had the lowest apparent interfacial shear strength with a reduction of 30% observed compared to the as-received QF. The fracture surfaces and corresponding post pulled-out fiber diameters were observed through SEM and these were used to determine the individual embedded fiber area for each tested sample [6]. Tabulated data from the single fiber pull-out tests are included in Table 1.

Sample	Interfacial shear strength (MPa)	Fiber diameter after pull-out (μm)	Number of specimens
As-received QF	80.9 ± 1.7	13.0 ± 0.2	16
Bi-cat. deposited QF	55.3 ± 0.9	13.1 ± 0.1	22
Heat-treated QF	70.3 ± 4.5	13.2 ± 0.1	14
CNT-g-QF (S)	90.3 ± 2.1	13.0 ± 0.1	16
CNT-g-QF (L)	79.2 ± 2.2	13.2 ± 0.2	17

Table 1: Single fiber pull-out test results with interfacial shear strength determined using fiber diameter and associated embedded after pull-out with standard error associated [6].

An additional benefit of grafting carbon nanotubes to a non-conductive fiber substrate, such as quartz, is that they can increase the electrical conductivity of the system. This electrical conductivity remains when the fibers are used to reinforce a composite, and unidirectional tow based samples were produced to investigate this effect under mechanical load (Figure 2). As the carbon nanotubes are localized at the fiber surface (at very low absolute loading, on the order of 0.3 wt.% and 0.8 wt.% for short and long nanotubes arrays, respectively), they provide an opportunity to probe their effect as in-plane electrical conductive gauges. This electrical conductivity detection is directly at the fiber-matrix interface and increases in relative resistance as a function of strain. Indeed high strain gauge sensitivity was observed for both CNT-g-QF samples (Table 2), with the highest sensitivity observed for CNT-g-QF (S) of 3.64 ± 0.43 when compared to literature values of 1×10^{-5} S/m to 2 S/m at carbon nanotube loadings suitable for conventional composite processing (i.e. $\leqslant$ 1 wt.%) [6, 9]. A linear response in electrical conductivity of the samples was recorded until just before the abrupt and catastrophic failure of the samples at ca. 2 % strain (Figure 3). Further analysis of the data and comparisons to the collected acoustic emission data can be found in [6].

Analysis of the mechanical composite tensile tests (Table 2) reliably demonstrated the primary fiber modulus was preserved, although for heat-treated QFs and CNT-g-QFs the tensile strength was halved. High temperature processing of quartz fibers leads to surface defects and damage, which has been observed previously in batch chemical vapor deposition conditions [3], however this may be circumvented at the commercial scale.

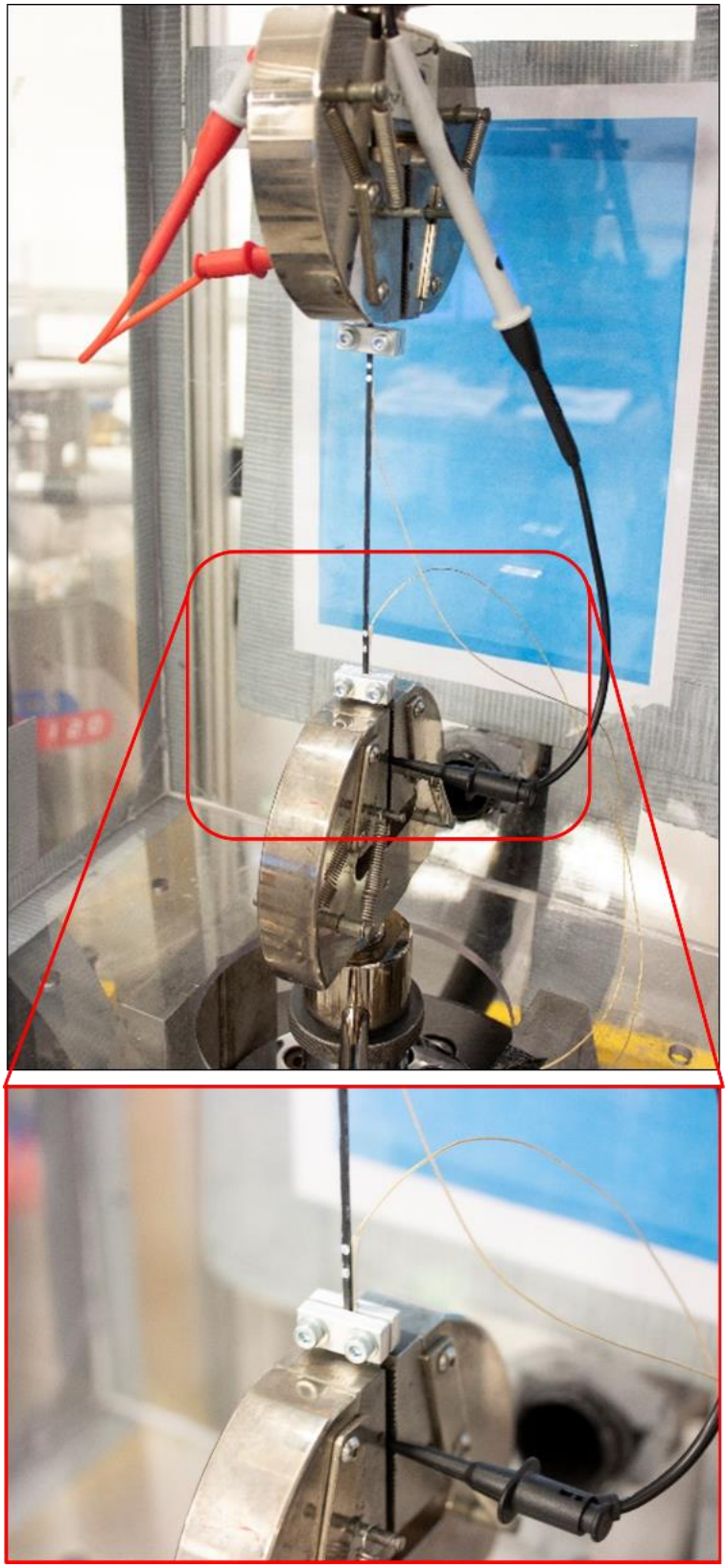

Figure 2: (Top) Photograph of the bundle composite test set-up following ASTM D4018. (Bottom) Close-up of the jaws, and in-situ detectors/targets, including acoustic emission microphone (contained within bolted rectangular aluminium clamp), white video gauge targets, and electrode (black) probe for electrical conductivity measurements. The second electrode (red) probe, targets, and additional microphone (in identical clamped arrangement) are shown in the top image above. Adapted from [6].

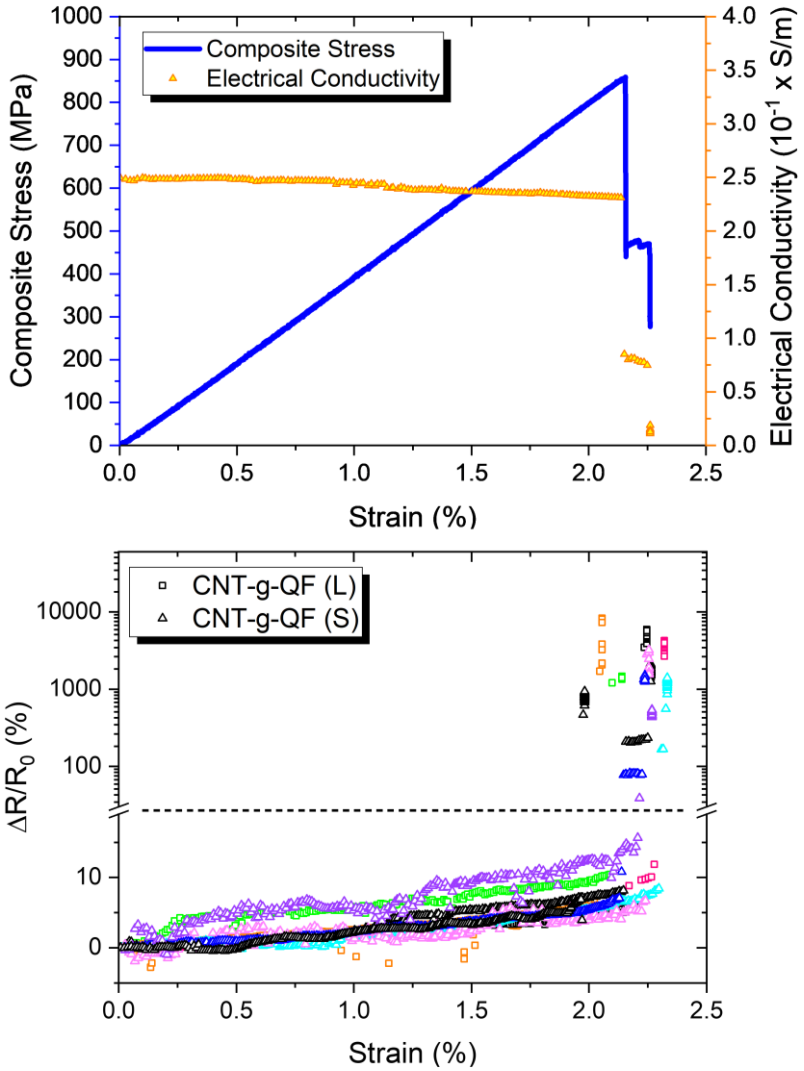

Figure 3: (Top) Stress-strain profile from a bundle composite test in tension, with corresponding in-situ measured electrical conductivity. (Bottom) Relative resistance changes, from initial, as a function of strain indicating a linear strain sensitivity up to ca. 2 %, with values reported above break in ordinate indicative of a significant increase in resistance from failure of specimen/significant number of fibers. Adapted from [6].

Sample	Composite strength (MPa)	Composite Young's modulus (GPa)	Initial resistance [R_0] (Ω) [$\times 10^4$]	Strain gauge sensitivity
As-received QF	1387 ± 52	38.9 ± 0.7	N/A	N/A
Bi-cat. deposited QF	1480 ± 53	38.8 ± 0.3	N/A	N/A
Heat-treated QF	1003 ± 10	38.7 ± 0.5	N/A	N/A
CNT-g-QF (S)	852 ± 18	38.8 ± 0.3	4.1 ± 0.5	3.64 ± 0.43
CNT-g-QF (L)	854 ± 16	39.7 ± 0.5	1.4 ± 0.1	2.79 ± 0.16

Table 2: Mechanical and in-situ electrical properties of the unidirectional bundle composites measured in tension with standard error provided. Tensile properties were normalized to a nominal fiber mass fraction of 65 wt.% following ASTM D4018 standard, which corresponds to a fiber volume fraction of 49 vol.%. strain gauge sensitivity calculated between 0.5 % and 2.0 % [6].

4 CONCLUSIONS

The resultant fiber-matrix interface was characterized with short and long grown nanotubes, 200 nm up to 30 µm respectively, using single fiber pull-out, and at the tow bundle level using the ASTM D4018 standard. During the bundle composite testing (Figure 2), in-situ measurements of electrical conductivity, solely as a component of the grafted nanotubes, displayed a linear piezoresistive sensitivity up to strains ca. 2% (Figure 3). The high sensitivity response, 3.6 ± 0.4, is a two-fold increase over traditional strain gauges. This was achieved even at very low absolute carbon nanotube composite loading (0.3 wt.%) for short grafted fuzzy fibers.

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