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CONTINUOUS PRODUCTION OF CARBON NANOTUBE-GRAFTED QUARTZ FIBRES: EFFECT OF CARBON NANOTUBE LENGTH ON FIBRE/MATRIX ADHESION

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ABSTRACT

Here, the continuous production of carbon nanotube-grafted-quartz-fibres was performed in an open chemical vapour deposition reactor with continuous in line catalyst deposition. Highly graphitic carbon nanotubes (CNTs) with controllable lengths ranging from 0.1 µm to 20 µm were grown on the quartz fibre surface by adjusting the reduction and growth times, with shorter fibres growing homogeneously and longer CNTs growing in a splayed "Mohawk" manner. The effect of CNTs length (and thus microstructure) upon the mechanical properties of CNT-grafted-quartz-fibre/epoxy composites was investigated through single fibre pull-out test. The presence of a uniform coverage of sub-micron long CNTs led to an increase in interfacial shear strength of 11% and 29% when compared to sized and de-sized quartz fibres, respectively.

1 INTRODUCTION

The mechanical properties of fibre-reinforced composites depend on the properties of the fibre-matrix interface, where stress concentrations prevail. *In situ* growth of carbon nanotubes (CNTs) on the surface of fibres produces "hairy" (or "fuzzy") fibres, incorporating both micrometre and nanometre reinforcement length scales. Common substrates are carbon [1], alumina [2] and silica [3] fibres with the former typically damaged during synthesis until recent developments by Anthony *et al.* [4, 5]. CNTs have provided the opportunity to enhance the efficiency (via mechanical interlocking) and quality of composites interfaces (i.e. interfacial shear strength) due to their high aspect ratio, low density, excellent stiffness and lateral flexibility [3, 6]. Simulations of neighbouring CNT-grafted-fibres carrying CNTs with different lengths, perpendicular to the fibre surface, showed a reduction in radial and shear stresses at the fibre-matrix interface. Stress concentrations are predicted to shift from the fibre matrix interface to the end of grafted CNT forest, effectively increasing the fibre diameter, resulting in higher stress concentrations in the resin rich region between the hierarchical fibres for longer CNTs [7]. This study not only allows direct comparison to the computational predictions on hairy fibres, but provides a route towards continuously grown CNT-grafted quartz fibres.

2 EXPERIMENTAL

2.1 MATERIALS

- Continuous 12K tow of sized Quartzel® fibres, 14 µm diameter, C14 1600 QS1318, Saint-Gobain, FR.
- The bi-catalyst solution consist of iron(III) acetylacetonate (≥99% ACS reagent, Merck, DE) 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.
- Epon 828 (Netmro, US) and Jeffamine T-403 (Huntsman, US) were both used as resin epoxy and hardener respectively.

3 CONTINUOUS SYNTHESIS OF CARBON NANOTUBE-GRAFTED-QUARTZ FIBRES

3.1 EQUIPMENT AND GROWTH PROCEDURE

The production of CNT-grafted-quartz fibres can be separated into two specific sections; the deposition of catalyst precursor particles on the fibres and the subsequent growth of CNTs from the catalyst precursor loaded fibres. In the same manner as the growth, catalyst precursor deposition was performed in-line by passing the fibre tow through a bath containing a mixture of 1 wt. % iron(III) acetylacetonate and nickel(II) acetylacetonate (1:2 mol.) in ethanol for two minutes. The coated fibres were then dried in two IR-furnaces (Figure 1) and collected on a spool. The bi-catalyst precursor deposited quartz fibres were then continuously pulled through the furnace and exposed to different gas conditions via an alterable arrangement of internal quartz tubing at speed ranging from 1 to 3 m h^{-1}. The hot-walled CVD set-up used in this project is a 3-zone tubular furnace (PTF 15/-/610, maximum temperature 1450 °C, Lenton, UK) (Figure 2). As the fibre tow entered the furnace, it was first exposed to nitrogen (7500 sccm), then in the hot-zone (760 °C) to hydrogen in nitrogen (2.4 vol. % hydrogen, 3400 sccm) for catalyst reduction. After reduction, the tow was then subjected to acetylene in nitrogen (1.3 vol. % acetylene, 325 sccm) which acted as the carbon source for CNT synthesis for a duration of ca. 5-10 min. The fibres were then passed through another nitrogen region (7500 sccm) to exit the reactor unimpeded.

3.2. CHARACTERISATION METHODS AND TESTING EQUIPMENT

The morphology of the CNT-grafted-quartz fibres was assessed using a high resolution field emission gun scanning electron microscope (SEM) (Leo Gemini 1525) to confirm the formation of CNTs and measure their length, perpendicular to the fibre surface. SEM samples were prepared on aluminium stubs using silver dag (Agar Scientific, UK). Single fibre pull-out tests were performed using an in-house apparatus, following procedures previously reported [3, 8]. The technique involves embedding a single fibre (ca. 40-100 µm) using an embedding kit (Figure 3.a), into an epoxy filled aluminium screw and curing the matrix (EPON 828/Jeffamine T-403, 1:0.42 w/w for 6 h at 100 °C). The sample is then mounted to a piezo-force sensor and the fibre free end is fixed to a piezo-translator (Figure 3.b). The test was operated at crosshead speed of 0.2 µm s^{-1} with a force accuracy of 1 mN.

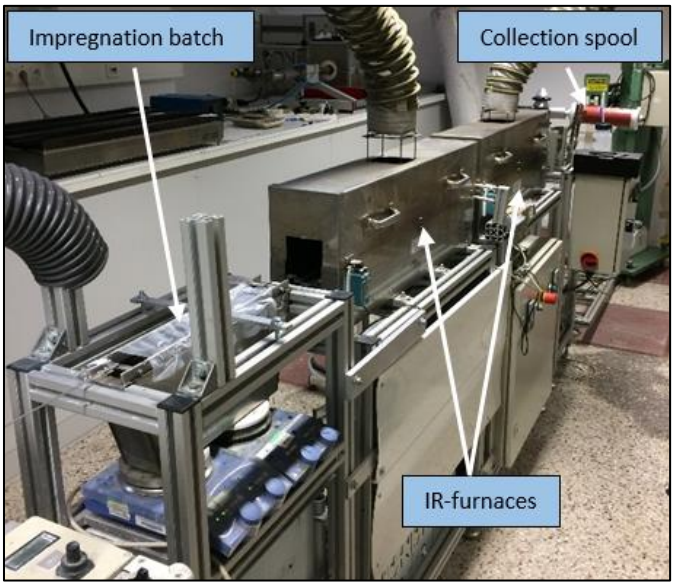

Figure 1. Photograph of the catalyst precursor deposition line.

Figure 2. Photograph of the continuous CVD line set-up.

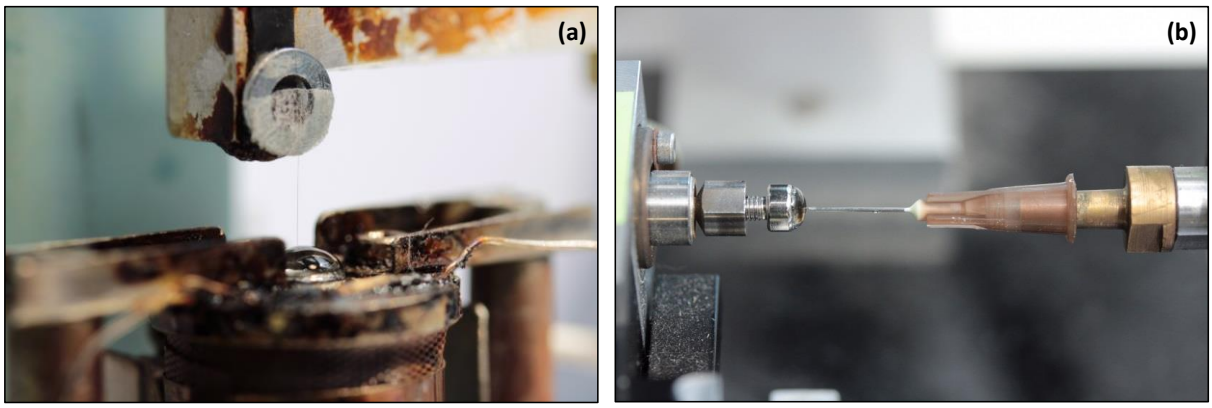

Figure 3. Photographs of (a) the fibre embedding kit and (b) the single fibre pull out set-up.

The apparent interfacial shear strength τ_{app} was calculated from equation 1. Where d_f is the fibre diameter, l is the embedded length and F_{max} the peak pull-out force. Embedded length and fibre diameter were measured after pull-out to determine the interaction area using electron microscopy (Figure 5). Interfacial shear strength was generated from at least 15 measurements for each specimen, with a linear fit of the population when max force is plotted as a function of embedded area.

$$\boldsymbol{\tau_{app} = \frac{F_{max}}{\pi l d_f}} \quad (1)$$

4 RESULTS AND DISCUSSION

4.1 MORPHOLOGY OF CARBON NANOTUBE-GRAFTED-QUARTZ FIBRE

Two different carbon nanotube configuration/length were obtained adjusting the speed from 2.4 m h^{-1} (Figure 4.a) to 1.2 m h^{-1} (Figure 4.b) corresponding to a two-fold increase of the reduction and growth time, with shorter CNTs (ca. 100-300 nm) growing homogeneously and longer CNTs (ca. 10-20 µm) growing in a splayed "Mohawk" manner. In order to establish which CNT configuration would be prevailing in terms of stress transfer and if its sized commercial counterpart can be surpassed, interfacial properties were assessed through single fibre pull-out.

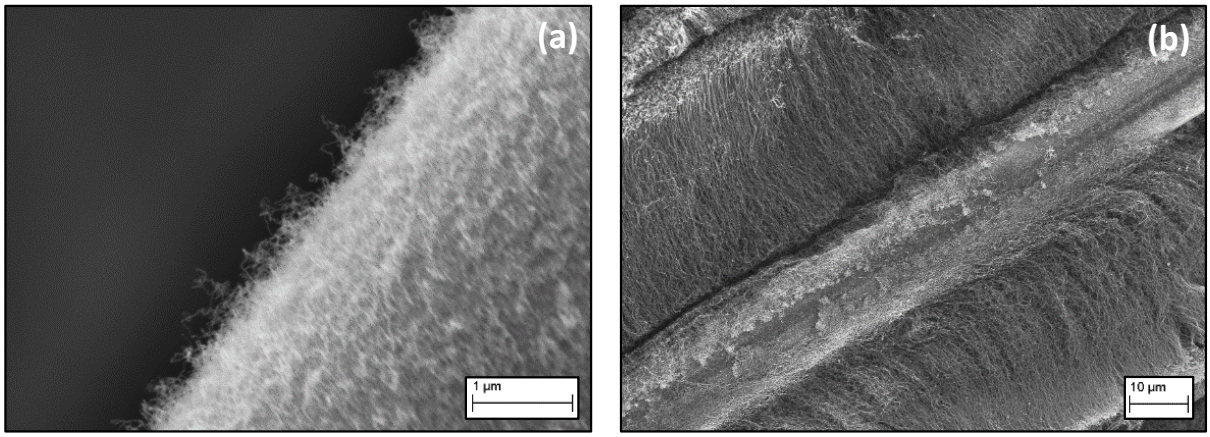

Figure 4. Carbon nanotube-grafted-quartz fibres exhibiting; (a) short (ca. 200 nm) and (b) long (ca. 20 µm) carbon nanotube growth.

4.2 FRACTOGRAPHY AND INTERFACIAL PROPERTIES OF CARBON NANOTUBE-GRAFTED-QUARTZ FIBRES

The trend in interfacial shear strength (IFSS) shows an improvement for both short and long CNT-grafted-quartz fibres, with the highest IFSS (89.6 MPa) obtained for the short CNTs, corresponding to an increase of 11% and 29% when compared to sized and desized quartz fibres, respectively. The lowest IFSS value (69.4 MPa) was obtained for desized quartz fibres which is expected as the chemical functionality has been removed. Long splayed CNTs showed similar interfacial shear strength than commercial sized quartz fibres (79.1 MPa) which can be explained by an inhomogeneity of the coverage leading to a different fracture mechanism than the short CNT configuration, as shown in Figure 6.

Table 1. Quartz fibres mechanical and fibre/matrix interfacial properties. *De-sized quartz fibres were obtained via thermal degradation of the sizing, fibres were run through the furnace at 760 °C for 1 h in the presence of nitrogen. Standard error is provided.

Sample	Fibre diameter after pull-out (μm)	Interfacial shear strength (MPa)
De-sized quartz fibres*	13.1 ± 0.1	69.39 ± 5.31
Sized quartz fibres	13.0 ± 0.2	80.92 ± 1.67
CNT-grafted-quartz fibres (short)	13.0 ± 0.1	89.6 ± 2.06
CNT-grafted-quartz fibres (long)	13.2 ± 0.2	79.15 ± 2.18

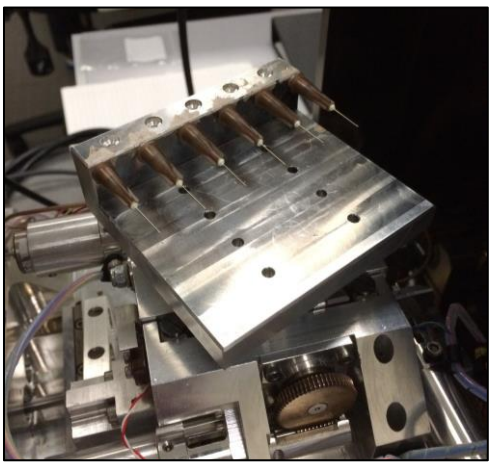

Figure 5. Photograph of single fibre pull out specimen holder for scanning electron microscopy.

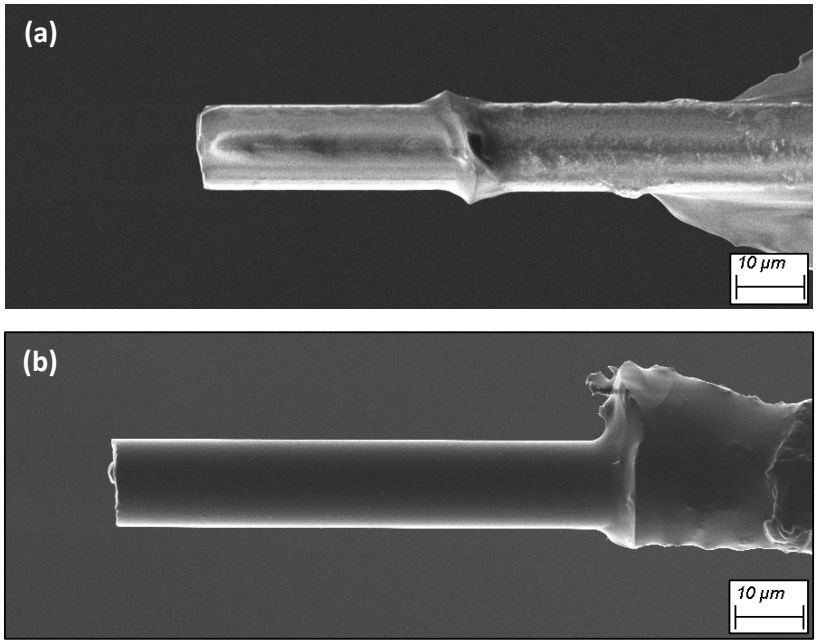

Figure 6. Scanning electron microscope of (a) CNT-grafted-quartz fibre (short) and (b) CNT-grafted-quartz fibre (long) fracture surface after pull-out.

5 CONCLUSION

The growth of both short and long carbon nanotubes (CNTs) on the surface of quartz fibres has shown to enhance the interfacial properties (IFSS) at the single fibre level with the highest value obtained for sub-micron long CNTs (89.6 MPa). Long "Mohawk" like CNTs formation led to an early failure when compared to short CNTs, with CNTs being stripped from the fibre surface in both instance indicating that the CNTs-quartz fibre interface is the weakest. The route could be further developed to increase production rate and manufacture larger composite parts and adapted for different fibril substrates.

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