

## OPTIMIZING HIERARCHICAL CARBON NANOTUBE-GRAFTED CARBON FIBER PRODUCTION

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### ABSTRACT

The promise of state-of-the-art-fiber reinforced composites containing carbon nanotube-grafted-carbon fibers has been in development since the early 90s. The main hurdle to manufacturing a hierarchical reinforced composite coupon/component, is the volume of modified fibers required. This requirement, is in turn dependent on repeatable, well-controlled and robust growth regime to ensure that the carbon nanotube coverage is uniform and consistent along the fibers, and subsequently throughout the composite. Failure to ensure that the modification is constant can result in stress concentrations in the regions of the fibers with variable length/coverage. Whilst there has been some limited development in woven fabrics being modified by growing carbon nanotubes in closed chemical vapor deposition (CVD) tubular reactors; to achieve a route towards industrial scale-up modification of the fiber tow is required, as well an open CVD reactor to facilitate the fibers being passed through the reactor unimpeded making the process continuous. The production of spool-to-spool open CVD on whole carbon fiber tows has been reported previously, but with limited evidence of prolonged and robust conditions, or a constant carbon nanotube-grafted-carbon fiber product over tens or more meters. Presented here are results of optimizing the carbon nanotube growth process on carbon fiber 12K tow in a bespoke open CVD reactor.

## 1 INTRODUCTION

The incorporation of high-performance nanomaterials like carbon nanotubes (CNTs) at the critical fiber-matrix interface in composites have been proposed to address an inherent weakness. One method to introduce these nanomaterials at this particular interfacial region is to produce hierarchical fibers (exhibiting two length scales of reinforcement), for example carbon nanotubes grafted/grown on the surface of carbon fibers (CNT-g-CFs). Particularly promising is the improved apparent interfacial shear strength of the fiber-matrix interphase of CNT-g-CFs with thermoplastic matrices shown at the single fiber level (+53%, polypropylene) when compared to an unsized carbon fiber baseline [1].

Yet, the increased production of hierarchical fibers is a challenge due to growth conditions for CNTs necessitating high temperatures and an inert environment, further complicated because carbon fibers are susceptible to damage in the process [2]. Parameters were identified to synthesize CNT-g-CF without loss of performance of the underlying fiber at the 12K tow level and in a continuous process (spool-to-spool) [3], and attention turned to increasing the scale of production. CNT chemical vapor deposition (CVD) growth conditions are notoriously sensitive to activation/reduction gases, availability of carbon feedstock as well as the catalysts composition/loading on the substrate, additionally influenced by the temperature on reaction rates and catalyst wettability kinetics; and in a continuous in-line process the fiber pull-through rate which is linked to dwell duration in reduction/growth regions. Achieving robust production of CNT-g-CFs for a prolonged duration and to modify a significant length of tow has therefore been difficult.

We present our latest work using a reaction snap-shot methodology developed from [4], which was employed to glean information at various positions inside the reactor. With these insights, reactor conditions were altered and extended CNT-g-CF production achieved with controlled lengths of 300 to 1000 nm growth of multiwalled CNTs with diameters  $\sim 10$  nm (+30 m 12K tow, 16 h in a single session). To fully evaluate the CNT-g-CF we developed a protocol which was reliable and provided an unbiased evaluation (using sections of up to 10 m long 12K tow). The protocol included a machine learning evaluation script inspecting electron micrographs and determining if CNTs were present on the fiber surface and the whole tow was examined to determine intra-tow regions (and full coverage of nanotubes). Average CNT coverage (uniformity) along the length of tow was evaluated through global methods for example, additional weight gain from CNT growth which was correlated to gas sorption analytical analysis (specific surface area). Mechanical properties of composites made wholly from CNT-g-CFs will also be presented at the conference.

## 2 MATERIALS AND METHODS

- Polyacrylonitrile (PAN)-based unsized carbon fiber (AS4-12K-7D, HS-CP-5000 grade) with diameter of  $7.1 \mu\text{m}$  was supplied by Hexcel Composites (Duxford, GB), and used as a continuous tow of 12K fibers.
- The precursor bi-catalyst solution for carbon nanotube synthesis consisted of nickel (II) acetylacetonate ( $\geq 98\%$ , VWR, GB) and iron (III) nitrate nonahydrate ( $\geq 98\%$  ACS reagent, Merck, DE) in ethanol (96%, Brenntag, AT) in a 1:0.64 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.

The equipment for CNT deposition and synthesis on carbon fibers is detailed elsewhere [3] and open CVD reactor shown in Figure 1. In short, unsized CFs were used as received, and then pre-deposited at a rate of 20 m/h with an in-line plasma oxidation pre-treatment, a bi-catalyst with a residence duration of 1 min and dried at  $40^\circ\text{C}$  and  $70^\circ\text{C}$ , producing approx. 200 m of treated tow. The collected and spooled precursor bi-catalyst deposited CFs were then passed, in inert conditions, through an open chemical vapor deposition reactor at  $550^\circ\text{C}$  at varied at pull-through speeds of 1.92 m/h and 3.36 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. Fiber morphology was characterized by scanning electron microscopy (SEM), using a Zeiss Sigma 300 (DE) at an operating voltage 5 keV where whole 12K section of carbon fiber samples were sampled. ImageJ software (version 1.52p, NIH) [6] was used for image analysis. The specific surface area of samples was characterized following ISO 9277 Standard with gas sorption isotherms using nitrogen using a Quantachrome NOVA touch gas sorption analyser (Anton Paar gmbH, AT) with Quantachrome TouchWin software (version 1.22, Anton Paar gmbH, AT) and BET (Brunauer, Emmett and Teller) method used to analyze collected data.

### 3 RESULTS

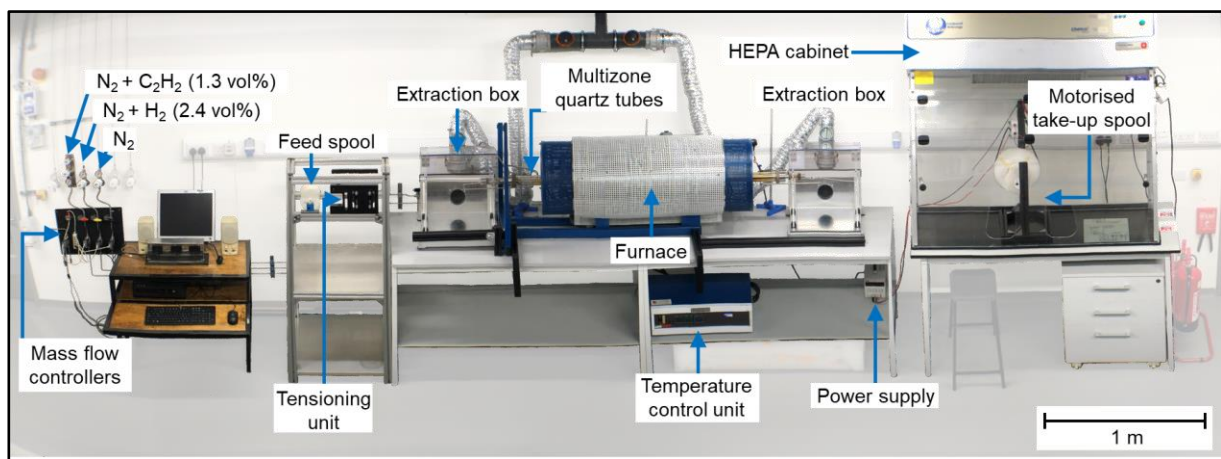


Figure 1: Overview of open CVD reactor showing continuous spool-to-spool configuration.



Figure 2: An example spool of CNT-g-CF used to determine the weight percentage of carbon nanotubes on the fiber after synthesis on open CVD line (12 m).

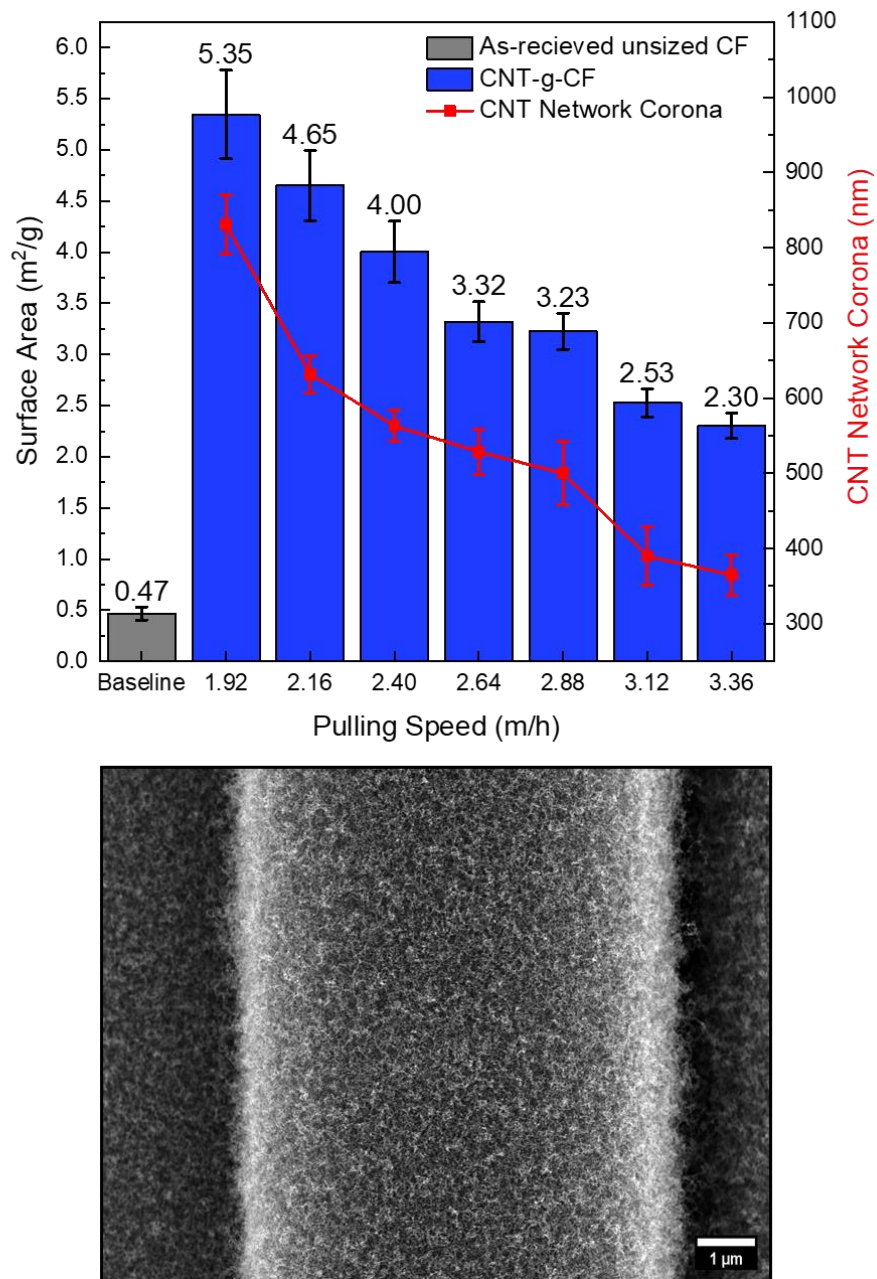


Figure 3: Top, Specific surface area measurements and CNT network corona length as a function of varying pull-through speeds, and Bottom, SEM micrograph of CNT-g-CF at a pulling speed of 1.92 m/h. Adapted from [5].

| Sample                           | Specific surface area<br>(m <sup>2</sup> /g) | CNT weight percentage<br>(wt. %) | CNT perpendicular thickness to fibre/corona<br>(nm) |
|----------------------------------|----------------------------------------------|----------------------------------|-----------------------------------------------------|
| As-received unsized carbon fibre | 0.47 ± 0.05                                  | NA                               | NA                                                  |
| CNT-g-CF (1.92 m/h)              | 5.35 ± 0.38                                  | 2.9 †                            | 856 ± 91                                            |
| CNT-g-CF [ref. 3, y2020]         | 0.53 ± 0.05                                  | 0.1 *                            | 126 ± 69                                            |

Table 1: Comparison between as-received fiber and previous CNT-g-CFs with optimized CNT-g-CF growth. Specific surface area determined BET analysis, relative increase in CNTs grown on the fiber surface as a weight percentage with † weight percentage determined though weighting spool using a balance and +10 m of modified 12K tow, \* from ref. 3 weight percentage using specific surface area and geometric considerations and a specific surface area estimate of CNTs of 260 m<sup>2</sup>/g to determine relative CNT loading (sample length ~0.15 m), and CNT length determined through scanning electron microscopy analysis.

#### 4 DISCUSSIONS

The open CVD reactor conditions including reactive gas flow rates/relative concentrations, temperature, and pull-through speed were changed to determine a stable growth regime of CNTs on the carbon fiber [7]. Further details on the protocols including a machine learning evaluation script inspecting electron micrographs and determining if CNTs are present will also be included in this publication. Stable CNT growth was achieved for a standard modulus commercially available unsized 12K carbon fiber tow over a length +30 m with the specific surface area and weight uptake (Figure 2), and an extensive microscopy analysis was completed. A uniform growth at the currently optimized synthesis parameters produced a CNT-g-CF with perpendicular CNT forest growth ca. 850 nm, which for a ~7 µm fiber diameter will not impact the potential fiber volume fraction in a composite considering ideal hexagonal packing [3, detailed in supplementary information]. Once a baseline set of conditions was established, a second test to determine the effect of varying pull-through rate was performed with CNTs length and specific surface area of the resultant CNT-g-CFs characterized (Figure 3, Table 1). Note that due to the arrangement of the reactor, altering the pull-through rate changed the relative catalyst reduction duration as well as the CNT synthesis duration (inherently linked), which in turn also altered the overall dwell duration in the reactor (in a fixed configuration). When the pull-through speed is altered it is clear that this impacts both the corona length (perpendicular forest height from the fiber surface), and the surface area. These two properties are fundamentally linked as the growth of CNTs provides the main contribution of the specific surface area. Considering that the reduction and the growth duration are currently altered, modification to the CVD parameters for CNT growth could be altered further to increase CNT growth (corona length) or conversely increase pull-through speed for a desired CNT corona length.

A comparison to the previously published results [3], which detailed the initial concept and reactor design, clearly indicates that an improved CNT growth has been achieved, with an increase in CNT weight percentage on the order 250% and an increase in corona length of about 5 times.

#### 5 CONCLUSIONS

The results presented are another step towards the scaled production of carbon nanotube-grafted-carbon fibers. The continued development to increase production of these hierarchical fibers over the past 5 years is clear, and a more robust growth regime with better understanding of the critical carbon nanotube open chemical vapor deposition synthesis parameters have been confirmed. The next stage of development for manufacturing carbon nanotube-grafted-carbon fibers should be directed toward implementation into larger furnaces and full tension creel-controlled systems. Further investigations into hierarchical fiber reinforcement should be made in parallel with larger coupons, and their performance in a range of matrices including thermoplastic and thermoset.

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