ECCM 20

26-30 JUNE 2022

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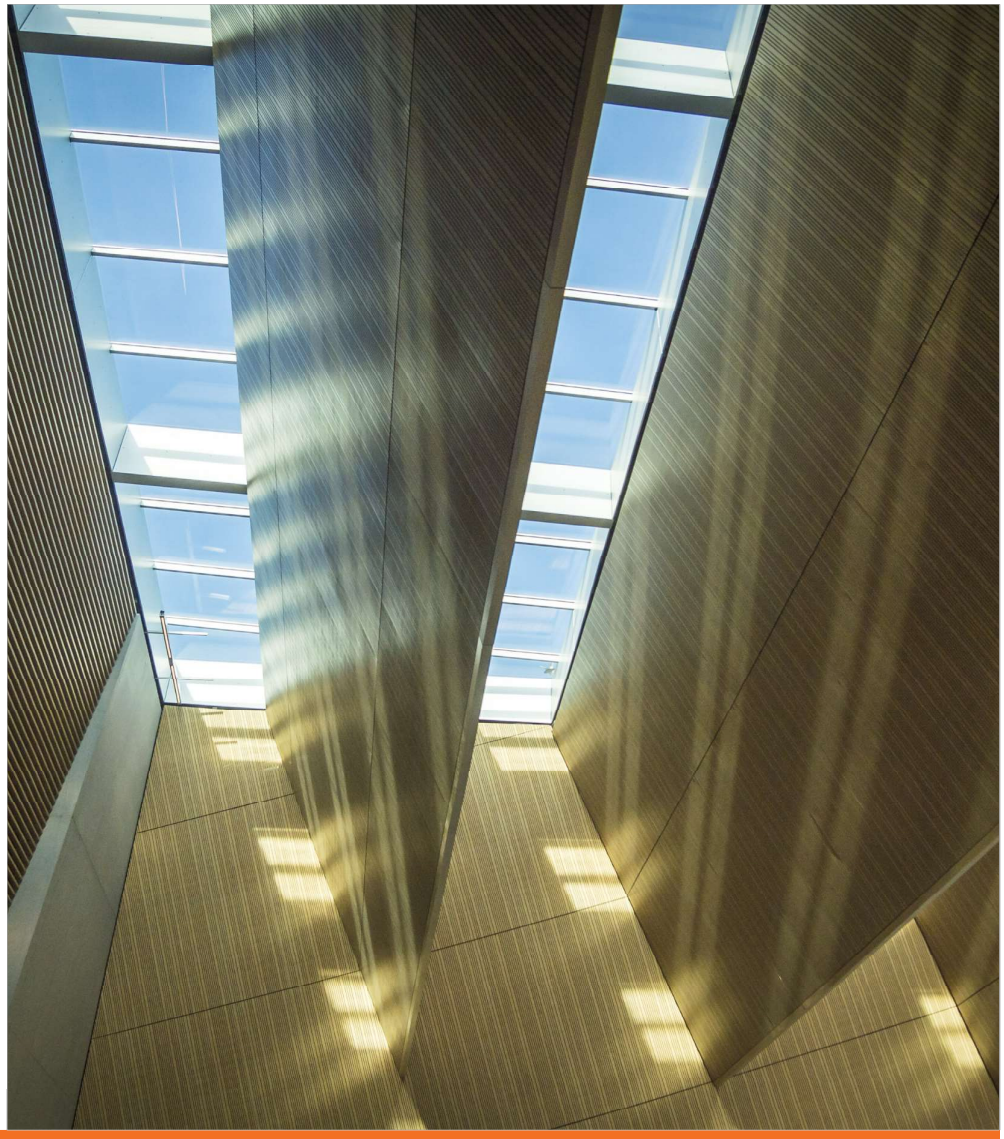

Proceedings of the 20th European Conference on Composite Materials

COMPOSITES MEET SUSTAINABILITY

Vol 1 – Materials

Editors : Anastasios P. Vassilopoulos, Véronique Michaud

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ESCM EUROPEAN SOCIETY FOR COMPOSITE MATERIALS

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EPFL CCLAB Composite Construction Laboratory LPAC Laboratory for Processing of Advanced Composites

Proceedings of the 20th European Conference on Composite Materials ECCM20 26-30 June 2022, EPFL Lausanne Switzerland

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Prof. Anastasios P. Vassilopoulos, CCLab/EPFL
Prof. Véronique Michaud, LPAC/EPFL

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Editorial

This collection gathers all the articles that were submitted and presented at the 20th European Conference on Composite Materials (ECCM20) which took place in Lausanne, Switzerland, June 26-30, 2022.

ECCM20 is the 20th edition of a conference series having its roots back in time, organized each two years by members of the European Society of Composite Materials (ESCM).

The ECCM20 event was organized by the Composite Construction laboratory (CCLab) and the Laboratory for Processing of Advanced Composites (LPAC) of the Ecole Polytechnique Fédérale de Lausanne (EPFL).

The Conference Theme this year was "Composites meet Sustainability". As a result, even if all topics related to composite processing, properties and applications have been covered, sustainability aspects were highlighted with specific lectures, roundtables and sessions on a range of topics, from bio-based composites to energy efficiency in materials production and use phases, as well as end-of-life scenarios and recycling.

More than 1000 participants shared their recent research results and participated to fruitful discussions during the five conference days, while they contributed more than 850 papers which form the six volumes of the conference proceedings. Each volume gathers contributions on specific topics:

Vol 1 – Materials

Vol 2 – Manufacturing

Vol 3 – Characterization

Vol 4 – Modeling and Prediction

Vol 5 – Applications and Structures

Vol 6 – Life Cycle Assessment

We enjoyed the event; we had the chance to meet each other in person again, shake hands, hold friendly talks, and maintain our long-lasting collaborations. We appreciated the high level of the research presented at the conference and the quality of the submissions that are now collected in these six volumes. We hope that everyone interested in the status of the European Composites' research in 2022 will be fascinated by this publication.

The Conference Chairs

Anastasios P. Vassilopoulos, Véronique Michaud

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Angélique Crettenand and Mirjam Kiener, Lausanne Tourisme
And all those who helped, colleagues who reviewed abstracts and chaired sessions, and CCLab and LPAC students and collaborators who worked hard to make this conference a success.

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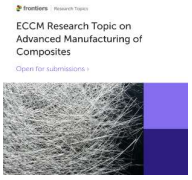

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Contents

ROBUST CONTINUOUS PRODUCTION OF CARBON NANOTUBE-GRAFTED STRUCTURAL FIBRES: A ROUTE TO HIERARCHICAL FIBRE REINFORCED COMPOSITES

Hassan Almousa[a], Hugo G De Luca[a], David B Anthony[b], Emile S Greenhalgh[c], Alexander Bismarck[d], Milo SP Shaffer[a,b]

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Abstract: *Growth of carbon nanotubes (CNTs) onto the fibre surface by direct chemical vapour deposition (CVD) offers a convenient means to integrate synthesis with assembly. This method delivers the nanostructures where they have the greatest influence on fibre-matrix interface or interphase. However, CVD is usually limited to small batches of short fibre lengths, and can damage the primary properties. Here, we describe a robust process to produce carbon nanotube-grafted-fibres continuously at tow level with a uniform coverage of short (sub-500 nm length), 10-20 nm diameter CNTs. Different CNT growth conditions, such as temperature [650-950 °C], duration [0.72-50 min], line speed [0.6-10 m/h], potential difference [0-1000 V], and reactive gas flow/compositions were investigated. Following optimisation, the fabrication of an entirely "fuzzy" fibre reinforced hierarchical composite was achieved.*

Keywords: Chemical vapor deposition; Carbon nanotubes; Carbon fibres; Hierarchical composites

1. Introduction

The structural response of fibre-reinforced composites is strongly influenced by the fibre-matrix interface or interphase. The inclusion of carbon nanotubes in conventional fibre composites promises to address many matrix- or interface-dominated failures. Research on these 'hierarchical composites' has focused predominantly on the addition of nano-reinforcement either in the bulk matrix, or locally on the fibre surface [1]. Grafting carbon nanotubes (CNTs) onto the fibre surface offers a convenient means to integrate synthesis with assembly and to deliver the nanostructures where they have the greatest influence. However, the outcome of direct chemical vapour deposition (CVD) growth depends on the underlying substrate material. On inorganic fibres, such as silica and alumina, long CNTs grow, often producing an undesirable "Mohawk" motif, which decreases the local fibre volume fraction and generates local high stress states that ultimately lead to premature failures. On carbon fibres (CFs), CVD can damage the primary fibre surface, as a result of the high temperature treatment in the presence of catalyst. In addition, CVD is usually limited to small scale batches of short fibre lengths. To make the process more applicable for industrial adoption, the production of continuous carbon nanotubes-grafted-fibres (CNT-g-Fs) must also be robust, uniform, and maintain the primary fibre characteristics.

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In this paper, we describe a process to produce upwards of 50 m of CNT-g-CFs continuously on 12K tow level [2]. A continuous in-line deposition of an efficient bi-catalyst precursor system, both in terms of composition and concentration was followed by CNT synthesis in an open CVD reactor. This patented technology [3] produces a uniform coverage of short (sub-500 nm length), 10-20 nm diameter CNTs, ideal for maintaining primary fibre loading fraction. The continuous process allows for various growth parameters to be studied systematically. Different CNT growth conditions, such as temperature, duration, line speed, potential difference, and reactive gas flow / composition were investigated. Following optimisation and scale-up, the production of 50 m per day, allowed the fabrication of an entirely "fuzzy" fibre reinforced hierarchical composites. The promising potential for CNT-g-CFs suitability as reinforcement in thermoplastic matrices (e.g., polypropylene) is due to the mechanical interlocking [4], and work is ongoing to evaluate our material in such systems. In due course, this approach has the potential to produce higher performance yet recyclable and sustainable composites.

2. Experimental

2.1 Materials

Commercially-availabe unsized polyacrylonitrile-based carbon fibres (AS4-12K) supplied by Hexcel Composites (Hexcel, GB) were used as a continous tow with a diameter of ~7 µm. Iron (III) nitrate nonahydrate (≥98% ACS reagent, Merch, DE), nickel (II) acetylacetonate (≥98%, VWR, GB) and ethanol (>99.7% BDH Prolabo, VWR, GB) were used to prepare the catalyst precursor. Acetylene in nitrogen (N2 98.7 vol% and C2H2 1.3 vol%, C certificate, BOC gases, GB), hydrogen in nitrogen (N2 97.6 vol% and H2 2.4 vol%, C certificate, BOC gases, GB), nitrogen (99.998 vol% minimum, BOC gases, GB) were used for continuous CVD CNT synthesis. EPON 828 liquid epoxy (Netmro, US) and Jeffamine T-403 curing agent were used as matrix for the short beam shear test. Carbon fibers and all chemicals were used as-received.

2.2 Continuous CVD set-up

Production of CNT-g-CFs is conducted over two consecutive processes. First, the deposition of catalyst precursor particles on unsized and plasma treated AS4 CFs. Second, the growth of CNTs from the deposited catalyst precursor. The catalyst deposition is performed in-line by passing the CFs through a bath consisting of 1 wt.% iron (III) nitrate nonahydrate and nickel (II) acetylacetonate (1:0.64 mol.%) in ethanol for 1 minute. After, the coated CFs are dried in two infared furnaces. The bi-catalyst deposited CFs are then pulled continuously through a three-zone CVD reactive chamber (Figure 1) and exposed to different gas conditions through adjustable arrangement of internal quartz tubes at a speed of 2.4 m/h. As the CF tow enters the furnace, it is first exposed to nitrogen (10000 sccm) then in the hot-zone (770 °C) to hydrogen in nitrogen (2.4 vol.% hydrogen, 3400 sccm) for catalyst reduction. Following reduction, the tow then is subjected to acetylene in nitrogen (1.3 vol.% acetylene, 325 sccm) which acts as the carbon source for CNT synthesis for a duration of ~ 12 minutes. Finally, the CFs then are passed through another nitrogen region to exit the reactor.

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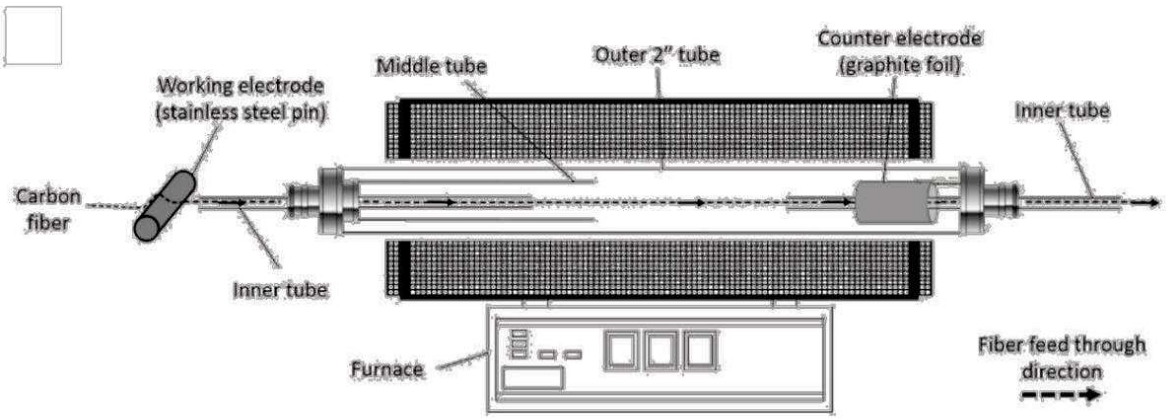

Figure 1. Continuous open spool-to-spool CVD reactor schematic [6].

3. Parameter space of CNT-synthesis via in-line CVD

CNT growth characteristics are strongly influenced by the temperature, active gas composition, reduction, and growth durations [5]. Varying these CNT growth parameters in a continuous process, allows the study of a wide range of conditions in-line and their effect on the produced CNT-g-CFs. A list of variables used to conduct a parametric study and the refinment of CVD conditions for CNT synthesis are listed in table 1. In this section, critical parameters for industrial adoption are discussed.

Table 1: CVD line associated process variables and refined synthesis conditions.

Variable	Unit	Range	Refined
Temperature	°C	[650 – 950]	770
Line-speed	m/h	[0.6 – 10]	2.4
Potential difference	V	[0 – 1000]	300
Reduction time	min	[0.72 – 10]	2
Growth time	min	[3.1 – 50]	12.5
C_2H_2:H_2	-	1:[10-80]	1:19.3
Gas-flow	sccm	[7500 – 12000] N_2	10000 N_2
		[3400 – 6800] H_2 in N_2	3400 H_2 in N_2
		[162 – 650] C_2H_2 in N_2	325 C_2H_2 in N_2

3.1 Effect of temperature

It is often observed when CNTs are synthesised at higher temperatures (above 800 °C) that less defective CNTs are grown. However, reduced temperatures are preferred as it reduces energy consumption and limits the damage to the primary CFs. Growth of CNTs on CF surface at temperatures below 720 °C in the continuous CVD reactor was not possible (Figure 2.a). At 770 °C, a dense and even coverage of CNTs were grown on CFs surface (Figure 2.b).

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Temperatures above 870 °C altered the appearance of the catalyst and particle size (observed *ex-situ*) resulting in poor growth (Figure 2.c).

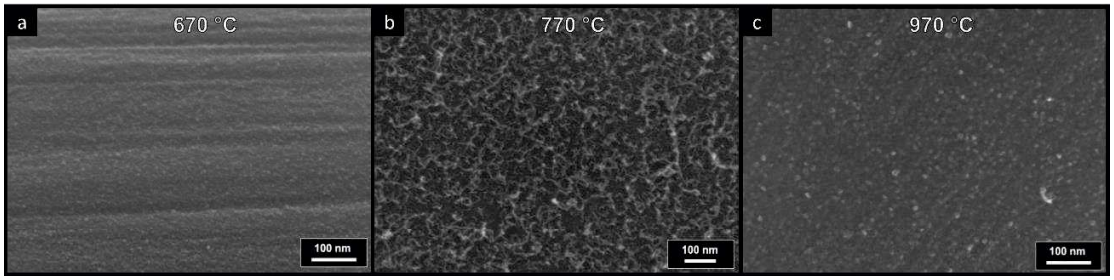

Figure 2. SEM micrographs of CNT-g-CF growth temperatures (a) 670 °C, (b) 770 °C, (c) 970 °C.

3.2 Effect of applied potential difference

Applying a potential difference of 300 V to the CFs was previously shown to enhance CNT growth and prevent catalyst pitting effect to CFs [6]. In the absence of a potential difference, the growth of CNTs was irregular and the CF surface was damaged. Therefore, a small step changes in potential difference applied to the CFs were conducted between 0 and 200 V. Potential differences over 200 V resulted in homogeneous and dense coverage of CNTs (Figure 3.c) that was comparable to applying potential different of 300 V. Any further increase in the potential difference up to 1000 V did not provide any significant improvement in CNT synthesis.

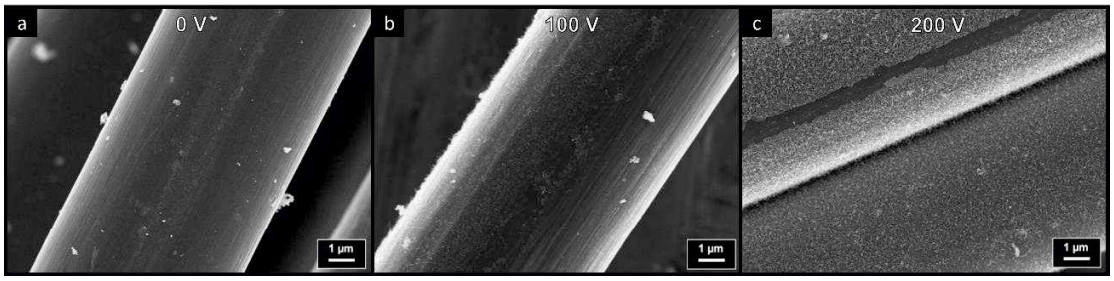

Figure 3. SEM micrographs of CNT-g-CF grown with an applied potential difference of (a) 0 V, (b) 100 V, (c) 200 V.

3.3 Effect of line speed

A conventional speed of carbon fibre production line is about 10 m/h. Therefore, matching this speed is important for future industrial adoption. A range of line speeds were investigated from 0.6 to 6.7 m/h (current design limitations). While longer growth dwell times can yield longer CNTs, premature termination of the growth can result from catalyst poisoning. Consequently, an increase of speed to 2.4 m/h resulted in uniform CNT coating with a thickness of ~ 200 nm (Figure 4.b). Further increases in the line speed up to 4.8 m/h led to thicker and homegenized CNTs coating as shown in (Figure 4.c). However, beyond this speed the growth declined due to incomplete catalyst reduction step.

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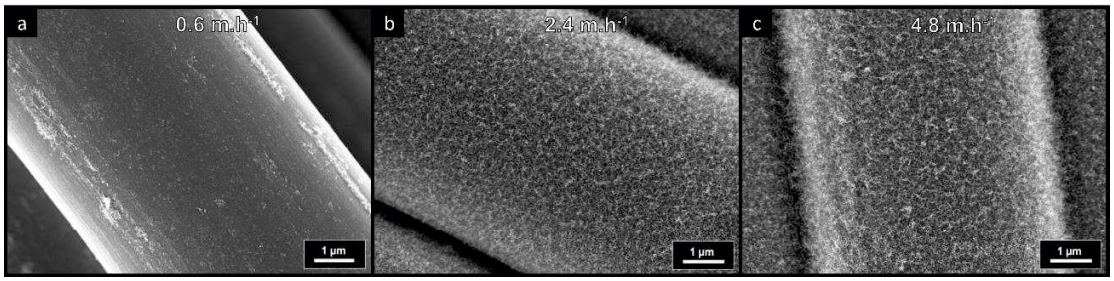

Figure 4. SEM micrographs of CNT-g-CF synthesized with line speeds (a) 0.6 m/h, (b) 2.4 m/h, (c) 4.8 m/h.

4. Processing CNT-g-CF composite specimen

Single-fibre measurement of apparent interfacial shear strength provide indications of the potential benefit of CNTs-g-CFs at the macroscale. However, a more complete mechanical evaluation accounting for macroscale deformation mechanism in a structural composite requires the fabrication of coupons. This step was unattainable until a scaled-up production of the CNT-g-CFs made it feasible to produce larger composite specimens. A process was developed for short beam shear (SBS) coupons fabrication within the specification of ASTM D2344 standard [7]. CFs were wrapped around stainless-steel pins (Ø 1.5 mm) to assemble four layers with an angle of 3.0° (±1.5°) between them. This method allowed for a fibre volume fraction of 50-69 vol.% in the final SBS hierarchical composite coupon.

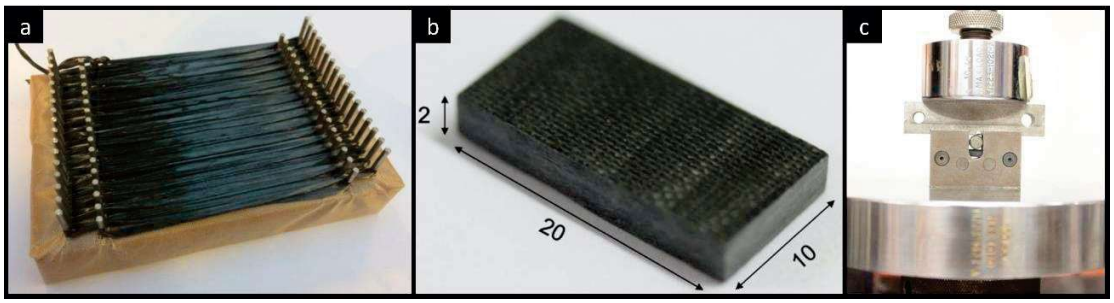

Figure 5. Images of (a) CNT-g-CFs 12K tow loomed around pins, (b) ASTM D2344 hierarchical composite sample (dimensions in mm), (c) SBS hierarchical composite coupon under load.

5. Conclusion

A continuous in-line deposition of bi-catalyst on fibres and continuous CVD system were successfully developed. In combination, these processes enabled comprehensive investigation of the effect of different parameters of CNT growth on CFs, such as temperature, duration, line speed, potential difference, and reactive gas flow/compositions. The refined conditions allowed for a robust route to producing CNT-g-CFs with dense and homogeneous growth of CNTs. After achieving a production of over 50 meters per day of CNT-g-CFs, a process for fabricating SBS CNT-g-CF specimen was developed to study the system's mechanical properties at macroscale. In due course, the CNT-g-CFs will be embedded in thermoplastic-based composite system to produce higher performance yet recyclable and sustainable composites.

Acknowledgements

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