



Uniform and scalable carbon nanotube growth on carbon fibers: Insights from experimental dynamic snapshots and computational fluid dynamics

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ABSTRACT

Carbon nanotube (CNT) grafted carbon fibers (CFs) are promising for multifunctional composites (CFRPs) but remain limited by scalability, non-uniform growth, and degradation of fiber tensile strength. This paper reports a continuous spool-to-spool chemical vapor deposition (CVD) process that achieves uniform CNT growth throughout 12k CF tows while preserving fiber tensile properties. The uniformity of CNT coverage, over meters of length and across thousands of fibers, was objectively established via a multi-length scale characterization protocol, combining machine learning-based SEM classification with macroscopic measurements of BET-based specific surface area (SSA) and gravimetric CNT content. Microscopic and macroscopic measurements are independently self-consistent. To understand and optimize CNT growth, a new dynamic snapshot method was developed and combined with steady-state computational fluid dynamics (CFD) modelling to resolve the spatial evolution of catalyst activation, nucleation, and CNT growth kinetics as a function of reactor temperature and species concentrations. These insights informed targeted modifications to gas flow and temperature conditions, enabling reproducible CNT growth at 550 °C. Under optimized CVD conditions, the CFs were grafted with a CNT corona of 850 nm in length, corresponding to a loading of 2.9 wt% on the fibers, which led to a ten-fold increase in SSA ($5.35 \text{ m}^2 \text{ g}^{-1}$). The process was shown to be stable for extended lengths (>50 m) and reproducible across multiple runs, establishing a scalable route for integrating CNT-grafted CFs into conventional manufacturing. This experimental-computational framework provides a rational approach toward high-performance multifunctional, hierarchical CFRPs.

1. Introduction

Carbon fiber reinforced polymers (CFRPs) have been widely used in high-performance applications across various industries due to their exceptional specific strength and high modulus [1]. CFRPs exhibit excellent in-plane tensile properties, but the overall mechanical performance including fatigue and fracture toughness is constrained to the strength of interface between carbon fibers (CFs) and the surrounding matrix. The performance of CFRPs is further limited by their inferior interlaminar and compressive performance, with compressive strength

often being less than 50 % of tensile strength [2]. Introduction of carbon nanotubes (CNTs) to CFRPs can enhance the fiber-matrix interface by improving the interfacial shear strength (IFSS), while also reinforcing the surrounding matrix to reduce matrix-dominated failures such as interlaminar shear, and compressive instability, without affecting the in-plane performance [3,4]. Additional functionality, including for example enhanced through-thickness electrical and thermal conductivities [5,6], electromagnetic interface shielding [7], and structural health monitoring [8] can be introduced by incorporating CNTs in composites. CNTs are typically introduced into CFRPs by dispersion into the matrix

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or attachment to the fiber surface [9]; more rarely, a combination of these methods has shown synergistic improvements [10]. The dispersion approach is most effective at relatively low concentrations (typically ~ 1 wt%), though limited by increased matrix viscosity and self-filtration effects [11]. Grafting or depositing CNTs directly on CF surface creates a hierarchical reinforcement, combining nanoscale and microscale reinforcements, compatible with a range of conventional composite processing methods. Computational models of hierarchical composites show significant benefits when CNTs are incorporated at the fiber-matrix interface [12–15]. The specific morphology of CNTs on the CF surface, including length, diameter, conformation, and density, influences the macroscale properties of the composite [16]. Studies suggest that the optimum configuration for improving the strength and toughness of unidirectional (UD) CFRPs is a uniformly distributed wavy CNT network to promote crack bridging and damage diffusion while suppressing stress concentrations [17,18]. Furthermore, grafting long CNTs onto fiber surfaces increase fiber-fiber separation [19], thereby reducing packing efficiency. To maintain a fiber volume fraction of 60 % with 7 μm diameter fibers, the separation must remain $\leq 1.6 \mu\text{m}$, corresponding to an ideal CNT length of ~ 800 nm (assuming no interpenetration of the networks) [20].

Various techniques can be used to deposit or grow CNTs on CF surfaces, including electrophoretic deposition [21], spraying [22], chemical grafting [23–25], and chemical vapor deposition (CVD) [26–28]. Wet deposition methods tend to generate random CNT networks parallel to the CF surface. CVD methods can grow radially oriented CNTs normal to the CF surface, allowing for enhanced interphase interaction volume between the CF and the surrounding matrix. CVD can also promote direct carbon-carbon bonding between CNTs and the CF substrate, reaching strengths of 200 MPa [29], compared to only 25 MPa for CNTs for typical wet coating methods [30]. On the other hand, CVD methods inherently involve a number of challenges that make them hard to optimize. The CNTs are usually grown from transition metal-based catalyst precursors at elevated temperatures (~ 600 – 800 °C), using hydrocarbon feedstock [31,32]. Several mechanisms can cause CF degradation during the CNT growth, reducing tensile strength [31,32], including carbon dissolution from the CF surface into catalyst particles or surface pitting [31,33]. Residual water, oxygen, or hydrogen used as a reducing agent may lead to hydrolysis [34] or hydrogenation [35] of the CF during high temperature CVD. Several approaches have been developed to minimize fiber damage during CNT synthesis, for example, optimizing gas stoichiometry and lowering the synthesis temperature to 500 °C [36] can reduce damage, though often at the expense of CNT quality. Alternative catalysts, such as copper, zirconium oxychloride [37], or sodium [38], avoid carbon dissolution, but then tend to grow carbon nanofibers instead of multiwalled CNTs (MWCNTs). Other reported strategies include repairing graphitic lattice damage through prolonged CVD exposure [39,40], limiting growth duration [41,42], applying tension to CF tow to mitigate thermally activated mechanochemical changes [43], or applying potential difference on sized CF to minimize surface damage [44]. The method of reducing CNT growth temperature to maintain the underlying CF tensile strength is conceptually simple, reduces energy consumption [5,45], and directly addresses the temperature-dependent nature of the degradation mechanisms.

Although lowering the processing temperature mitigates fiber degradation, it does not address the broader challenges of CVD. The sensitivity of the CVD process to reaction conditions, the large parameter space, and difficulties in quantifying product quality have hindered development. In addition, the complexity of CVD equipment and the use of flammable gases at elevated temperatures has limited much of the research literature to small-scale batch processing, where problems of reproducibility are exacerbated. A scalable, reliable and continuous process is required both to explore composite applications effectively, and as a route towards industrial implementation. Over the past ~ 30 years [26], only limited studies have explored open CVD systems for

continuous CNT growth on CF. Only a few configurations have reported continuous CNT growth on moving fiber substrates [20,46–50], highlighting the inherent challenges of designing such systems. However, most of these studies focused on non-CF tow substrates due to the inherent difficulty of growing CNTs directly on CF surface, and early attempts produced short CNTs without demonstrating uniformity or reproducibility at larger scale.

Although early studies on continuous CNT growth on CF were limited, subsequent efforts have sought to optimize such open CVD systems. Such systems typically follow sequential steps of catalyst precursor deposition, reduction to nanoparticles, and CNT growth. Different strategies have been reported to optimize CNT growth density. For example, electrochemical anodization has been used to enhance catalyst deposition uniformity, enabling a systematic study on growth time through varying pulling speeds which resulted in 30 % improvement in IFSS while preserving CF tensile strength [51]. Further optimization was achieved by varying hydrogen and acetylene concentrations, growth temperature and pulling speed within a two-furnace configuration that separated catalyst reduction from CNT growth [52]. While effective, two-furnace arrangements are less practical for scalable CF production, motivating single-furnace designs. Early single-furnace attempts involved back-and-forth motion [53], whereas later continuous pull-through approach systematically varied temperature, pulling speed, gas ratio, and catalyst concentrations to maximize IFSS improvements of up to 84 % while maintaining CF tensile strength [54,55]. Despite these advances, most studies relied on single-variable optimization within bespoke reactor designs. Treating the reactor as a ‘black box’ and adjusting one parameter at a time cannot yield the mechanistic insights required for scale-up. Therefore, a comprehensive understanding of the coupled chemical, thermal and fluid dynamic processes, together with statistical confirmation of CNT growth uniformity and reproducibility across thousands of fibers in a tow, is still needed.

This study addresses the challenge of non-uniform CNT growth on CFs in scalable CVD systems, by combining new approaches to material characterization, computational modelling, and dynamic growth analysis to capture CNT growth kinetics. We first established a robust, multi-length-scale characterization protocol that combines statistical SEM analysis using a machine learning-based image classifier to quantify CNT coverage, with independent macroscopic measurements of linear density and specific surface area (SSA) over several meters of CNT-grafted CFs. In parallel, we developed a steady-state non-reactive computational fluid dynamics (CFD) model to map reactive gas concentrations and flow fields, providing a detailed view of the open CVD reactor environment during CFs processing. These conditions are correlated to the experimental growth by introducing a dynamic snapshot method to capture the spatial evolution of CNT nucleation and growth along the CF axis via *ex-situ* SEM analysis. These tools enabled the rational progression from an initial unstable CVD process configuration to a reliable and effective CVD system for CNT grafting on CF tows.

2. Methodology

A detailed list of materials, including carbon fiber specifications, gas sources, and chemicals used in the following processing and fabrication are provided in [section S1](#).

2.1. Continuous catalyst precursor deposition on carbon fibers

A spool of the unsized 12k CF tow mounted on a creel equipped with a closed-circuit tension control system (Max. 10 N, Ogura Clutch Corp., JP) to maintain a constant tension of 0.5 N and pulling speed of 20 m h^{-1} , underwent in-line atmospheric plasma oxidation (2.5 bar, 35 L min^{-1}) using open air plasma (FLUME Jet RD1004, Plasmatrete, DE) for a residence time of 4 min [56]. The surface activation step increases the

fiber surface energy and introduces oxygen-containing functional groups that may aid catalyst precursor deposition. Surface activated CFs were then passed through an impregnation ethanol bath containing 1 wt % bi-catalyst precursor solution (Ni:Fe molar ratio 1:0.64) with a dwell time of 1 min, followed by sequential drying in infrared ovens at 40 °C and 70 °C before the bi-catalyst-loaded CFs (Bi-cat-CF) tow was wound onto a collection spool. The process ensured uniform catalyst deposition across the entire 12k tow and along individual filaments.

2.2. Continuous synthesis of carbon nanotubes on carbon fibers

The Bi-cat-CFs were processed in a continuous, open-ended CVD reactor system that had been described previously [20,57], and was successfully recommissioned in a new location (Fig. S1) for scalable synthesis of carbon nanotube-grafted-carbon fiber (CNT-g-CF). The reactor consists of a tubular furnace (PTF 15/-/610, Lenton, GB) with three adjustable concentric quartz tubes, each with a dedicated gas inlet

to control gas composition and create distinct catalyst reduction and CNT growth zones (Fig. 1A). The fiber tow passes through tension pins (2 N, measured as detailed in section S3.1) to maintain alignment and prevent sagging, equivalent to about 0.1 % of the tow's tensile strength, which does not affect catalyst behavior or CNT growth. Before entering the furnace for heating, the tow first passes through an inert nitrogen region (5 bar) to prevent premature reactions or oxidation. Upon reaching the hot-zone (region of uniform set-point temperature), the fibers are exposed to a reducing environment of 2.4 vol% H₂ in N₂ (2 bar) to facilitate catalyst reduction. The fibers then enter a CNT growth zone and exposed to 1.3 vol% C₂H₂ in N₂ (2 bar). Finally, the fiber tow exits the furnace into a cooling stage, again under an inert nitrogen atmosphere (5 bar). The CFs are continuously collected on a motorized winding spool within a HEPA filtered cabinet. Detailed parameters, including temperature, winding speed, gas flow rates, and applied voltage, are listed in Table 1. The static electric field (SEF) was applied as described previously [20] and only used in the reference case (CVD α);

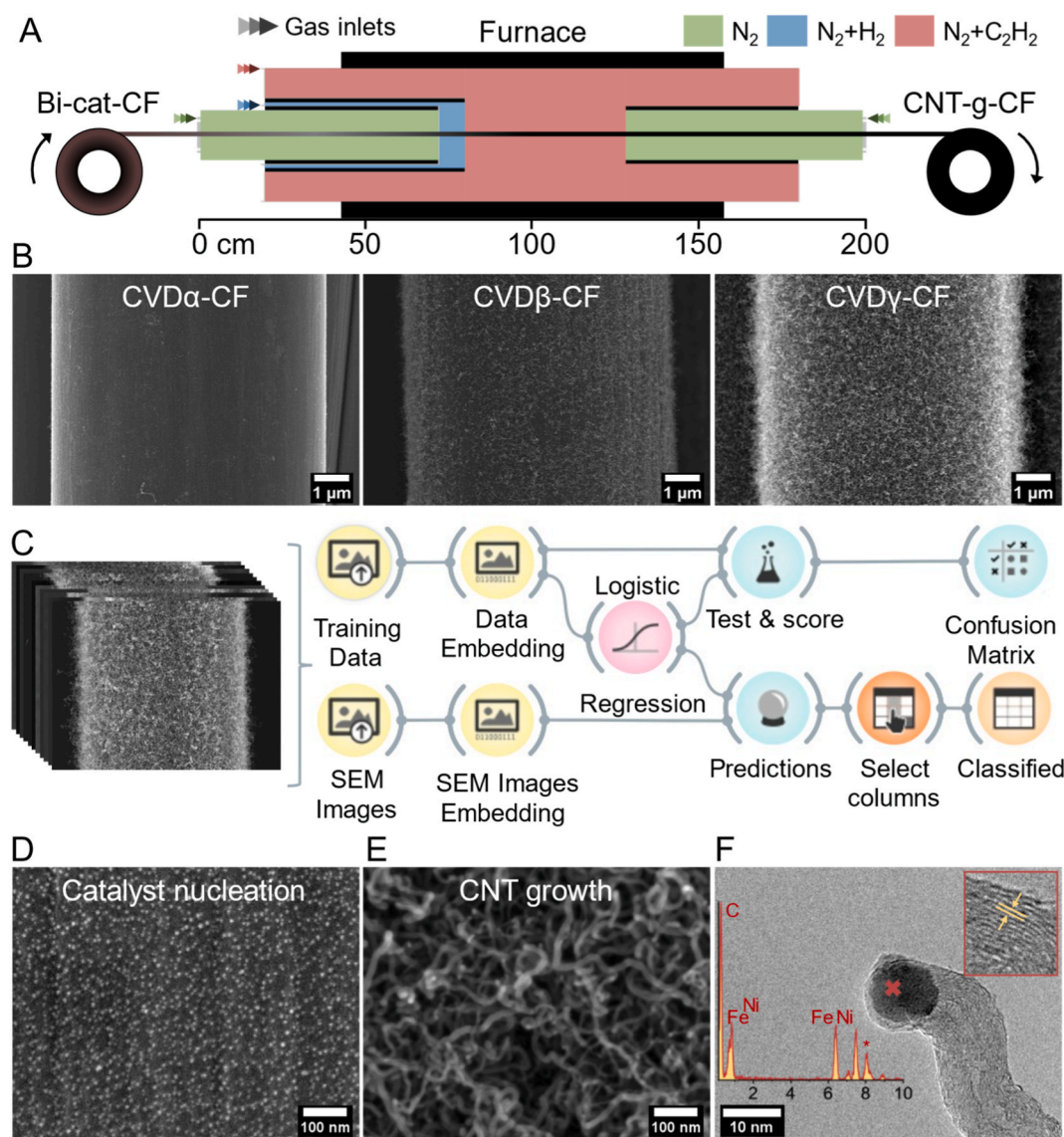


Fig. 1. Continuous CNTs synthesis on CFs via an open-ended CVD reactor. (A) 2D schematic of the CVD reactor showing gas inlets, fiber pull-through, and gas zones processing bi-catalyst coated carbon fibers (Bi-cat-CF) to carbon nanotubes-grafted carbon fibers (CNT-g-CF). The length of the reactor is to scale; height is scaled up by factor of five for clarity. (B) SEM images of CNT-g-CFs prepared under three different CVD conditions (CVD α -CF, CVD β -CF, CVD γ -CF). (C) Machine-learning workflow for classification of CNT growth on CF. (D, E) SEM images of catalyst nucleation and the resulting fully grown CNT network of CVD γ -CF, respectively. (F) TEM image of multi-walled CNT, highlighting graphitic interlayer spacing (0.34 nm) with EDS spectrum of catalyst particle composition (* indicates Cu peak, originating from TEM grid).

Table 1

Summary of key CVD process parameters for three investigated cases.

Variable	Unit	CVD α	CVD β	CVD γ
Temperature	°C	770	550	550
Line-speed	m.h ⁻¹	2.40	2.40	1.92
Potential difference	V	300	0	0
N ₂ gas-flow	sccm	10000	10000	10000
2.4 vol% H ₂ in N ₂ gas-flow	sccm	3400	528	1760
1.3 vol% C ₂ H ₂ in N ₂ gas-flow	sccm	325	325	40

it was excluded in subsequent cases.

2.3. Evaluation of carbon nanotube growth on carbon fibers

Raman spectroscopy was used to assess structural changes on the CF surface associated with CNT growth. The degree of disorder in the sp² graphitic structure was evaluated using the D-to-G band intensity ratio (I_D/I_G). Spectra were collected using a Renishaw inVia micro-Raman spectrometer equipped with a 532 nm (2.33 eV) DPSS diode laser. For further details on acquisition parameters, sample size, and processing methods, see [section S3.2](#).

Surface morphology and CNT growth features were characterized using high-resolution scanning electron microscope (SEM, Sigma 300 Zeiss, DE) operated at 5 keV using the in-lens detector to capture both low- and high-magnification images across statistically sampled CFs. High-resolution transmission electron microscope (HRTEM, JEM-2100F, JEOL, JP) equipped with energy-dispersive X-ray analysis (EDS) was used to assess CNT structure and catalyst composition. For full imaging parameters, sampling protocols, and analysis see [section S3.3](#).

A supervised machine learning classifier was developed and applied to SEM micrographs to classify CNT coverage as uniform and non-uniform ([Fig. 1C](#)), using Orange data mining software (Orange3-39 version). For model development details, see [section S3.4](#).

The preceding characterization relied on microscopic measurements sampled over relatively large, centimeter-scale sections of CF tow. The following macroscopic measurements sample several meters of fiber tow to obtain representative bulk values. Specific surface area (SSA) was measured by N₂ adsorption using the BET method (ISO 9277) [58] with a Quantachrome NOVAtouch gas sorption analyzer (Anton Paar gmbH, AT). Samples were degassed at 100 °C for 12 h prior to measurement. The CNT content was determined gravimetrically using bi-cat-CFs as the baseline. All sample preparation and measurement details are provided in [sections S3.5 and S3.6](#).

2.4. Computational modeling

A computational fluid dynamics (CFD) model was developed in COMSOL Multiphysics v6.0 to simulate velocity, temperature, pressure, and reactive gas concentrations in the open-ended CVD reactor by solving the continuity, momentum, energy, and species transport equations. A 2D-axisymmetric model comprising of four inlets, two outlets, and four quartz tubes was developed to represent the reactor geometry. The gas mixture was treated as a continuum, incompressible, with laminar flow and negligible gravitational effects. The model is considered to operate in a continuum regime, as indicated by a Knudsen number (Ke) of 8.6×10^{-5} , and is treated as incompressible, given a Mach number (M) of 0.005. The presumption of a laminar flow is supported by a calculated Reynolds number (Re_{max}) of 560. Furthermore, a no-slip laminar boundary layer condition is assumed, justified by a Grashof number (Gr) of 5.2×10^5 , and the effects of gravitational forces are deemed negligible, based on a Richardson number (Ri) of 1.6. All equations and regime analysis of the dimensionless numbers are detailed in [section S4.1](#). Gas outlets and inlets were set to 20 °C, while both outlet pressure were set to 1 bar, and the gas inflow volumetric rates for N₂,

N₂+H₂, and N₂+C₂H₂ were converted to flow velocities that matched the set experimental values ([Table 1](#)). Wall temperatures were assigned based on experimental measurements using a temperature probe (KHX-IM30U-RSC-1000, Omega, GB and thermocouple data logger EL-USB-TC-LCD, Lascar Electronics, GB), with linear interpolation applied between recorded points. Thermal conductivity, dynamic viscosity, and diffusion coefficients for all species were assigned from the built-in material library, which estimates transport properties based on kinetic gas theory. The Lennard-Jones parameters for the species are obtained from the CHEMKIN-PRO database [59]. The 2D-axisymmetric domain was meshed using the COMSOL meshing tool, yielding 64,056 elements with an average quality of 0.78 over a 0.045 m² area. The governing equations for the numerical solution are detailed in [section S4.2](#).

2.5. Dynamic snapshot for carbon nanotube growth kinetics

The kinetics of CNT growth on continuously moving CFs were examined by employing an *ex-situ* dynamic snapshot technique, inspired by a method originally developed to capture a moment in time of CNT growth along glass fiber substrates as they passed through the reactor [46]. The method captures discrete growth stages along a 2-m (reactor length) CF tow. After stabilizing the CVD conditions, the tow was rapidly extracted by cutting the CF tow at the fiber exit and reversing the freely rotating feed spool at the fiber entrance within 1 s to preserve the near-real-time spatial growth profile. The tow was then sectioned for SEM analysis to identify catalyst nucleation ([Fig. 1D](#)) and CNT growth progression ([Fig. 1E](#)). Samples were collected at specific points along the CVD reactor, with their exact positions recorded to correlate with local growth conditions. To examine the growth kinetics, the lengths of the CNT corona network were quantified via SEM imaging analysis in relation to timestamps, determined by position and pulling speed, then fitted to a sigmoid-Boltzmann curve using the fitting tool in OriginPro 6.1 software (version 10.1.0.178). The growth rate was subsequently determined by taking the first derivative of the fitted Boltzmann curve, allowing for an estimation of the CNT corona network growth rate at different points along the reactor.

2.6. Fabrication and mechanical testing of composite rods

Unidirectional (UD) composite rods were fabricated using as-received and CNT-g-CFs prepared from three different CVD conditions. The CF tow was fed through tension pins into an epoxy bath, then drawn through a 1.2 mm nozzle to control resin content and achieve 40 % fiber volume fraction (V_f). Composite rods were mounted under 8 N tension and cured at room temperature for 24 h, then post-cured at 50 °C for 16 h.

Tensile tests were performed on cured composite rods according to ASTM D4018-23 using an Instron 5980 (50 kN load cell) at a strain rate of 1 mm min⁻¹. Gripped regions of the samples surface were keyed lightly with sand paper then cleaning with isopropanol, and end-tabbed with prepared glass-fiber reinforced epoxy panels (1.6 mm thick Croylam FR4, Croylek, GB which were grit-blasted and cleaned) using epoxy (3 M Scotch-Weld DP490, 3 M, GB), and tested at a 150 mm gauge length with strain measured using a video extensometer (MG223B, iMETRUM GB). Flexural strength was measured by performing a three-point bending (MFS with 200 N load cell, Linkam, GB) test with a 30 mm span length and 1 mm min⁻¹ displacement rate, using 60 mm-long samples. Full testing protocols and equations are provided in [section S3.7](#).

3. Results and discussion

A novel workflow was developed to understand continuous CNT growth on CFs by integrating material characterization, computational modelling, and an experimental dynamic snapshot process. These methods were first applied to the best existing CVD conditions known

for our reactor (CVD α) and used to evolve improved conditions (CVD β and CVD γ). However, the results are presented by method, given their novelty and for ease of comparison. The analysis begins with the new multi-length-scale characterization protocol used to evaluate CNT coverage and uniformity. CFD simulations are then introduced to resolve flow regime and spatial molar concentration profiles of reactive gases. These insights are combined with an experimental dynamic snapshot method to reconstruct the evolution of CNT growth along the reactor. The three examined cases represent sequential process refinements: Case 1 (CVD α) is a high-temperature growth (770 °C) that served as the reference condition; based on an initial single-variable parametric study reported previously [60], to explore the influence of temperature, gas composition, reduction and growth time of CNT growth on unsized CF compared to previous work conducted on sized CF [20]. Although this method does not capture interactions between variables, it remains a standard approach in CNT growth optimization. Among the 46 experimental variations [60], the CVD α condition summarized in Table 1 resulted in the greatest extent of regional CNT formation. Case 2 (CVD β) operates at a lower temperature (550 °C), and case 3 (CVD γ) retains the lower temperature while optimizing gas-phase molar ratio to achieve uniform and reproducible CNT growth. The experimental dynamic snapshot method captures the transitions between these cases, demonstrating how process refinements guided by characterization of CNT growth kinetics and CFD modelling facilitated transition from sparse to uniform and dense CNT growth. Additional findings address CNT length control via line speed variation, and mechanical performance of the fabricated composites.

3.1. Multi-length-scale characterization

CNT growth on CFs is commonly assessed using Raman spectroscopy and SEM, with TEM occasionally used for high-resolution structural analysis. Although these techniques provide detailed local information, they are inherently limited in spatial coverage; comprehensive evaluation of growth uniformity across multifilament tows is rare, if not entirely absent, from the literature. The challenge is amplified by the intrinsic variations in surface morphology, chemistry and local conditions within tows containing many thousands of CFs [61]. Analyzing only a few fibers in heterogeneous CNT growth can result in misleading conclusions and false correlations, compromising the effectiveness of process optimization. New methods to quantify CNT uniformity are therefore needed, supported by objective, statistically significant, multi-length-scale characterization techniques. In this study, the CNT growth on CF surface was examined on sample sizes ranging from few centimeters to several meters for the three different reactor conditions.

The post-growth multi-length-scale analysis begins with SEM, which provides the most reliable indicator of CNT grafted morphology when applied rigorously and statistically. To assess CNT morphology and distribution, several centimeters of the CF 12k tow were spread across a large stub (32 mm diameter, Fig. S2) and examined following the statistical protocol described in the methods. The CVD α -CF exhibited sparse CNT growth within the tow, whereas CVD β -CF and CVD γ -CF showed uniform coverage, with CNT corona network lengths extending to 319 ± 43 nm and 856 ± 91 nm, respectively (Fig. 1B). Additional representative SEM micrographs for each case are provided in Fig. S6. However, to enable high-throughput and unbiased quantification of CNT growth uniformity, a dataset for each condition was generated through large-objective statistical SEM imaging (as detailed in S3.3) and analyzed using a pre-trained machine learning (ML) model (Fig. 1C). The model was trained on an independent dataset compiled from previous CVD runs. The image classifier model showed that only 15 % of CVD α -CF fibers were identified as uniform, whereas >90 % of CVD β -CF and CVD γ -CF fibers were classified as uniform, highlighting a significant improvement in CNT growth uniformity. Details of the ML model and classification accuracy are provided in Section S6.

Having established the morphology of each case, the structural

nature of the observed nanorods/nanofibers was next examined to determine whether they were indeed CNTs. Raman spectroscopy, widely employed to characterize carbon nanomaterials, was used as a rapid method to investigate crystallinity and nanostructure type. However, interpretation is not straightforward for CNTs grafted on CFs due to the overlapping carbonaceous signals; nonetheless, the ratio of the D-band and G-band intensities (I_D/I_G) remains a useful indicator of changes in disorder and graphitic domain formation associated with nanostructure growth. The spectra of CVD α -CF showed no significant change in I_D/I_G (0.89 ± 0.01) compared to the as-received CF (AR-CF), consistent with sparse growth. In contrast, CVD β -CF and CVD γ -CF exhibited a clear increase in D-band intensity and I_D/I_G ratio (Table 2), consistent with the formation of nanostructured sp^2 domains and surface defects. Furthermore, the second-order D band (2D) became more pronounced in CVD β -CF and CVD γ -CF, providing stronger evidence for the presence of well-developed graphitic shells characteristic of multiwalled CNTs (MWCNTs).

HRTEM was used to resolve the nanostructure directly, revealing a graphite interlayer spacing of 0.34 nm (Fig. 1F), and a MWCNT structure in all cases (Fig. S8), despite the relatively low growth temperature of 550 °C used in CVD β and CVD γ . Across the different growth conditions, CNTs consistently exhibited an average diameter of 10 nm (Table 2), indicating a critical nucleation site dictated by the catalyst–fiber interaction. TEM (Fig. S8) and TEM-EDS (Fig. 1F) analysis of CVD γ -CF provided clear evidence for a tip-growth mechanism, consistent with previous reports on small-diameter CNT formation on carbon fibers [62, 63]. Other studies, however, have identified mixed tip- and base-growth behavior [64] or predominantly base-growth modes [65], depending on the catalyst–substrate interaction and local reaction environment. Elemental analysis of the catalyst nanoparticles showed a Ni:Fe molar ratio of 1:0.87 (Fig. 1F), confirming the bi-catalytic nature of the growth.

Following the microscopic analyses, characterization was extended to bulk samples given the sufficient material available from the continuous CNT growth process (Fig. S4). Gravimetric analysis of several meters of CNT-g-CF tow provides a direct macroscopic measure of the total mass of CNTs grafted, relative to the catalyst-deposited fibers. The linear density of CVD α -CF shows no difference to the baseline (indicating poor overall CNT growth), however CVD β and CVD γ growth regimes resulted in CNT grafting of 1 wt% and 2.9 wt%, respectively.

Specific surface area (SSA) was then quantified via BET using nitrogen adsorption–desorption measurements. All samples exhibited a Type II isotherm profile (Fig. S9), characteristic of non-porous or macroporous materials, confirming that any measured change in SSA from baseline predominantly originates from the external CNT network. The

Table 2

Physical properties of different carbon nanotube-grafted carbon fibers from three different chemical vapor deposition conditions. Listed properties include the average intensity ratio of the characteristic Raman bands (I_D/I_G); supervised machine learning classification (MLC); CNT network corona length (L_c); carbon nanotube diameter (d_{CNT}); specific surface area (SSA); and carbon nanotube content on carbon fibers (wt.%).

Fiber	CVD α -CF	CVD β -CF	CVD γ -CF
I_D/I_G^a	0.89 ± 0.01	0.97 ± 0.01	1.00 ± 0.01
MLC	Sparse	Uniform	Uniform
L_c (nm)	193 ± 54	319 ± 43	856 ± 91
d_{CNT}^b (nm)	10.1 ± 1.8	10.3 ± 1.3	10.4 ± 1.7
SSA ^c ($m^2 \cdot g^{-1}$)	0.82 ± 0.12	2.48 ± 0.37	5.35 ± 0.38
CNT content ^d (wt.%)	0.11 ± 0.01	1.02 ± 0.01	2.90 ± 0.01

^a As-received AS4 carbon fiber $I_D/I_G = 0.84 \pm 0.02$.

^b Measured with point resolution of 0.19 nm via transmission electron microscopy.

^c As-received AS4 carbon fiber measured specific surface area = $0.47 \pm 0.17 m^2 \cdot g^{-1}$.

^d Bi-catalyst coated carbon fiber linear density = $0.862 g \cdot m^{-1}$.

SSA of CVD α -CF increased only slightly ($0.82 \pm 0.12 \text{ m}^2 \text{ g}^{-1}$) compared to the AR-CF ($0.47 \pm 0.17 \text{ m}^2 \text{ g}^{-1}$), confirming the observed low and non-uniform CNT growth. CVD β -CF and CVD γ -CF exhibited five-fold ($2.48 \pm 0.37 \text{ m}^2 \text{ g}^{-1}$) and ten-fold ($5.35 \pm 0.37 \text{ m}^2 \text{ g}^{-1}$) increases in SSA, respectively. Based on the CNT diameter (10 nm) from TEM and a simple geometric estimation, the synthesized CNTs SSA was $200 \text{ m}^2 \text{ g}^{-1}$ (Tables S2–S3), consistent with typical reported values for pristine synthesized MWCNTs [66]. Combining this estimate with the gravimetric uptake ($2.9 \text{ wt}\% \times 200 \text{ m}^2 \text{ g}^{-1}$) gives an approximate SSA increase that agrees with the measured BET values, providing quantitative confirmation of the uniform CNT coverage observed in SEM. These characterization techniques span different length scales and, critically, are independent methods. The collated results (Table 2) are in agreement, providing confirmation of the uniform CNT growth achieved under CVD β and CVD γ conditions.

While gravimetric analysis was performed on several meters of CNT-g-CFs, the technique inherently averages out any local variations introduced by fiber-fiber contact, heterogeneous catalyst distribution, or variations in surface morphology [67]. To verify that the macroscopic measurements arise from uniform CNT coverage for CVD β -CF and CVD γ -CF, a semi-empirical method (section S7) was developed to estimate the bulk CNT content from SEM-derived microscopic parameters, such as catalyst particle size, catalyst coverage, catalyst utilization, and CNT contour length. Determining these parameters is challenging due to the processing of multi-thousand filaments through a continuous line. Catalyst coverage prior to CNT growth was assessed using high-resolution SEM images captured through the dynamic snapshot experiment (section 3.3). Image-based particle analysis (Fig. S13) quantified nanoparticle surface coverage on the CF surface (14 % and 13 % for CVD β -CF and CVD γ -CF, respectively) and provided average nanoparticle diameter of 7 nm, consistent with the 10 nm MWCNT outer diameter. Catalyst utilization was estimated as the proportion of active particles, defined as those producing CNTs, by extending the image analysis method (as detailed in Section S7.2). Finally, the CNT contour length was estimated using a Kuhn segment model, commonly applied to describe the extension of flexible polymer chains, adapted here for CNTs (Fig. S15). The resulting contour lengths were approximately 400 nm for CVD β -CF and 1900 nm for CVD γ -CF (Table S7). From the quantified microscopic parameters obtained by SEM and semi-empirical calculations, the CNT-g-CF SSAs were estimated to be 1.5 and $5.0 \text{ m}^2 \text{ g}^{-1}$ with corresponding CNT contents of 0.6 and 2.4 wt% for CVD β -CF and CVD γ -CF, respectively (Table S8). These values are consistent with the bulk SSA measured by BET and gravimetric mass uptake. The agreement across these independent methods confirms that similar CNTs grow throughout the CVD β -CF and CVD γ -CF tows.

3.2. Computational fluid dynamics simulation

CVD reactors are almost always regarded as a ‘black box’ due to the complex physical and chemical interactions in the reaction zone and the challenge of *in-situ* analysis. A multiphysics CFD tool can resolve gas flow, temperature and reactive species concentration within the reaction zone, providing insights into the conditions under which CNT growth occurs. The actual conditions are particularly complex and uncertain in an open-ended furnace, featuring multiple competing gas flows. Here, a model was developed to represent the bespoke open-ended CVD reactor (Fig. 1A) used in the experiments, comprising two opposing inlets for nitrogen flow to preserve an inert atmosphere within the reactor. The counterflow configuration due to the upstream inlet introduces additional complexity to the resulting flow field. Two additional inlets are in the downstream direction, where reactive gases (H_2 and C_2H_2) are introduced at distinct axial positions through a series of nested quartz tubes to create spatial control of different gas compositions along the pulled through fiber. All the steady-state simulations converged within 80 iterations or below, indicating numerical stability and model reliability.

The spatial distribution of reactive species within the reactor governs key transport phenomena, including molar ratio and zones of gas species depletion. To quantify these effects, the molar concentrations of hydrogen (Fig. 2A) and acetylene gas (Fig. 2B) were simulated and mapped across the reactor domain for each CVD case study (Table 1). The molar concentration maps (shown with aspect ratio 1:5 for clarity) reveal localized enrichment zones near each gas inlet, reflecting the multi-inlet configuration. Each gas stream maintains its inlet concentration until it meets the subsequent quartz tube, ensuring physical separation from the point of gas injection to the region of interaction with the fiber tow. For instance, all cases show a region of elevated hydrogen concentration confined initially to its inlet zone. These localized enrichment zones transition into broader zones downstream, where diffusion and dilution occur progressively along the axial direction (fiber tow path). The rate of dilution varies across the different CVD cases, depending on the inlet flow rates. Molar concentrations, temperature, and velocity vectors were extracted along the fiber axis at discrete axial positions across all three cases to quantify local conditions relevant to CNT growth (Fig. 2C).

3.2.1. Temperature and velocity profiles at fiber axis

The velocity and temperature fields were coupled in the CFD simulations to capture how flow dynamics influence temperature stability along the fiber axis. The reactor region from 60 to 120 cm was specifically analyzed because the temperatures in this zone exceeded 350°C (Fig. 2C), marking the beginning of Ni-Fe catalyst reduction. The catalyst reduction can continue progressively with an increase in temperature up to 550°C in all cases [68]. Within this segment, a distinct velocity inversion occurs as opposing nitrogen streams interact, producing a localized flow along the fiber axis; this feature could influence the stability of the flow around the fiber and the delivery of reactive gases. Among the three CVD cases, CVD α with the highest total combined flow rate shows the strongest velocity inversion and the most pronounced disturbance of the temperature gradient. This inversion could contribute to shifting the stable hot-zone and thereby affect local gas species distributions. Minimizing velocity inversion may help maintain a more stable temperature field, which could support more consistent catalyst reduction and uniform CNT growth.

3.2.2. Hydrogen molar concentration

Hydrogen plays a critical role in catalyst activation by reducing metal precursors into nanoparticles and etching of excess carbon deposition during hydrocarbon decomposition on catalyst surface [69, 70]. While equimolar hydrogen-nitrogen gas mixture is introduced at the inlet of all three simulated cases, the spatial distribution along the fiber axis varies considerably depending on the flow dynamics (Fig. 2C).

In case 1 (CVD α), hydrogen maintains its inlet concentration (1.97 mol m^{-3}) at the fiber entry region before decreasing by 35 % and becoming stable throughout the hot-zone. In case 2 (CVD β), the hydrogen concentration along the fiber begins below the starting concentration at only 1.48 mol m^{-3} and undergoes a rapid 95 % loss of concentration at the start of the stable hot-zone, which could reduce the extent of the hydrogen-rich region available for catalyst reduction. In contrast, case 3 (CVD γ) shows only a slight drop in hydrogen concentration of 10 % from the starting hydrogen concentration at the hot-zone, resulting in a relatively stable and hydrogen-rich environment along the fiber axis. Notably, the CVD γ case also exhibits lateral diffusion of hydrogen toward the acetylene inlet zone, suggesting the potential of early gas-phase interactions that could promote CNT nucleation. Although these trends are derived from non-reactive simulations, they provide a much improved understanding of the reaction conditions inside the furnace. Qualitatively, the consumption of hydrogen is minimal to negligible under constant flow, thus the model can be aligned with established growth mechanisms and provide a framework for interpreting differences in CNT yield and catalyst activation efficiency across the experimentally studied cases.

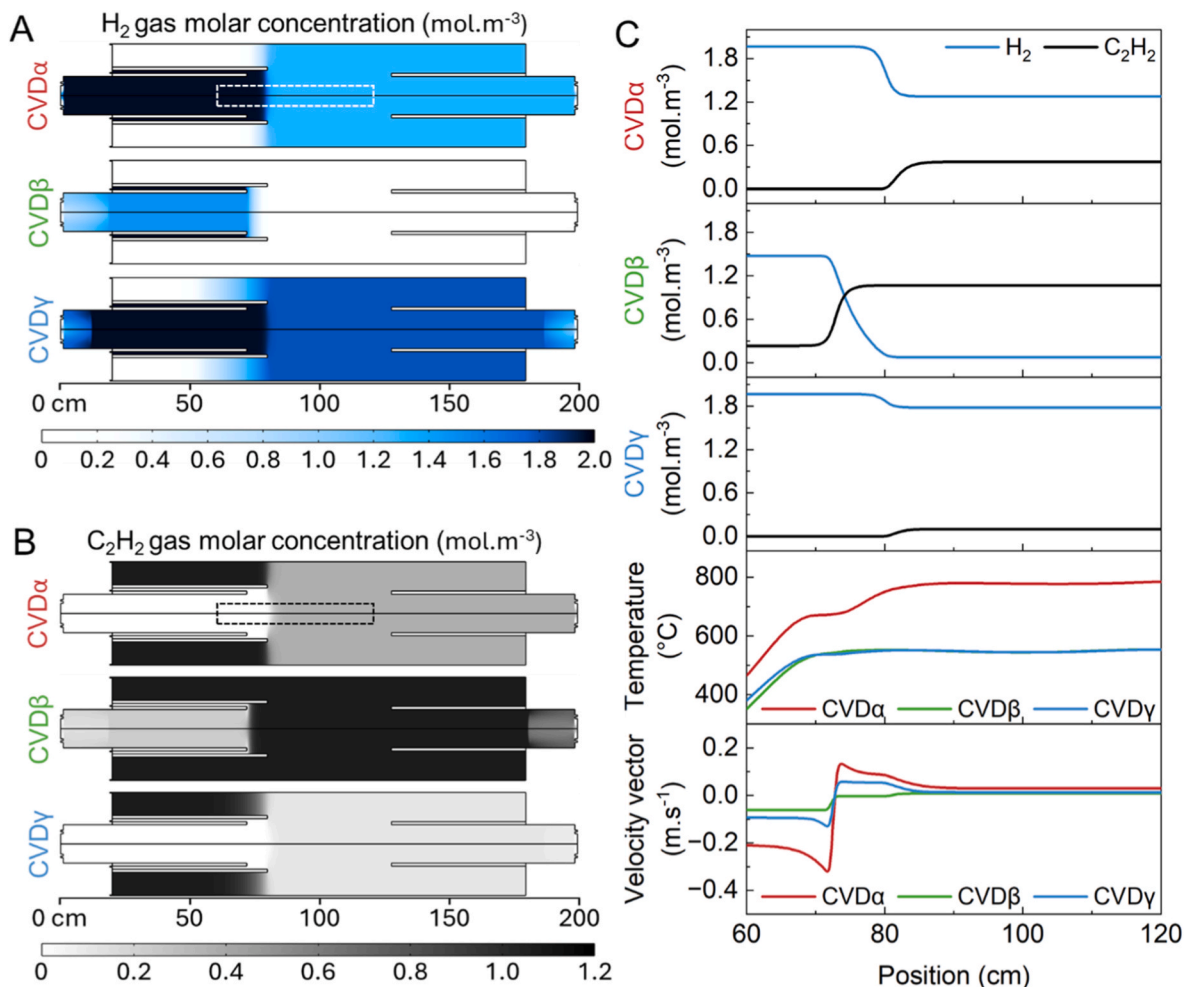


Fig. 2. CFD modeling of gas composition and temperature profile within the CVD reactor (2D-axisymmetric model). (A, B) Contour plots of hydrogen and acetylene molar concentrations, respectively, on a central 2D cross-section plane of the reactor for three different CVD conditions (CVD α , CVD β , CVD γ). Reactor length is shown to scale, while height is scaled by 1:5 for clarity. (C) Stacked line plots display hydrogen and acetylene concentrations together with temperature and velocity vector along the fiber pathway. The fiber centerline is shown in black on the 2D plots, and the dashed boxes in (A) and (B) indicate the extended section of interest in (C).

3.2.3. Acetylene molar concentration

Acetylene is widely recognized as an effective hydrocarbon precursor in catalytic CVD for CNT synthesis due to its efficient decomposition into reactive carbon species at temperatures typically ranging from 350 to 600 °C [71]. In this model, acetylene was introduced into the reactor with an inlet concentration of 1.12 mol m^{-3} , based on the volumetric fraction of the gas mixture. The spatial positioning of acetylene relative to the hydrogen-rich zone is critical; premature CF exposure prior to catalyst reduction can cause carbon encapsulation and catalyst poisoning [72]. Conversely, delayed exposure of hydrocarbon feedstock risks the diffusion of active catalyst nanoparticles into the CF substrate [31], limiting their catalytic availability and impairing CNT nucleation and growth.

In the CVD α case, the higher hydrogen-to-acetylene flow rate ratio maintains clear segregation of streams at the fiber inlet region, minimizing the presence of acetylene from the hydrogen-rich reduction zone. However, acetylene emerges downstream in the reactor at lower concentrations (0.30 mol m^{-3}) within the region of elevated temperatures (770 °C), conditions known to facilitate gas-phase radical reactions [73]. At this elevated temperature, acetylene-derived carbon species can rapidly deposit onto catalyst surfaces, causing premature deactivation or limited CNT growth [74].

Case 2 (CVD β) features a reduced flow rate difference between hydrogen and acetylene streams, resulting in immediate mixing and a

moderate initial acetylene concentration (0.24 mol m^{-3}) that extends to the hypothesized catalyst reduction zone. This premature acetylene exposure could accelerate carbon deposition, causing catalyst deactivation via encapsulation. Further downstream, the acetylene concentration significantly increases (up to 1.07 mol m^{-3}), which may result in carbon over-deposition, limiting CNT yield. Case 3 (CVD γ) achieves a spatially balanced distribution (Fig. 2B), preventing the mixing of acetylene with the hydrogen-rich catalyst reduction zone. Consequently, catalyst nanoparticles could be sufficiently reduced and activated before encountering acetylene. The stable and low acetylene concentration (0.10 mol m^{-3}) extended downstream may create optimal conditions to maintain catalyst activity, suggesting better nucleation and growth of CNT.

3.3. Experimental dynamic snapshot investigation

While CFD provides detailed predictions of temperature gradients, gas composition, and flow regimes within the reactor, the non-reactive model cannot reveal the positions where catalyst nucleation or CNT growth occur within reactor. An experimental dynamic snapshot method was, therefore, developed to compare the evolving state of the CNTs on CF with the computed conditions, as a function of time and position along the reactor. By extracting and analyzing fiber segments at defined spatial intervals, critical stages of CNT growth were successfully

identified for all CVD cases (Fig. S16). Namely, the catalyst reduction to nanoparticles, CNT nucleation, and CNT growth. Each stage was mapped to the CFD-predicted temperature, and gas environment, to construct a comprehensive multidimensional map of CNT growth progression inside the open-ended CVD reactor, forming the basis for the subsequent case-specific discussion. This multidimensional correlation enables, for the first time, a direct linkage between internal reactor conditions and CNT-g-CF surface evolution in a continuous reactor.

3.3.1. Case 1 (CVD α): Localized CNT growth

Continuous CNT growth is challenging because of the moving substrate and the non-uniform thermal and chemical conditions in the open-ended CVD reactor. Under the CVD α processing condition, CVD α -CF exhibited CNT growth, although the coverage was non-uniform, as confirmed by the multi-length-scale characterization in section 3.1. To investigate the cause of the localized growth, a dynamic snapshot experiment was performed and presented in Fig. S17. Although the furnace set-point was 770 °C in the intended growth region, CNT growth was observed to initiate earlier in the temperature gradient region, closer to 550 °C. At this position and temperature, acetylene concentration was negligible (10^{-12} mol m $^{-3}$), yet growth proceeded once the catalyst had become active. Additional sparse growth was observed at the hot-zone (770 °C) under a stable C $_2$ H $_2$:H $_2$ molar ratio of 3.4, likely driven by secondary reduction and high-temperature CNT growth kinetics. These observations revealed that CNT growth under CVD α was non-uniform because the conditions required for catalyst activation and CNT nucleation existed only within a narrow transient region of the reactor, rather than in the intended steady growth zone. Extending these conditions should enable more uniform and sustained CNT growth. The dynamic snapshot study of CVD α -CF helped to define an improved temperature and gas-phase environment required for catalyst activation and CNT growth.

3.3.2. Case 2 (CVD β): Enhanced thermal stability

Based on the study of CVD α , new growth conditions were formulated for case 2 (CVD β). The reactor temperature was reduced to 550 °C, the optimal temperature identified by comparing the dynamic snapshot to the CFD calculation, to create an extended, stable thermal environment spanning approximately 60 cm along the reactor. Gas flow rates were adjusted to achieve a controlled molar ratio of 1:3 (C $_2$ H $_2$:H $_2$) by adjusting hydrogen flow rate (525 sccm) while maintaining the acetylene flow rate (325 sccm). The updated CVD β parameters resulted in uniform CNT growth across the entire tow as shown in section 3.1. The characteristics of these CNTs were similar to those in the sparse regions of CVD α where growth had occurred, presumably due to the similar growth conditions, deliberately extended from the original transient into an extended zone. The resulting uniform CVD β growth now serves as a robust reference condition. Subsequent variations in CVD parameters can be rigorously evaluated against this established baseline to determine their influence on CNT growth. A unique feature of the CVD α parameters was the application of a static electric potential across the CFs and a counter electrode during CNT growth. This potential difference was initially hypothesized to enhance CNT formation and preserve fiber tensile strength [20,44]. However, once stable growth was achieved using the revised CVD β conditions, comparable experiments with and without an applied potential showed no measurable difference in CNT morphology or coverage (Section S10). Electric potential was therefore excluded in subsequent work, although it may have played a role under the CVD α transient growth conditions. The improved CNT uniformity observed under the new operating conditions was primarily attributed to the optimized temperature and gas flow parameters, which collectively defined the CVD β condition yielding uniform CNT growth with an average CNT corona length of 319 ± 43 nm.

To investigate the growth kinetics of these relatively short CNTs, dynamic snapshot measurements were repeated using the CVD β conditions. A correlation between the experimental CNT growth rate and the

CFD-predicted gas concentrations and temperature distributions (Fig. 3) can identify the local conditions at different stages of CNT growth. The observed reduction zone, defined as the region extending from the initial catalyst nanoparticle nucleation on CF surface to the onset of CNT growth initiation (Fig. S16), corresponded to a residence time of approximately 2 min (2.4 m h $^{-1}$ for 8 cm). The short catalyst reduction dwell time may restrict catalyst activation prior to CNT growth [75,76]. The maximum CNT growth rate occurred immediately before the transition from a hydrogen-rich to a hydrocarbon-rich region, where the local molar ratio of acetylene to hydrogen (C $_2$ H $_2$:H $_2$) was approximately 0.23. Further downstream, in the stable hot-zone, the hydrogen concentration decreased, reducing the molar ratio to 0.10 which coincided with a notable reduction in CNT growth rate. This observation is consistent with previous studies showing that elevated hydrocarbon concentrations can suppress catalyst activity and limit the CNT yield [77]. Extending the hydrogen-rich region upstream of the growth zone is therefore expected to sustain catalyst activity, prolong growth duration, and improve CNT yield.

3.3.3. Case 3 (CVD γ): Optimized gas flow

Building upon the previous results, CFD simulations were used to modify the CVD parameters to stabilize the hydrogen concentration within the hot-zone while simultaneously lowering the acetylene content. The hydrogen and acetylene flow rates were adjusted to 1760 sccm and 40 sccm, respectively, achieving a molar ratio of approximately 1:17 (C $_2$ H $_2$:H $_2$) in the central reactor region. This revised flow regime created an extended hydrogen-rich region upstream of the acetylene-rich region, as well as extending the reduction region within the reactor. SEM analysis of CNT-g-CF produced under these conditions at the baseline pulling speed of 2.4 m h $^{-1}$ showed a marked increase in the growth density of CNTs on the fiber surface, with an average length of the CNT corona network of 550 ± 85 nm. Although these adjustments improved CNT growth relative to the previous cases, the question remained whether the CNT length can be further extended by adjusting residence times. The effect of dwell time under reducing and growth conditions was investigated by systematically varying the pulling speed in small increments (± 10 %, up to ± 40 %). SEM measurements revealed that the CNT corona length increased with longer dwell times, reaching a maximum at a pulling speed of 1.92 m h $^{-1}$, where the average CNT corona length was 856 ± 91 nm (Fig. 4A). This peak was independently confirmed by bulk measurements, where BET analysis showed a corresponding maximum in SSA (5.35 ± 0.38 m ^{2} g $^{-1}$) at the same pulling speed (Fig. 4B; BET plots shown in Fig. S19). The agreement between the nanoscale SEM observations and macroscopic BET results provides strong evidence of enhanced and uniform CNT growth under these conditions. Below this speed, the CNT corona length and SSA decreased, which is hypothesized to result from time-dependent effects associated with prolonged exposure to catalyst reduction or CNT growth conditions. A possible mechanism is that prolonged reduction allows the active catalyst to react with the underlying CF substrate, causing pitting [78,79]. To determine the effect of prolonged reduction, an independent experiment was conducted in a hydrogen-nitrogen only environment which indeed resulted in CF surface pitting (Fig. S20, experimental details in section S12).

The optimal pull-through speed of 1.92 m h $^{-1}$ was then selected for dynamic snapshot testing to resolve whether the catalyst reduction or CNT growth stage was the rate-limiting step to the CNT growth process. Under these conditions, CNT formation initiated further downstream within the thermally stable hot-zone (Fig. 3). The catalyst reduction dwell time was 6 min, followed by 4 min of CNT growth, during which the CNT corona network extended at a rate 2.5 times higher than CVD β condition. When converted from corona extension to absolute nanotube length using the Kuhn model, the growth rate was essentially equivalent, indicating that corona measurements provide a reliable representation of CNT growth kinetics. Under these optimized conditions, the maximum CNT growth rate was 0.3 μ m min $^{-1}$, consistent with reported

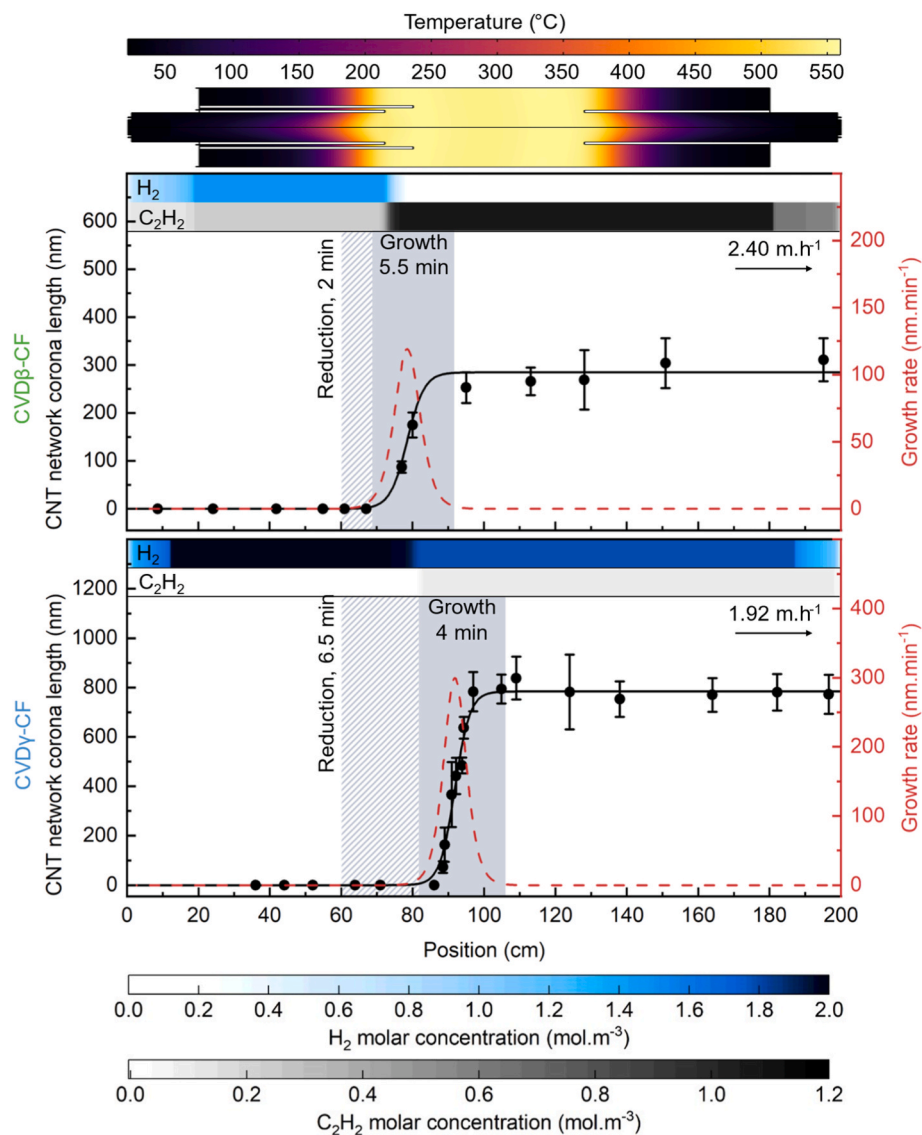


Fig. 3. Multi-dimensional mapping of CNT growth kinetics via dynamic snapshot. Temperature contour plot of CVD reactor linked spatially to evolving CNT corona length (black scattered dots) for both CVD β -CF and CVD γ -CF cases. The measured corona lengths fitted using a sigmoidal curve (solid black line). CNT corona network growth rate represented as red dashed curve. Hydrogen and acetylene molar concentrations along the fiber pathway overlaid as contour stripes. Key zones of catalyst reduction and CNT growth marked with solid and diagonal strips, respectively. Dwell times in each zone indicated along with the corresponding fiber pulling speed. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

values for low-temperature CVD growth [80]. The spatial separation of gas profiles effectively decouples the reduction and growth stages, establishing distinct regions for catalyst activation and CNT nucleation along one continuous reactor. These observations align with studies indicating that catalyst reduction is a rate-limiting step in CNT synthesis, emphasizing the necessity of a well-defined hydrogen-rich reduction zone for consistent catalyst activation [78,80]. SEM imaging at multiple magnifications (Fig. 4C) confirmed uniform and dense CNT coverage across the fiber tow. Supplementary Video 1 presents a continuous SEM examination along the 12k CF tow of CVD γ -CF, effectively demonstrating the uniformity of CNT growth achieved under the CVD γ growth conditions. The stability of the continuous CNT growth process was evaluated by producing a 50 m-long CVD γ -CF in a single uninterrupted run (Fig. 4D), with samples extracted from different sections for SEM and SSA analysis (Fig. S11). Reproducibility over time was also evaluated through five additional production runs (≥ 5 m) performed over the course of one year (Fig. 4E), CNT network corona length analysis, and BET measurements yielded consistent results (Fig. S13).

3.4. Mechanical properties

Tensile strength and stiffness are generally the most important properties of CFRPs. Any reduction in fiber strength caused by the surface modification (process) undermines the primary advantage of CFRPs. A persistent drawback of CVD-based CNT grafting has been fiber strength degradation. The continuous process developed in this study produced sufficient material for composite scale testing on full 12k CF tows. Tensile tests on fiber bundle composites are dominated by the fiber properties and provide statistically reliable strength data relevant to composite applications. The tensile strength of CVD α -CF composites showed a 25 % reduction compared to the AR-CF baseline (Fig. 5A). This reduction is attributed to the harsher processing conditions of CVD α at 770 °C, where the elevated temperature likely promoted catalyst pitting and surface defects. In contrast, CVD β -CF and CVD γ -CF composites retained their primary tensile strength, confirming that uniform CNT growth at 550 °C can be achieved without compromising fiber integrity. The tensile modulus remained unchanged in all CNT-g-CFs (Fig. 5A), consistent with the intrinsic stiffness of the fibers being unaffected by

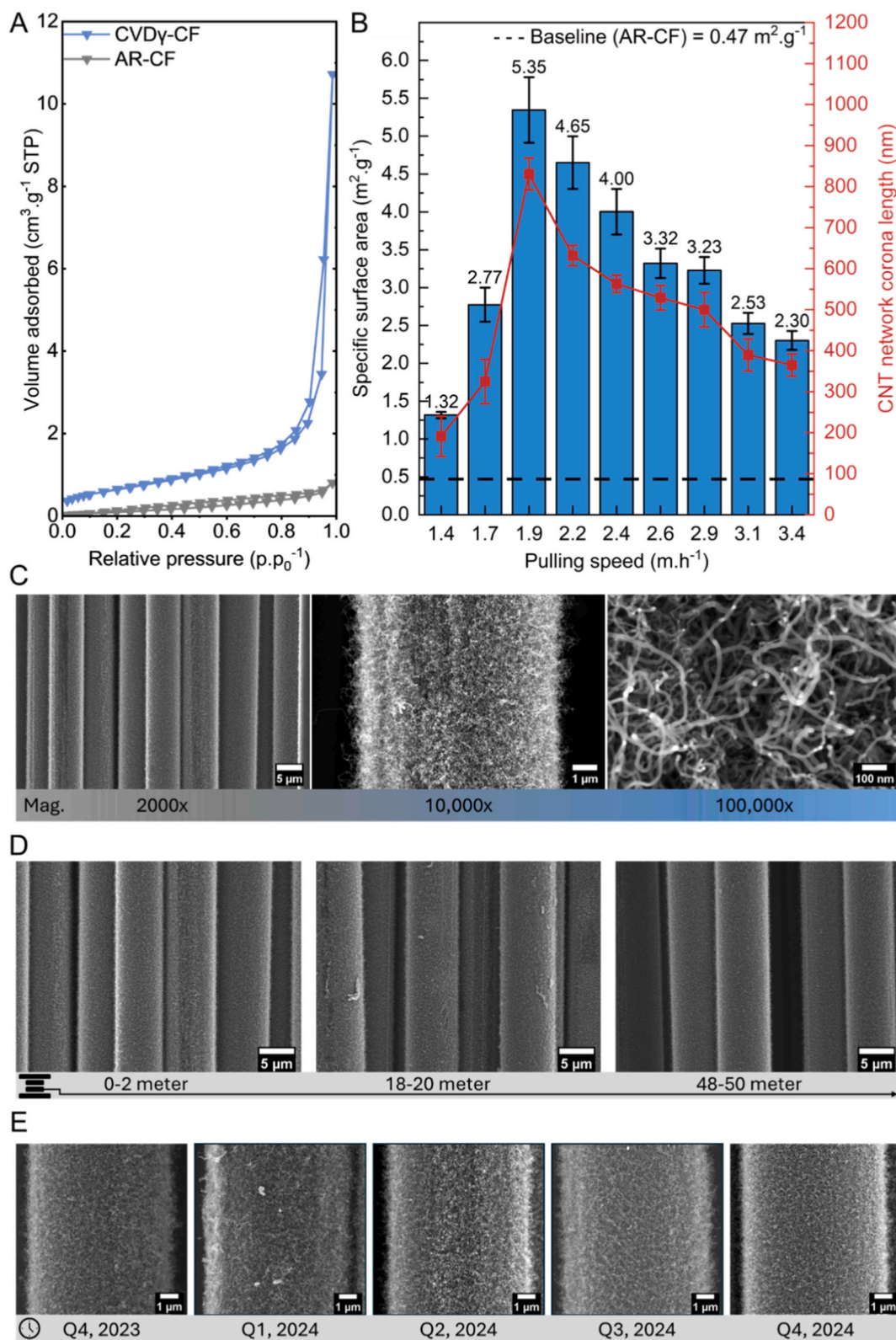


Fig. 4. Characterization of CNT-g-CF produced under CVD γ . (A) Nitrogen adsorption-desorption isotherms of CNT-g-CF grown using CVD γ condition compared to as-received unsized CF. (B) Correlation between measured specific surface area and CNT corona length, plotted as a function of fiber pulling speed grown using CVD γ parameters. Error bars are standard errors. (C) SEM micrographs at increasing magnifications, illustrating the spatial uniformity of CNT coverage across all fibers. (D) SEM images of CVD γ -CF taken along 50 m of continuous growth, and (E) across different times over a one-year period, demonstrating the repeatability and consistency of the process.

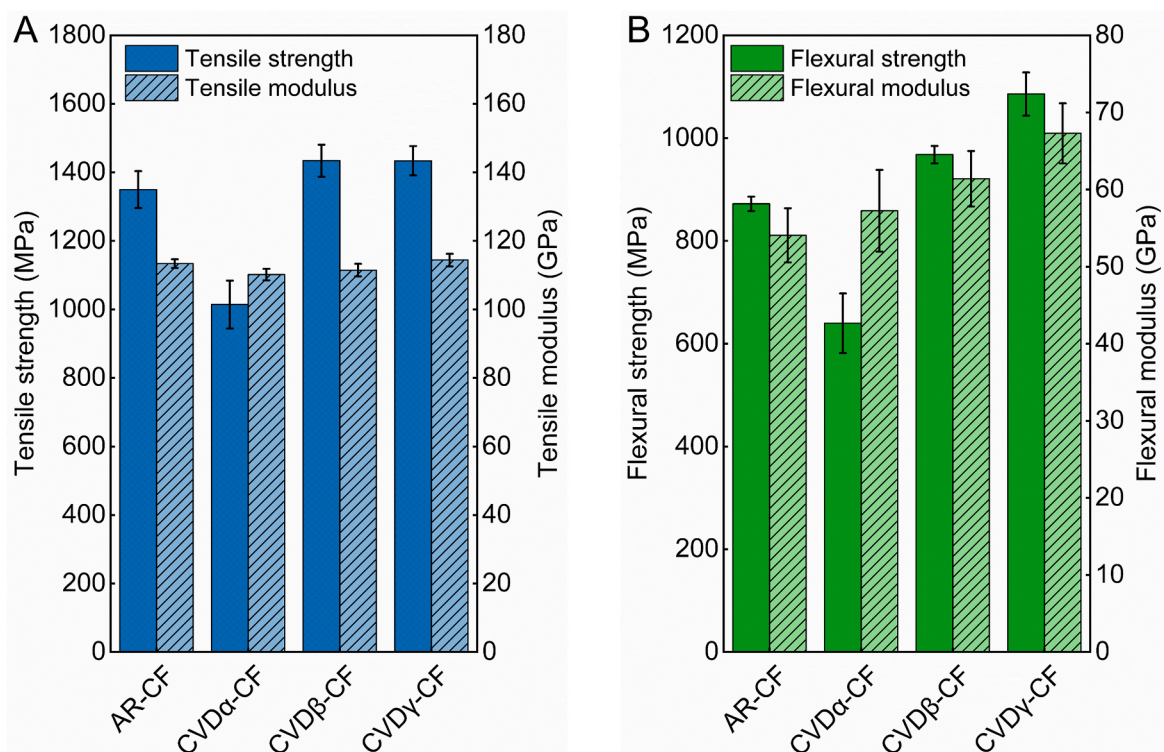


Fig. 5. Mechanical properties of baseline carbon fiber and CNT-grafted carbon fiber composites. (A) Tensile strength and modulus of carbon fiber reinforced composite rods. (B) Flexural strength and modulus of carbon fiber reinforced composite rods. Comparing all CNT-grafted-CF cases to baseline as-received carbon fiber (AR-CF). All data is normalized to nominal diameter and 40 % fiber volume fraction. Error bars are standard error.

surface modification [81]. These results demonstrate that the optimized CNT grafting condition (CVD γ) overcomes a key limitation of CVD-based modification by preserving fiber tensile strength.

To evaluate composite flexural performance, three-point bending tests were performed on the pultruded rods (40 % V_f , void content below 3 %), which subjects specimens to combined tensile, compressive, and shear stresses. The flexural strength of CVD α -CF also showed reduction compared to the baseline of AR-CF, while CVD β -CF and CVD γ -CF exhibited improvements of 11 % and 24 %, respectively (Fig. 5B). The flexural strength of CFRPs is often primarily governed by compressive performance, which is known to be matrix/interface dominated, particularly in the current system, where tensile performance is, at best, unchanged. The observed flexural improvement can be attributed to the CNT grafting reinforcing the fiber–matrix interphase and the surrounding matrix, thereby hindering local shear and delaying fiber microbuckling [82]. Interestingly, the flexural modulus improved progressively, with CVD γ -CF reaching a 25 % increase over AR-CF (Fig. 5B), likely associated with reinforcement of the fiber–matrix interphase, which improves stress transfer efficiency and reduces local compliance in matrix-rich regions. Since the fiber modulus remains unchanged, the observed increase arises from these interfacial and matrix effects rather than any change in the intrinsic fiber properties. These results show that optimized CNT grafting, achieved under CVD γ conditions, preserves tensile strength while enhancing flexural composite performance. Interface-dominated mechanical performance may be enhanced further by applying surface oxidation and sizing techniques to the CNT-grafted fibres, taking advantage of their increased surface area. Improvements in other matrix-dominated functional characteristics, such as electrical and thermal transport characteristics, can be anticipated.

3.5. Toward implementation

CNT-modification is a strong candidate to deliver multifunctional reinforcing fibres, of current interest in a range of contexts [83], through

improved interfacial strength, toughness, and electrical conductivity [84]. Continuous CNT-g-CF offers a scalable route to realize these advances via straightforward integration into existing production infrastructure. In this study, catalyst-coated carbon fibers were processed in a continuous CVD reactor under optimized CNT growth conditions (CVD γ). The processing temperature of 550 °C lies within the operational window of industrial polyacrylonitrile (PAN)-based carbon fiber production, which involves sequential oxidation in ovens followed by carbonization and graphitization in low-temperature (LT) and high-temperature (HT) furnaces, respectively. In practice, residence time in oxidation ovens is typically 55 min, achieved through 11 passes across 6–8 ovens with heated lengths of 10 m (15 m total) [85]. In comparison, carbonization and graphitization are conducted in LT and HT furnaces with heated lengths of 15–20 m, operating in a single pass with a residence time of 1.5 min [85]. Within the framework established in this study, CNT growth can be integrated as an additional module comprising catalyst deposition, hydrogen reduction to activate the catalyst, and subsequent CNT growth. The findings of this study illustrate plausible reactor conditions, namely a hydrogen reduction dwell time of 6 min and a CNT growth dwell time of 4 min at 550 °C. These catalyst reduction and CNT growth dwell times could be accommodated within an 18 m furnace by introducing approximately four and three fiber passes, respectively, consistent with the established use of multiple passes during oxidation and demonstrating potential compatibility with existing furnace designs. Despite this plausibility, clearly extensive gas flow and reactor design, with detailed CFD modelling, will be needed to develop appropriate conditions; this study shows that temperature is a primary factor in catalyst activation and CNT nucleation, but that its influence is coupled with gas composition, flow dynamics, and residence time.

The process satisfies many key criteria for industrial adoption, including stability, reproducibility, and preservation of mechanical properties. CNT growth was maintained by over 50 m of CF without degradation in tensile strength, demonstrating compatibility with the

fiber structure. SEM analysis confirmed uniform CNT coverage and indicated potential for interfacial enhancement. Tensile modulus remained consistent, confirming that axial stiffness is preserved. Sonication tests in water, ethanol, and acetone showed no removal of CNTs, confirming strong adhesion to the fiber surface (see SEM images, [section S14](#)). This adhesion is essential for downstream processes such as tow spreading, resin impregnation, and composite fabrication, with initial tests indicating no detachment during lab-scale trials of these steps. Previous tribological studies have further demonstrated the mechanical robustness of CNT-grafted CFs, evidencing strong adhesion and surface integrity under frictional loading [86–88]. These results establish a practical and scalable method for introducing CNT-based surface functionality into continuous CF production.

4. Conclusions

This study explores a comprehensive framework for the continuous grafting of carbon nanotube (CNT) onto carbon fibers (CFs) surface, addressing longstanding challenges related to scalability, growth uniformity, and the preservation of CFs tensile properties. A multi-length-scale characterization protocol was developed to quantitatively verify uniform CNT coverage across thousands of fibers. To ensure unbiased analysis, a machine learning-based classification model of scanning electron microscopy (SEM) images was implemented for evaluating uniformity. The consistency of microscopic datasets with macroscopic measurements of CNT mass and specific surface area (SSA), provide further reassurance of consistent and uniform growth. A steady-state computational fluid dynamics (CFD) model of an open-ended chemical vapor deposition (CVD) reactor was developed for the first time to resolve internal flow fields and species distributions, thereby addressing the ‘black box’ nature of conventional CVD systems. In parallel, a dynamic snapshot method was developed to experimentally identify the progression of catalyst reduction and CNT growth stages, to be mapped spatially against local reactor conditions. The insights gained from this approach informed process modifications that achieved uniform CNT growth at 550 °C, resulting in CNTs corona network with an average length of approximately 850 nm, within the threshold required to preserve high fiber volume fraction, and producing a tenfold increase in specific surface area ($5.35 \text{ m}^2 \text{ g}^{-1}$), while maintaining the tensile strength of the fibers. Despite the reduced temperature, the grafted CNTs show a hollow core with organized outer shells, representing an effective balance between CNT quality, fiber preservation, and scalable uniform growth. The optimized CVD process demonstrated stability over 50 m of CNT-grafted CFs and reproducibility across multiple iterations over the course of a year. Significantly, the optimized CNT-grafted fibers also improved the flexural strength of composites by 24 %, by addressing matrix-dominated failure, verifying their utility for enhanced composite performance. This integrated experimental-computational framework delivers fundamental insights into continuous CNT growth through open-ended CVD system and establishes a scalable, industry-compatible pathway for producing next-generation high-performance composites.

CRedit authorship contribution statement

Hassan A. Almousa: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Hugo G. De Luca:** Investigation. **David B. Anthony:** Writing – review & editing, Resources, Methodology, Investigation. **Emile S. Greenhalgh:** Resources. **Alexander Bismarck:** Resources. **Milo S.P. Shaffer:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbon.2025.121138>.

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