LOW TEMPERATURE PLASMA ENHANCED GROWTH OF CARBON NANOSTRUCTURES ON QUARTZ FIBRES

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ABSTRACT

This work investigates the growth of carbon nanostructures (CNSs) on quartz fibres through chemical vapour deposition (CVD). As the high temperatures (600-1000 °C) required in traditional thermal CVD are known to degrade the tensile strength of quartz fibres, a plasma enhanced chemical vapour deposition (PECVD) technology is here proposed to achieve low temperature (≤ 550 °C) growth of CNSs. Both a thermal CVD and a PECVD process are performed on quartz fibres at temperatures of 640 °C and 540 °C, respectively. As opposed to the 74% fibre strength loss resulting from the thermal CVD process, only a 13% strength loss is measured after the PECVD process through single fibre tensile test, confirming the effectiveness of this strategy in preserving the fibre mechanical response. Scanning electron microscopy is employed to characterize the surface morphology of quartz fibres after catalyst precursor deposition, hydrogen annealing pre-treatment and CNS growth for both processes. CNS morphologies are compared in terms of CNS length, orientation, and spatial arrangement and the effect of plasma and catalyst morphology is addressed.

1 INTRODUCTION

Hierarchical fibre reinforced composites are emerging as a novel class of advanced high-strength and multifunctional materials. Mimicking hierarchical natural materials, e.g., bones, hierarchical composites combine nanoscale fillers with microscale reinforcing fibres, resulting in unique properties that arise from the synergic interaction of each constituent across a range of length scales [1]. Specially, grafting carbon nanostructures (CNSs), such as carbon nanotubes (CNTs) and carbon nanofibres (CNFs), on the surface of fibres produces nanostructured fibre/matrix interfaces, thus improving interfacial properties and providing additional electrical, thermal, or chemical functions [2].

CNS deposition onto the surface of fibres has been achieved by dip coating [3], spray coating [4], electrophoretic deposition (EPD) [5], chemical grafting [6] and direct growth through chemical vapour deposition (CVD) [7]. Among these techniques, the CVD method provides higher densities of CNSs, which result in higher levels of interfacial shear strength (IFSS), and excellent control over CNS orientation. In general, conventional thermal CVD growth involves the decomposition of carbonaceous gases on nanoparticles of a transition metal catalyst (e.g., Fe, Ni, Co) in the temperature range of 600-1100 °C. However, the exposure to the high-temperature environment, which supplies the energy for the chemical reactions, can significantly degrade the tensile properties of the fibre substrate. Carbon fibres are usually attacked by the iron catalyst particles at high temperatures (~700 °C) and substantial loss of tensile strength has been reported when heated above 550 °C in both hydrocarbon-containing and inert atmospheres [8]. More severe strength loss occurs for glass fibres, starting at temperatures as low as 250 °C [9]. Even for high-temperature quartz fibres, a 50 % strength loss was detected following heat treatment at 760 °C [10].

Therefore, an important challenge to produce hierarchical fibres is lowering the growth temperature to mitigate its effects on the strength of underlying fibres. To this aim, a plasma-enhanced CVD

(PECVD) technology is proposed herein as an alternative to thermal CVD. During the PECVD process, a high energetic plasma supplies some of the energy for hydrocarbon decomposition and CNS formation, allowing lower operating temperatures. Moreover, PECVD technology permits to finely control the alignment of the tubes due to the interaction with the electric field.

PECVD synthesis of CNTs has been reported at temperatures as low as 300 °C on metal, silicon, and silica substrates, predominantly intended for electrical applications [11]. Recently, Sha et al. [12] and Zhang et al. [13] produced hierarchical carbon fibres through direct PECVD growth at temperatures as low as 400 °C and 450 °C, respectively, demonstrating the effectiveness of this strategy in preserving the mechanical properties of carbon fibres and achieving notable increases in IFSS with epoxy.

In this work, the growth of CNSs via PECVD is investigated at low temperatures (≤ 550 °C) on quartz fibres. The effects of thermal CVD and PECVD process on the fibre mechanical properties are quantified by single fibre tensile tests. Morphological and chemical characterizations of modified fibre surfaces are provided by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

2 MATERIALS AND METHODS

2.1 Materials

A continuous roving of commercially sized quartz fibres (Quartzel® C14 1600 QS1318) was kindly provided by Saint-Gobain. These fibres have a nominal diameter of 14 μm. Iron (III) nitrate nonahydrate was dissolved in 2-propanol as catalyst precursor for the CVD process.

2.2 Growth procedure of carbon nanostructures

The growth of CNSs on quartz fibres was achieved both by thermal (TCVD) and plasma enhanced (PECVD) processes. To this aim, an iron-based catalyst precursor was deposited on quartz fibres by dip-coating into a 0.05 M solution of iron (III) nitrate nonahydrate in 2-propanol. Subsequently, a high-vacuum reaction chamber equipped with a RF-plasma module with a gas-shower cathode was used for CNS growth. In this chamber, an annealing treatment was carried out in H_2 atmosphere for 4 minutes to reduce the catalyst precursor and promote the formation of evenly distributed catalyst nanoparticles. Afterwards, acetylene was introduced for the growth of CNSs for 10 minutes. These parameters are based on previous studies involving the growth of vertically aligned CNTs on different substrates [14–17]. In the case of the PECVD process, the growth step was performed with a plasma power of 30 W. Temperature was measured with two thermocouples: one on the heater and the other anchored to the substrate. The former was about 100 °C higher than the latter. As one of the main purposes of this work is to highlight the effect of temperature on the substrate, the discussion will refer to the temperature experienced by the substrate. Substrate temperatures in the two processes are reported in Table 1.

Process	Annealing Temperature (°C)	Growth Temperature (°C)
TCVD	620	640
PECVD	520	540

Table 1: Substrate temperatures selected for the thermal CVD (TCVD) and plasma-enhanced CVD (PECVD) processes.

2.3 Mechanical characterization of single fibres

The effect of CVD temperature on quartz fibres mechanical properties was evaluated by performing the exact growth protocol described in section 2.2 on as-received fibres (with no pre-deposited catalyst). Afterwards, single fibre tensile tests were carried out at room temperature with a Zwick/Roell Z010 tensile machine. A 100 N range load cell, displacement control, a cross-head speed of 2 mm/min and a sample gauge length of 20 mm were used. The system compliance was evaluated by testing samples of

as-received quartz fibres at three different gauge lengths (20, 30, 40 mm) in accordance with ASTM C1557. At least 10 samples were tested for each condition.

2.4 Morphological, chemical and structural characterizations

Morphological and chemical investigations were performed through a Mira3 field emission scanning electron microscope (FESEM) by Tescan equipped with an energy dispersive X-ray (EDS) detector.

3 RESULTS AND DISCUSSION

Prior to CNS growth, an iron catalyst precursor was deposited on the fibre surface by dip-coating. The morphology of dip-coated fibres is shown in Fig. 1a along with the EDS spectrum (Fig. 1) corresponding to a portion of the fibre surface shown in Fig. 1b. EDS investigation confirms the deposition of the iron nitrate on the fibre surface, while the peak of carbon suggests that the organic sizing is still on the fibre surface after the dipping process. The catalyst precursor morphology features both aeras with large clusters of catalyst precursor and areas with a smooth morphology, comparing quite favourably with the one reported by Yamamoto et al. [18] for alumina fibres dip-coated under the same conditions adopted in the present study.

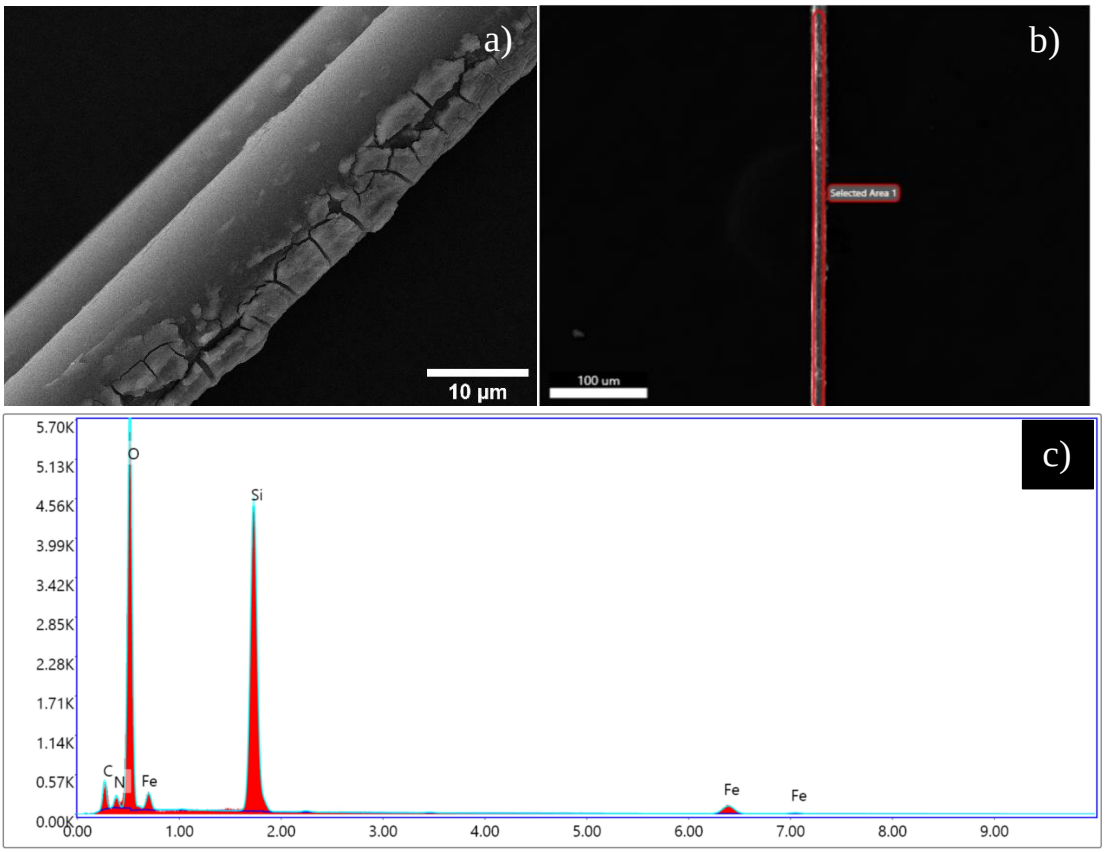

Figure 1: (a) SEM micrograph of a dip-coated quartz fibre; (b) a portion of a dip-coated quartz fibre selected for EDS analysis; (c) EDS spectrum for a dip-coated quartz fibre.

As a baseline for CNS growth onto quartz fibres, a thermal CVD process was performed on dip-coated quartz fibres at temperatures above 600 °C. As previously observed for basalt fibres [17], this process led to the growth of highly dense forests of vertically-aligned carbon nanostructures (Fig. 2). The CNS arrays, whose length ranged from 15 to 80 µm, were organized in a Mohawk morphology, which is typically observed for nanostructures whose length exceeds the fibre diameter [18]. During the growth of CNSs, the high density of nucleation sites, i.e. iron nanoparticles, generates proximity (also

known as crowding) effects which force the CNSs to grow perpendicularly to the substrate due to mechanical interactions between nearby CNSs [19]. As the CNSs become longer than the fibre diameter, the radial symmetry is broken due to van der Waals forces among nearby CNSs which split them into two or more arrays, generating a Mohawk morphology.

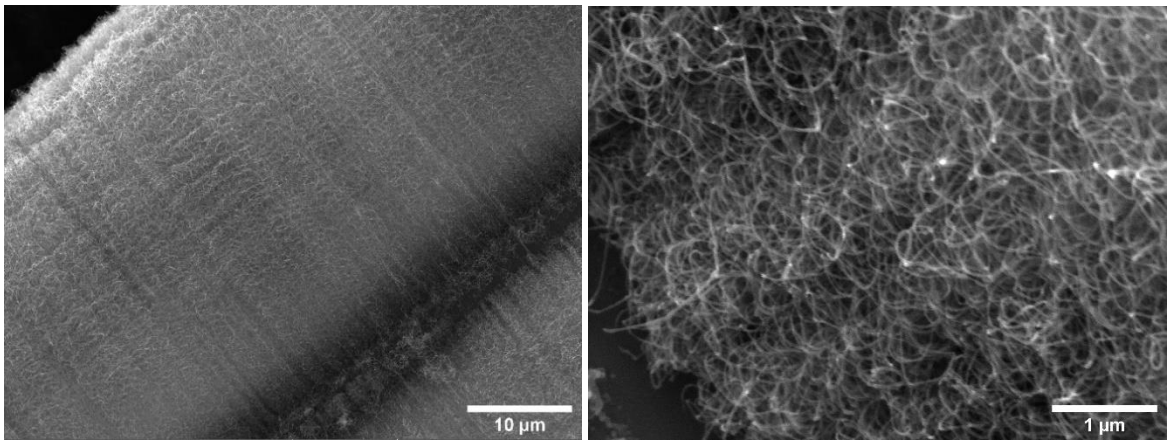

Figure 2: SEM micrographs of CNSs grown on quartz fibre surface following the TCVD process.

The effect of this exemplary thermal CVD process on the tensile properties of quartz fibres was evaluated by exposing as-received fibres to the same process conditions, without any pre-deposited catalysts. As a result, a 74% strength loss was highlighted through single fibre tensile tests, confirming the need for a low temperature process (Fig. 3).

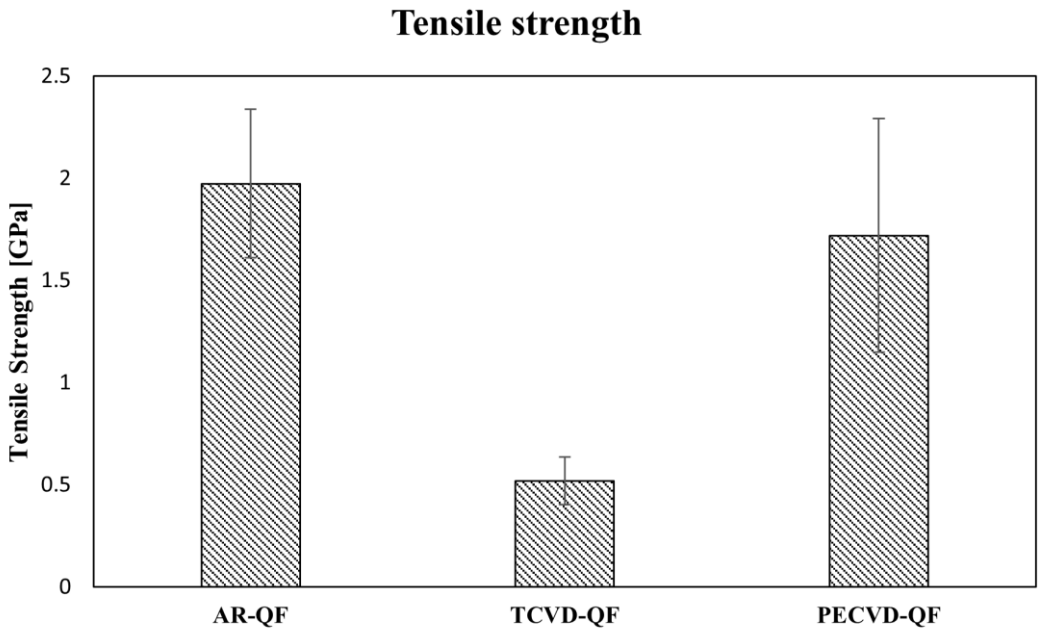

Figure 3: Tensile strength of quartz fibres as-received (AR-QF) and exposed to thermal (TCVD-QF) and plasma-enhanced (PECVD-QF) process with no catalyst.

The temperatures of the annealing and growth steps were therefore reduced to 520 °C and 540 °C, respectively, while a high energetic plasma was introduced during the growth step to promote the growth at reduced temperature. As reported in Fig. 3, this process effectively minimized the strength loss of the fibres, which retained around 87% of their original strength.

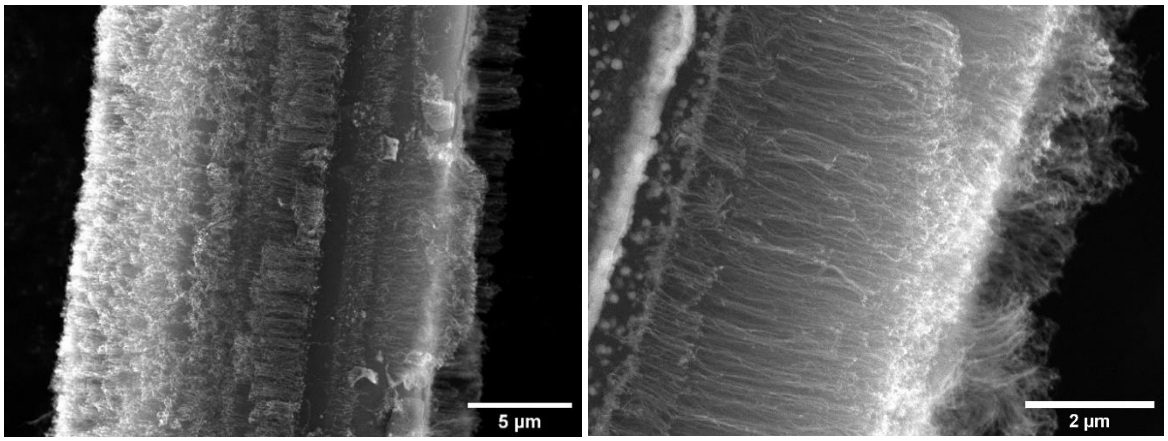

Figure 4: SEM micrographs of CNSs grown on quartz fibre surface following the PECVD process.

The morphology of CNSs grown by PECVD on quartz fibres is shown in Fig. 4. Conformal growth of radially aligned CNSs was achieved. The length of CNSs fluctuated from about 1 to 3 µm. As shorter CNSs were obtained through this process, no Mohawk arrangement was observed. However, it is worth noting that single nanostructures were straight, while thermal CVD-grown CNSs appeared curly and highly entangled with each other. This is in accordance with the findings of Bower et al. [20] who performed an alternating plasma and thermal process resulting in a straight/curled nanotube structure. Due to the presence of an electric field during the growth, CNSs are likely to be forced to grow along the electric field lines which are oriented perpendicularly to the substrate surface.

In addition to the effect of the electric field, the density and distribution of catalyst nanoparticles following the annealing step [14, 18] have to be considered as factors determining CNS morphology.

In the present work, the annealing step of the thermal CVD process (620 °C) produced densely distributed Fe nanoparticles (Fig. 5a) which are responsible for the proximity effects during growth. On the other hand, after the annealing step of the PECVD process (520 °C), the catalyst seems to be in the form of a layer on the fibre surface, with no obvious formation of Fe nanoparticles (Fig. 5b). Different annealing conditions led to different templates for CNS growth, thus contributing to the different CNS morphologies obtained following the two processes.

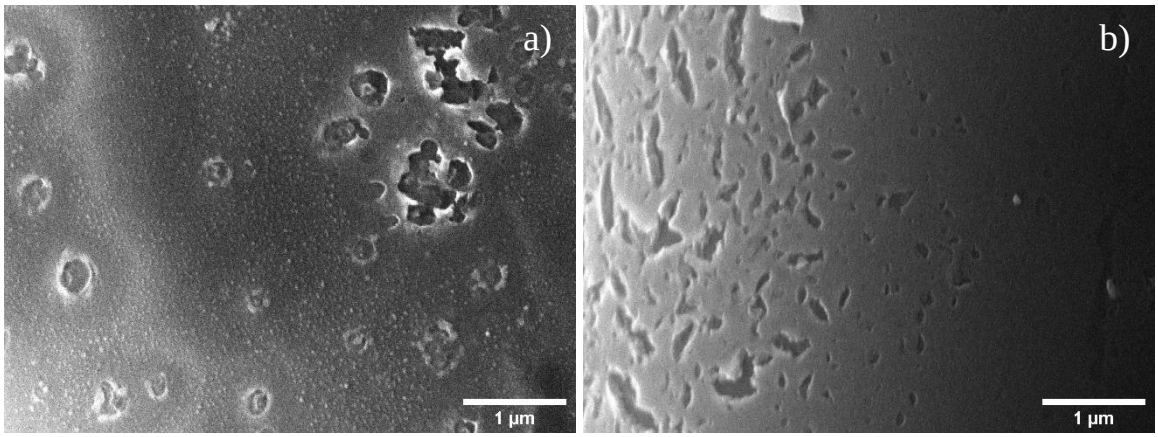

Figure 5: SEM micrographs of quartz fibre surface after the annealing step of (a) the thermal CVD process, (b) the PECVD process.

4 CONCLUSIONS

Direct CNS growth on the surface of reinforcing fibres is an effective way to improve interfacial adhesion and functionalities of fibre reinforced polymers. However, the high temperatures involved in the CVD process can seriously degrade the fibre mechanical response.

In this work, a plasma-enhanced CVD technique is employed to reduce the process temperature, thus mitigating the effect on the mechanical properties of quartz fibres. Two different CVD growth processes have been performed on quartz fibres: (i) a conventional thermal CVD process at temperatures of 620-640 °C, and (ii) a low-temperature PECVD process at 520-540 °C. Single fibre tensile testing confirmed the effectiveness of the PECVD technique in preserving the fibre mechanical properties as a strength loss of only 13% was measured after this process, while the thermal CVD process resulted in a strength loss of 74%. The different morphologies of CNSs obtained through the two processes are compared in terms of CNS length, orientation, and spatial arrangement. Different annealing conditions and the presence or not of plasma are reported as the main causes of morphological differences. The straight CNSs obtained by PECVD, as opposed to the curly nanostructures produced by thermal CVD, are believed to be caused by the electric field. However, further investigations under the same annealing conditions are needed to conclusively assess the effect of plasma on CNS morphology.

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