PLASMA-ENHANCED GROWTH OF CARBON NANOTUBES WITH IN-SITU CATALYST GENERATION FOR MULTIFUNCTIONAL BASALT FABRICS

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Abstract
Hierarchical reinforcements offer the opportunity to produce high-performance composite materials with multifunctional properties. In this work, the growth of carbon nanotubes (CNTs) is achieved on basalt fabrics at low temperatures (400-600 °C) without the addition of any external catalyst by combining *in-situ* catalyst generation and plasma assistance. First, an alkaline etching pre-treatment is performed to promote the segregation of the native iron oxides of basalt to be exploited as catalysts upon thermal annealing in H_2 atmosphere. Afterwards, a plasma-enhanced chemical vapour deposition (PE-CVD) technique is employed for the synthesis of CNTs at low temperatures to mitigate the well-known degradation of the fibre strength following high-temperature exposure in traditional thermal CVD. As a result, SEM investigation revealed an abundant growth of vertically aligned CNTs at 585 °C, with catalyst activation through H_2-annealing pre-treatment at temperatures as low as 485 °C. At lower temperatures (440-500 °C), only short and sparse CNTs were obtained. Moreover, the CNT-modified basalt fabric, in combination with a conductive polymer, showed promising responses in the electrochemical characterization, opening for possible applications as electrochemical devices, such as energy harvesting devices, to be further investigated in future research.

1. Introduction

Nowadays, the use of glass fibre within polymer matrix composite materials occupies a prominent slice of the global composite market, gaining attention due to the limited end-life disposal options of these materials. In this context, natural fibres of mineral origin, such as basalt fibres, are regarded as a promising greener alternative to glass fibres, thanks to their mechanical properties comparable to those of glass fibres and superior resistance to chemical agents, to high temperatures, and lower moisture absorption compared to natural fibres of vegetal origin [1]. Unfortunately, the widespread use of basalt fibre reinforced composites is hindered by the weak interface between the fibres and the polymer matrices. Among the strategies explored by the scientific community for interphase optimization in fibre reinforced composites, the production of hierarchical reinforcements offers the opportunity to improve the mechanical properties of basalt fibre composites while implementing additional functions for a wider class of industrial applications.
Significant research activity adopted chemical vapour deposition (CVD) to directly grow high loadings of carbon nanostructures, particularly carbon nanotubes (CNTs), on the surface of reinforcing fibres,

thus enhancing the interfacial adhesion with the polymer matrix and providing additional functions, such as damage sensing [2], electromagnetic wave absorption [3], and electrochemical properties [4]. The CVD method generally requires the presence of metal catalysts, commonly based on Fe, Ni and Co, which act as nucleation sites for the growing CNTs. While the addition of an external catalyst precursor is required for most fibre substrates, *in-situ* catalyst generation has been demonstrated for basalt fibres by promoting the microstructural segregation of iron oxides via basic or acidic pre-etching and the subsequent reduction in hydrogen atmosphere to nanocrystalline metallic iron. This approach, reported for the first time by Forster et al. [5], was employed for the growth of high density vertically aligned (VA)-CNTs by Sarasini et al. [6]. However, the high temperatures used for the process (above 700 °C) caused a significant deterioration of the fibre mechanical properties, with a reported strength loss of 39%.
In this work, a plasma-enhanced CVD (PE-CVD) technology is proposed as an alternative to thermal CVD. Thanks to a high energetic plasma, which supplies some of the energy for hydrocarbon decomposition and CNT formation, the PE-CVD method allowed lower operating temperatures which can mitigate the loss of mechanical strength of the substrate fibres. Moreover, a preliminary assessment of the electrochemical response of the CNT-modified basalt fabric has been carried out to investigate its potential as multifunctional fabric for applications in the field of electrochemical sensors and supercapacitors.

2. Materials and methods

2.1. Materials

A commercially available basalt woven fabric (220 g/m^2) was provided by Basaltex (BAS 220.1270.P). Individual fibres were coated with an epoxy-compatible sizing. NaOH (by Sigma Aldrich, reagent grade ≥98%) was dissolved in water for chemical pre-treatment of the basalt fabric.

2.2 CNT synthesis procedure

Prior to the CVD process, a chemical pre-treatment was carried out in a NaOH 2M aqueous solution for 3 hours at room temperature. The CNT synthesis was performed at the Sapienza-INFN CVD facility equipped with a RF-plasma module with a gas-shower cathode.
The basalt substrate (20 mm × 20 mm) was placed on the heating element of the high vacuum reaction chamber and thermally annealed in hydrogen atmosphere for 8 minutes to reduce the iron oxides to active metallic iron and promote the formation of nanoparticles catalysing the growth of CNTs. Afterwards, acetylene was introduced in the chamber as the carbon feedstock for CNT synthesis for 14 minutes while a plasma power of 45 W was employed. Finally, the samples were allowed to cool down to room temperature under the base pressure. These growth parameters were tuned based on the CVD protocol previously reported by Sarasini et al. [6] for the growth of VA-CNTs on basalt fabric via thermal CVD, which was replicated for the assessment of the electrochemical properties of the CNT-modified fabric. The temperature was measured with two thermocouples: one placed inside the heating element and the other anchored to the top surface of the fabric substrate. As the focus of the work is to reduce the temperature experienced by the fibre substrate, the substrate temperatures will be addressed. Two different temperature conditions were investigated, as reported in Table 1.

Table 1. Substrate temperatures investigated for the growth of CNTs on basalt fabric via PE-CVD.

Process	Annealing Temperature (°C)	Growth Temperature (°C)
PE-CVD-1	485	585
PE-CVD-2	440	500

2.3 Characterization techniques

A Mira3 field emission scanning electron microscope (FESEM) by Tescan was used for the morphological investigation of CNT-modified basalt fabric.

All electrochemical measurements were conducted by using an Autolab PGSTAT204 apparatus. The setup for the measurements consisted of two CNT-modified basalt electrodes separated by a conductive polymer synthesized by solvent casting from starch and an ionic liquid.

3. Results and discussion

The aim of this work is to investigate the use of PE-CVD for the low temperature growth of CNTs on basalt fibres. Based on a previous work by our group [6], an innovative approach of exploiting the native iron oxides of basalt fibres as catalysts was used for the growth of CNTs. An alkali etching pre-treatment was therefore carried out on the basalt fabric samples before the CVD process to promote the exposure of iron oxides on the surface of basalt fibres. In fact, the corrosive attack experienced by basalt in alkaline environment involves the breaking of the siloxane bonds and consequent silicates migration in the solution, thus exposing calcium, titanium, and iron oxides on the fibre surface. This iron content can seed the growth of CNTs from the basalt surface upon reduction during the H_2-pre-synthesis annealing treatment. Whereas in the previous work both annealing and growth steps were conducted at typical thermal CVD temperatures (above 700 °C) at the expense of a severe fibre strength loss, in this work a plasma-enhanced CVD technique was used to achieve a lower temperature growth.

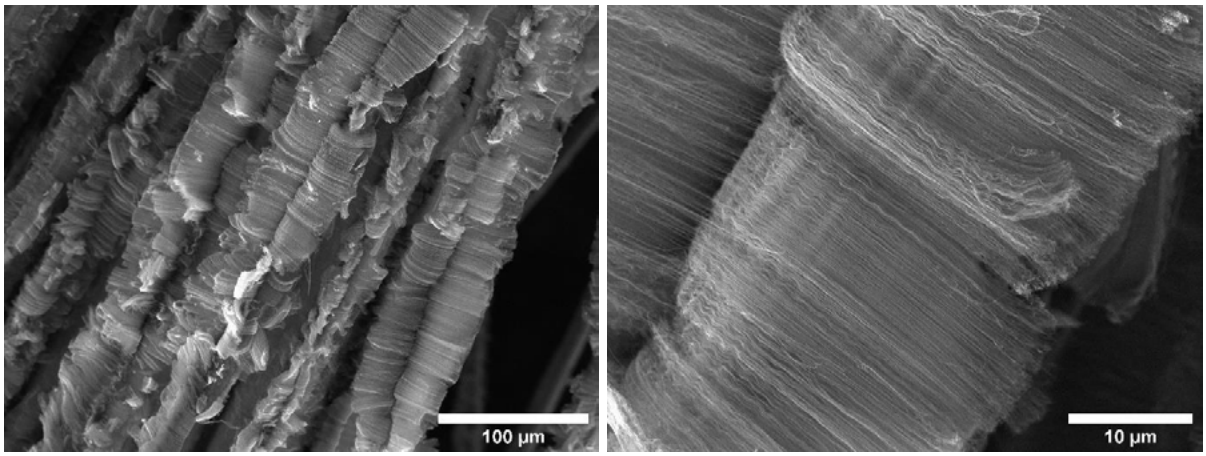

Figure 1. SEM micrographs of basalt fibres following the PE-CVD process at 485-585 °C.

As shown in the representative SEM micrographs reported in figure 1, the PE-CVD-1 process led to an abundant growth of dense VA-CNTs arrays, with lengths ranging from 30 to 40 µm. Such morphology is completely comparable to the one obtained via thermal CVD at temperatures above 700 °C, demonstrating that the plasma power introduced during the growth step was able to compensate entirely for the temperature difference in terms of energy needed for the growth. Moreover, the obtained morphology demonstrates that the native iron oxides exposed on the fibre through the alkaline etching can be reduced to a uniform and dense distribution of iron catalyst nanoparticles at temperature as low as 485 °C. In fact, a dense distribution of nucleation sites is required to generate proximity effects and force the tubes to grow in a common direction due to van der Waals interactions between nearby CNTs [7]. As observed by Tolga Gul [8], the density of the catalyst nanoparticles also affects the tortuosity of individual tubes in the VA-CNT forest. By comparing the higher magnification SEM micrograph in figure 1 to the one reported by Sarasini et al. [6], it can be assumed that in both cases the density of nanoparticles was sufficient to guarantee the growth of well-aligned CNTs.

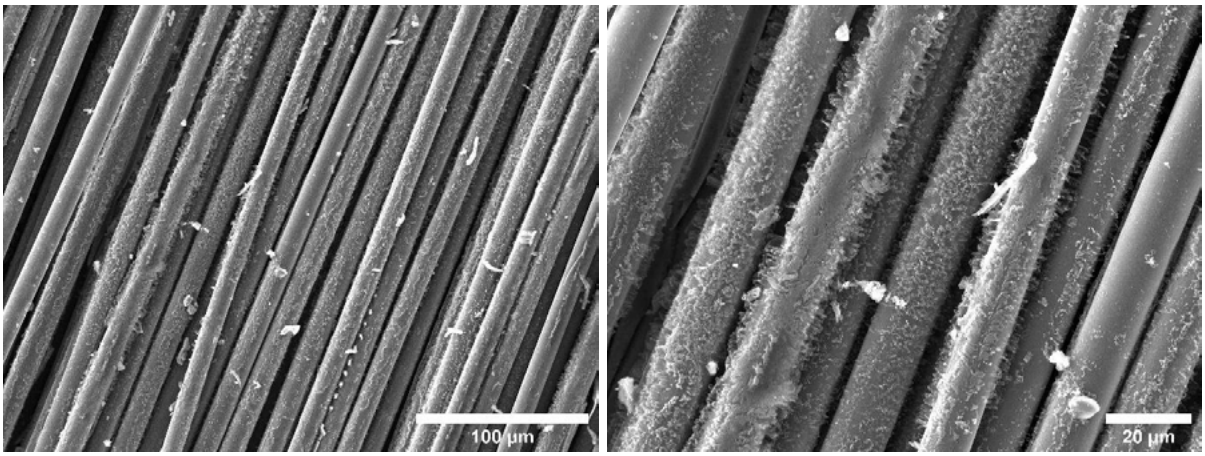

Figure 2. SEM micrographs of basalt fibres following the PE-CVD process at 440-500 °C.

A further reduction of process temperatures was made for the PE-CVD-2 process. The SEM investigation (figure 2) revealed the growth of sparse and much shorter CNTs (~3 µm). As opposed to the previous process, the poor coverage indicates that the lower temperature annealing was probably not sufficient to completely activate the iron catalyst into suitable-sized and evenly distributed nanoparticles. It is worth noting that, despite the low density, the CNTs grew with a radial orientation and relatively low tortuosity. The radial orientation and low waviness of the tubes in this case is mainly determined by the plasma which, along with the catalyst distribution, contributes to the final CNT morphology and orientation. As reported by Bower et al. [9], in fact, the interaction with the electric field during the growth tends to align the CNTs perpendicularly to the fibre surface in the direction of the electric field lines.

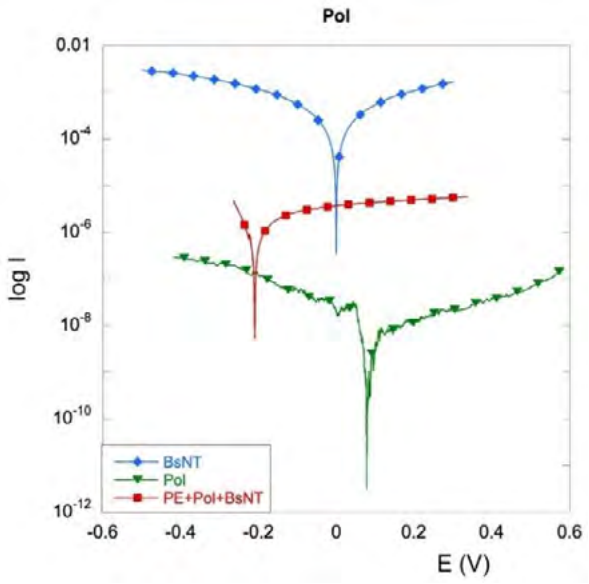

Figure 3. Polarization curves of the materials tested individually and in combination.

In contrast to conventional silane-based sizing coatings, CNTs directly grown on basalt fabrics might provide enhanced interfacial adhesion with the polymer matrix as well as multifunctional opportunities. In addition to the electrical conductivity measured in [6], a preliminary assessment of the electrochemical response of the material was carried out in this work. Fig. 3 illustrates the potentiodynamic polarization curves of basalt with nanotubes and the polymer alone at a scan rate of 1

mV/s. The combined system presents an intermediate current value compared to the individual components and stability in the potential range investigated. This behaviour opens possibilities for applications in the field of electrochemical devices, such as those for energy harvesting.

4. Conclusions

The *in-situ* growth of CNTs without external catalyst was investigated at low temperatures (400-600 °C) by means of a PE-CVD technique. Two synthesis processes were conducted at different temperatures to highlight the potential of this technique for temperature reduction and the resulting CNT morphologies were compared to the thermal counterpart from a previous work performed at temperatures above 700 °C [6]. The PE-CVD-1 process (485-585 °C) allowed to achieve a CNT morphology completely comparable to the thermal one with a consistent temperature reduction which is expected to mitigate the strength loss experienced by the basalt substrate. On the other hand, the PE-CVD-2 process (440-500 °C) led to a non-uniform coverage of short CNTs, identifying a lower temperature limit under the selected process conditions. Future works will be focused on the proper tuning of the process parameters in the identified temperature range to further investigate the low temperature opportunities of PE-CVD on basalt fabrics.
Moreover, the electrochemical investigation carried out in this work showcases promising potential for the application of hierarchical basalt fabrics in the field of electrochemical devices, such as supercapacitors, to be further investigated in future works.

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