Hierarchical composites for advanced multifunctional structures

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Abstract

The concept of hierarchical composites is based on the idea of coupling reinforcements of different scales following a biomimetic approach so as to establish maximum synergy between the different scales. This synergy may guarantee optimal bulk properties via a controlled engineering approach of the hierarchical phase. These properties may target various functionalities like structural reinforcement, structural health monitoring, energy harvesting, power storage and generation or even actuation. This approach poses multiple challenges which are related to the preparation of the reinforcement. In this study, two different production methods, i) the Chemical Vapor Deposition (CCVD) and ii) a wet chemical impregnation technique were implemented to fabricate hierarchical reinforcements. These multiscale reinforcements consist of structural carbon fibres (CFs) coated with carbon nanotubes (CNTs). Both production processes were optimized by adjusting crucial experimental parameters so as to finally obtain homogeneously deposited coatings on the surface of the fibres. The morphological characteristics of the hierarchical fibres were assessed via Scanning Electron Microscopy. Subsequently, the mechanical, interfacial and targeted functional properties of the hierarchical fibres were evaluated in order to provide a roadmap for the scaling-up towards structural laminated composites.

1. Introduction

The incorporation of nanofillers in structural fibre reinforced composites (FRCs) is a research area, which attracted immense scientific interest during the last decades [1]. The promising properties of nanoreinforcements such as carbon nanotubes (CNTs) have driven numerous research efforts towards their successful integration into FRCs [2]. In this context, two distinct approaches have been generally followed, namely the dispersion of the nanomaterials in the polymeric matrix or the attachment of the nanomaterials onto the primary fibrous reinforcement as a "thin nano-coating". The resulting nano-reinforced FRCs are referred to as hierarchical, multiscale or hybrid composites. A basic distinction between the aforementioned production routes is the enhancement of specific properties in the final FRCs. As is obvious, the dispersion of CNTs in the matrix focuses on the matrix dominated properties, while the attachment of the CNTs onto the CF surface mainly leads to the enhancement of the interfacial and interlaminar properties with a possible accompanying degradation in the fibre tensile strength.

Various methods like CCVD growth, electrophoretic deposition (EPD) and wet chemical modifications were reported for the effective attachment of CNTs onto the CF surface [3]. The interconnection of phases of different length scales at the interface of the hierarchical composites renders the interfacial region and the study of it indispensable in order to safely predict the properties of the final composites [4,5]. In addition to the enhancement of the interfacial properties the hierarchical composites can also demonstrate other non-structural functionalities [3]. These functionalities are mainly attributed to the nanostructured CNT-rich interfaces which are formed in the hierarchical composites. Temperature [6] and strain sensing [7], UV sensing and curing monitoring [8], as well as thermal energy harvesting [9] have been reported in literature mainly for glass FRPs.

The development of advanced multifunctional FRPs may lead to the exploitation of the full potential of the nano-reinforcements in terms of mechanical, electrical, thermal and optical properties. In this respect, this study involves the characterization and comparison of the microstructure, mechanical properties and additional targeted functionalities of hierarchical carbon based reinforcements. The study focuses on the evaluation of the aforementioned properties at the single fibre and fibre tow level with a view of optimizing the implemented experimental protocols and then scaling up to multifunctional hierarchical composites.

2. Materials and methods

2.1. Materials

The unsized (un_CF) and the sized (s_CF) M40 high modulus PAN fibres (Torayca) with a tensile strength of 2.74 GPa, a modulus of 392 GPa and failure strain of 0.7%, as stated by the manufacturer were used in this study. The fibre diameter was 6.6 μm as determined by density measurements. A two component MY-750 / HY-951 epoxy system was employed as the matrix for the production of the single fibre model composites. This matrix exhibits a tensile strength of 75-90 MPa along with an elongation at break of 3-4% and a modulus of 3.5-4.0 GPa. Additionally, the ONEX MW 1000C1 CNTs, with diameters ranging from 20 nm to 45 nm and lengths ≥ 10 μm, purity ≥ 94%, metallic inclusions ≤ 5.9%, amorphous carbon <0.1% and bulk density ≤ 80–120 kg/m3, provided by Glonatech SA, were used for the wet chemical treatment protocol.

2.2. Methods

2.2.1 Wet chemical deposition of CNTs on the surface of CFs

The wet chemical protocol for producing hierarchical CFs included oxidation of sized CFs and commercial multi-walled CNTs in HNO_3 (65 % v/v) for 60 min and in a mixture of sulfuric and nitric acid (ratio 3:1 v/v) under reflux and magnetic stirring for 6h, respectively. Then, the oxidized CNTs were filtered and neutralized with deionized water, this also applied for CFs after oxidation. The oxidized CNTs were then dispersed in distilled water at 0.1% w/v and used as an ink for coating the surface of the oxidized CFs. The coating procedure was conducted by submerging the oxidized CFs in the CNT ink in an in-house made semi-automated set up [10]. The hierarchical CFs produced by this process will be referred to as CF/CNT_wet throughout this study.

2.2.2 Growth of CNTs on the CF surface via CCVD

The CNT growth process was conducted in a horizontal tubular furnace (Carbolite) using a FeCo bimetallic catalyst. Details on the catalyst preparation and the CVD procedure can be found elsewhere [11]. Acetylene was used as the gaseous hydrocarbon source for the CNT growth, which was achieved for 30 min at 850°C using unsized CFs. The hierarchical CFs produced by this process will be referred to as CF/CNT_cvd in this study.

2.3. Morphological evaluation and mechanical characterization

The morphology of the CFs, the CF/CNT_wet and the CF/CNT_cvd was evaluated by Scanning Electron Microscopy (SEM) using the JEOL JSM 6510 LV SEM/Oxford Instruments. The mechanical strength of the reference un_CF and s_CF were studied via single fibre tensile testing. Reference and hierarchical CFs were tested at three gauge lengths, i.e. 10 mm, 25 mm and 40 mm (more than 50 tests for each fibre type), following the ASTM C1557-14 [12].

The Interfacial Shear Stress (IFSS) developed at the interface of the reference and the hierarchical CFs with the epoxy matrix was also assessed via Single Fibre Fragmentation Tests (SFFT). Dog bone-shaped specimens comprised of a single fibre embedded axially in the middle of epoxy resin were produced as described elsewhere [11]. Subsequently, their surface was appropriately prepared (sanding and polishing) for microscopic characterization. During the fragmentation test these specimens were loaded to tension, with a custom made horizontal tensile stage which was placed under the polarized optical microscope objective. The birefringence patterns were used to measure the fragments of each fibre. Five samples were tested for each category and each fibre diameter was evaluated before testing by averaging 10 optical measurements along its length.

The study also targeted to assess the thermoelectric efficiency of the reference and the hierarchical CFs as an additional functionality of these structural reinforcements. The DC electrical resistance (R) of the CFs was measured by a standard two-probe method using an Agilent34401A6½ digital multimeter, at 25 mm electrode-electrode distance and stabilized with silver paste. The distance between the two electrodes defines the fibre's length and was used further for the resistivity (ρ) and electrical conductivity (σ) calculations. For the thermoelectric (TE) measurements a custom made set-up was developed to obtain the Seebeck voltages. CF tows were mounted on two metal blocks, which enabled the thermopower generation upon being exposed to a temperature gradient.

TE materials obey the well-known thermoelectric or Seebeck effect (opposite to Peltier effect) described by the thermoelectric power (TEP) or thermopower or Seebeck coefficient (S), which is the direct solid state conversion of thermal energy to electrical [13]. An electric current is created through the diffusion of charge carriers, either electrons or holes from the hot side of the material to the cold. The Seebeck coefficient is defined then as: $S=\Delta V/\Delta T$ (1), where ΔV is the electric potential difference created by a temperature gradient ΔT.

3. Results and discussion

The morphology of the reference CFs and the hierarchical CF/CNT is depicted in the SEM micrographs of Figure 1. The s_CF and un_CF exhibited typical high modulus CF surfaces. A rough texture was observed for both the reference CFs resulting from the alignment of the outer graphitic sheets parallel to the CF axis. A homogeneous surface coverage with CNTs was observed for the hierarchical CFs regardless of the production method. A thin veil of CNTs was formed on the CF surface in the case of CF/CNT_wet with the nanotubes lying parallel to the surface of the CF. On the contrary, the CNT growth method resulted in the formation of a rather thick CNT coating, normal to the CF surface in the CF/CNT_cvd.

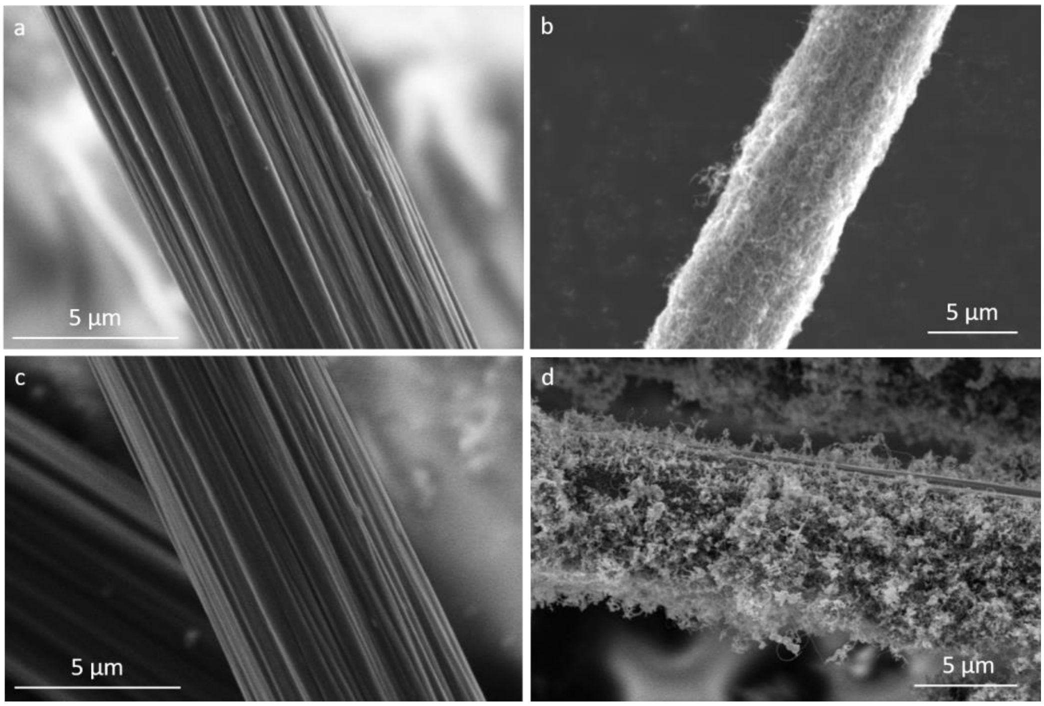

Figure 1. SEM micrographs of the reference and the hierarchical CFs, a) s_CF, b) CF/CNT_wet, c) un_CF and d) CF/CNT_cvd.

The effects of the CCVD and wet chemical processes on the mechanical properties of the CFs were evaluated via single fibre tensile tests. As can be seen in Figure 2 both processes were found to negatively affect the CF strength to a small extent. The reference and hierarchical CF strength to length relationships were derived by measuring single fibres at three different lengths. These equations were subsequently used for assessing the fibre strength at the sub millimeter lengths recorded during the SFFT.

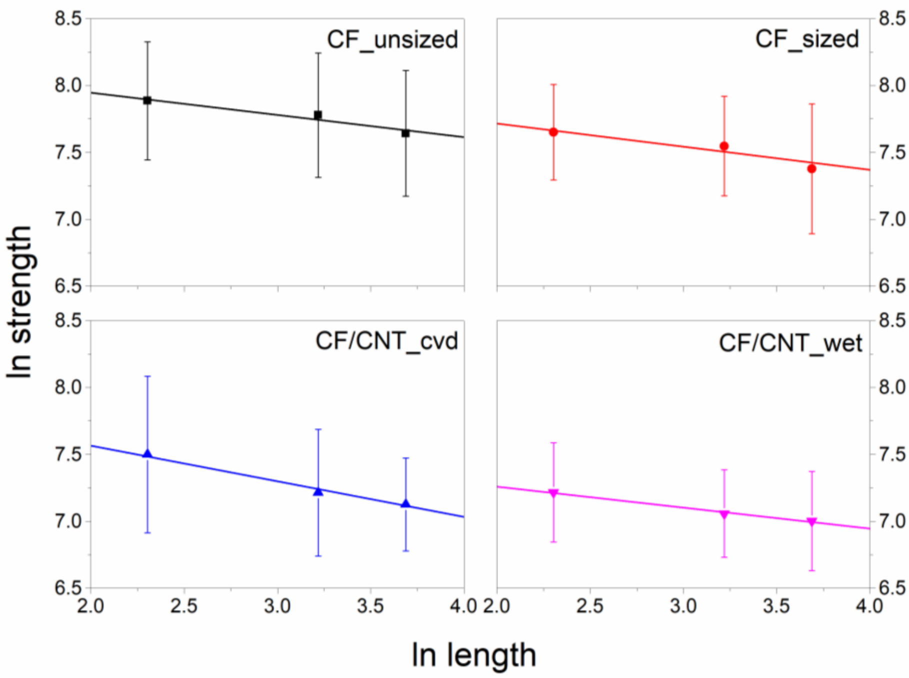

Figure 2. Experimentally derived relationships of the fibre strength with respect to the fibre length.

Subsequently, the interfacial properties of model composites consisting of either a single reference CF or a single hierarchical CF were evaluated. The incorporation of the CNTs on the CF surface was found to positively affect the IFSS which was developed at the interfacial region. The CF/CNT_wet exhibited a 17% enhancement in comparison to the reference s_CF, while the CF/CNT_cvd exhibited an even more pronounced enhancement (77%) in comparison to the reference un_CF. Characteristic Break Density vs Tensile strain plots for the reference and hierarchical CFs are depicted in Figure 3. The onset of the fragmentation process was found to happen at the same strain level for both the reference and the hierarchical CFs. On the other hand, the hierarchical CFs exhibited obviously enhanced break densities at the saturation stage. Additionally, the CF/CNT_cvd presented an increased rate of breaks accumulation in comparison to both the reference fibres as well as the CF/CNT_wet. These results indicate that although the incorporation of the CNTs onto the CF surfaces have a negative effect on the CF tensile properties, the interfacial mechanical characteristics of the hierarchical CFs with the epoxy matrix are essentially improved.

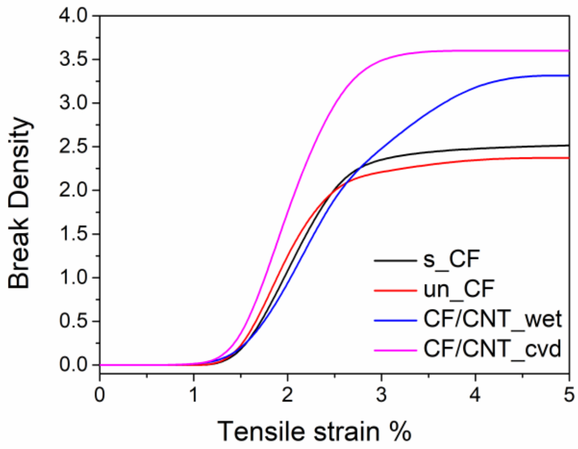

Figure 3. Characteristic Break density vs tensile strain plots for the reference and hierarchical CFs as measured by SFFT.

Finally, the electrical characteristics and the thermoelectric response of the reference and the hierarchical CFs were evaluated as additional non-structural functionalities stemming from the hierarchical nature of the produced reinforcements. Figure 4 summarizes the a) resistance values and b) Electrical conductivities of the hierarchical and the reference CFs. The resistance was found to increase after the CNT deposition on the CF surface both for the CF/CNT_wet and the CF/CNT_cvd. This change was more pronounced for the CF/CNT_cvd. Regarding to the thermoelectric characteristics, the Seebeck coefficient slightly increased for the CF/CNT_wet in comparison to the reference s_CF, while a more obvious enhancement was observed for the CF/CNT_cvd in comparison to the reference un_CF.

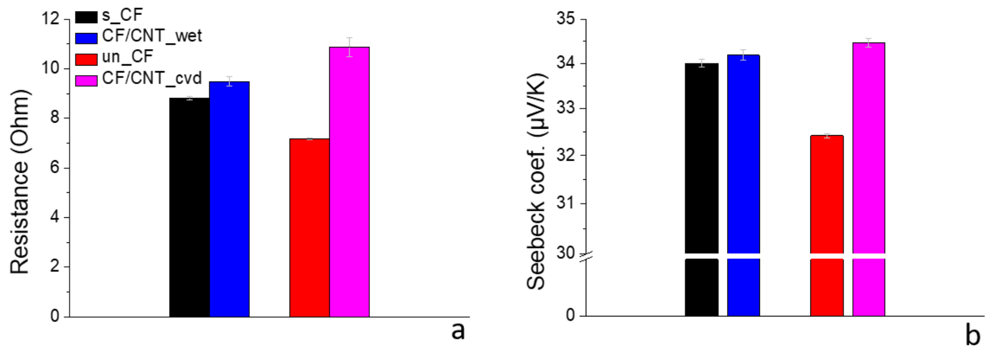

Figure 4. a) Electrical resistance and b) Seebeck coefficient of the reference and the hierarchical CFs.

4. Conclusions

This study focused on the production of hierarchical carbon based reinforcements by two different experimental processes, namely CCVD and wet chemical treatment. The study assessed the effects of the two procedures on the mechanical properties of the hierarchical CFs and evaluated the shear stresses which are developed on the nanostructured interfaces by SFFT. The strength of the hierarchical CFs was slightly reduced due to both processes but this reduction was counterbalanced by the increased IFSS values which were more pronounced for the CF/CNT_cvd in comparison to the CF/CNT_wet. Finally, the electrical and thermoelectric properties of the hierarchical reinforcements were also assessed during this study, demonstrating the multifunctionality of the produced structures.

Acknowledgments

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