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Optimal synergy between micro and nano scale: Hierarchical all carbon composite fibers for enhanced stiffness, interfacial shear strength and Raman strain sensing

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ABSTRACT

Multifunctional hierarchical reinforcements are fabricated by growing multi walled carbon nanotubes (CNTs) onto carbon fibers (CFs) via chemical vapor deposition. In contrast to typical hybrid multi scale reinforced composites, the biomimetic approach of hierarchical interconnection between CFs and CNTs is followed in order to provide the dimensional confinement required for the effective synergy between the nanophase i.e. the CNTs and the micron phase i.e. the CFs. Compared to the reference CF: (i) ASTM single fiber tensile tests reveal up to 50% increase in tensile modulus together with the expected decrease in tensile strength, (ii) Single Fiber Fragmentation Tests (SFFT) reveal up to 134% enhancement for Interfacial Shear Strength (IFSS), (iii) the frequency of the Raman 2D graphitic vibrational mode with strain shows a strain sensitivity enhancement up to 87.4% and (iv) fractographic investigation shows bridging of the CNTs only for specific growth conditions, which correspond to the optimal IFSS. Furthermore, a direct correlation between the Raman strain sensitivity with the young moduli of the CF and the hierarchical CF-CNT is found, proving the efficient stress transfer from the nano to micron scale in a "composite" fiber. Overall, an optimal synergy between the reinforcing graphitic phases is achieved, attaining for the first time an equivalent stiffness for the CNT reinforcement close to theoretically obtained values. Thus, biomimetic hierarchical reinforcements provide the roadmap for the full exploitation of the unique properties of the nanophase in advanced structural composites.

1. Introduction

Multiscale reinforced hierarchical composites have drawn the attention of the scientific community during the last decade due to their capability of enhancing inherent weaknesses, like flexural properties and interlaminar adhesion, of Fiber Reinforced Polymer Composites (FRPs) [1–6]. Thereby, a concept of structural hierarchy mimicking paradigms given by natural materials and structures, i.e. wood, bone and flower stems, was implemented in advanced multiscale FRPs. In practice, a combination of different material length scales, micro-dimensional - carbon fibers (CFs) and nano-dimensional - carbon nanotubes (CNTs), and different material properties led to the realization of a hierarchy in these designed engineered composites.

The exploitation of the exceptional properties of CNTs by their incorporation into composites was attempted via two different methods, (i) dispersion into the polymeric matrix and (ii) attachment or growth onto the reinforcing fiber surfaces. Typical hybrid systems, where fibers constitute the main reinforcement and nano phases are dispersed in the composite matrix, seldom manage to attain the expected properties that should stem from the unique properties of nano sized graphitic entities such as CNTs. This is due to several manufacturing problems, i.e. agglomeration issues due to strong Van der Waals forces, or subsequent filtration issues due to high viscosities, generated during the incorporation of the CNTs directly into polymeric matrices (hybrid composites) hampered the full exploitation of their strengthening ability [7,8]. Alternatively, the attachment of CNTs onto CF surfaces and the subsequent incorporation of that hierarchical CFs into the respective matrices was reported by catalytic chemical vapor deposition (CVD) [9,10], anchoring via the formation of chemical bonds [11–13] or coating of CFs with CNT containing sizing mixtures [14,15]. Among these techniques, CVD was extensively studied by many researchers [16–18]. In cases where the substrate was fibrous (carbon, glass and

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alumina fibers), the effects of the growth parameters on the mechanical strength of the produced hierarchical fibers were evaluated [19,20]. CVD growth resulted in some loss of the fiber strength in most of these studies [21,22]. This was counterbalanced by the resulting enhanced interfacial adhesion, commonly attributed to the increased surface roughness, and the subsequent mechanical interlocking with the polymeric host matrix [23,24].

Although the knowledge and the research effort on advanced multiscale FRPs has ever been increasing during the last decade, there is ample space for further enhancement in their mechanical properties, as the composite properties do not fully reflect the potential of the reinforcing phases. Moreover, recent research reported that, the detrimental effects on fiber strength can be reduced [25,26] or even reversed [27], by careful choice of the CVD parameters - mainly growth temperature, catalyst and hydrocarbon source, by subjecting the fibers to tension during the growth process [20], or by coupling the CVD process with an electric field [28]. On the other hand, the stiffness of the produced hierarchical fibers is seldom studied in the literature. In the few existing relevant studies the young modulus was either found unaffected [19,21,23,29], or in some cases it was reported to decrease [20,23] depending mainly on the orientation of the grown CNTs onto the CF surface as well as the growth temperature. It should be noted at this point that, the CNT coated fiber is a "composite" on its own with both different diameter and strength. These differences have to be considered in the evaluation of the strength and the stiffness of the resulting hierarchical systems, for if they are neglected they definitely lead to overestimations in the calculated properties.

At the same time, a corollary of the hierarchical nature of such reinforcements is often demonstrated by various added functionalities. Gao et al. reported on the strain, humidity and temperature sensing ability of hierarchical glass fibers, coated with commercial oxidized CNTs by electrical measurements [30]. Tzounis et al. presented the thermoelectric response of single glass fibers coated with CNTs [31]. Furthermore, Raman spectroscopy has extensively been employed for stress or strain sensing of crystalline carbon micron and nano scaled reinforcements, whereby the inclusions act as sensing elements with sub-micron spatial resolution [32,33]. The basic principle underlying the employment of Raman spectroscopy for strain monitoring is the change in the frequency of distinct vibrational modes when an external load is applied, due to the anharmonicity of the molecular bonds [33]. Thus, a molecular displacement is translated to an actual strain or equally stress profile that in the case of a composite material, can describe its stress and strain state. This method can potentially be applied as a nondestructive evaluation technique for in field applications using modern portable spectrometers [34], or fiber optic based systems [35].

Raman sensing from commercial CNTs deposited onto glass or carbon fiber surfaces has been reported by Liu et al. who studied strain induced Raman shifts of hierarchical glass fibers coated with a silane coating containing dispersed single walled CNTs. The strain induced Raman shift exhibited a dependence on the coating thickness, with thicker coatings resulting in increased values, namely 16.6 cm^{-1}/% strain [36]. In a similar study, Jin et al. reported on the strain induced Raman sensing ability of high (5.8 cm^{-1}/GPa) and low modulus (4.8 cm^{-1}/GPa) CFs coated with silane containing single walled CNTs [37]. Both studies referred to the 2D graphitic vibrational mode, and to our knowledge are the only studies referring to hierarchical fibers. However, the strain induced Raman sensing ability of hierarchical reinforcements where the nano reinforcement is grown on the fiber surface, has not as yet been reported. This is the approach adopted in the current study, where the covalently bonded CNTs on the CF surface prove to provide an optimal synergy between the two scales.

More analytically, in this study, hierarchical CF-CNT reinforcements were produced using different CVD conditions. The relationship between the crystalline structure of the hierarchical CF-CNT, their reinforcing ability and their additional strain sensing functionality was demonstrated for the first time. The morphology and thermal stability of the CF-CNT reinforcements were evaluated by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). In terms of mechanical properties, the effect of the growth parameters on the stiffness and strength of the CF-CNT was assessed via Single Fiber Tensile tests. The dependence of fiber strength on length was also experimentally measured and represented in logarithmic plots. Additionally, the utilization of CF-CNT as reinforcing material in epoxy model composites was evaluated via Interfacial Shear Strength (IFSS) measurements. The resulting IFSS enhancements in all CF-CNT samples were further corroborated via SEM fractography. Raman spectroscopy was employed for both the qualitative and quantitative structural evaluation of the produced CNTs and the measurement of the strain induced Raman sensing ability of the CF-CNT as a function of the CVD growth conditions. Finally, the established correlation between the enhanced stiffness and Raman strain sensitivity demonstrated that the hierarchical concept developed in this study fully exploits the CNT potential in FRPs for the first time, via architectured scale interaction. In this way, hierarchical systems proved to be by far more efficient in exploiting the properties of the CNTs via an engineered interphase which was both enhancing the load bearing ability of the primary reinforcement and the stress transfer at the interface.

2. Experimental section

Materials: The M40 unsized high modulus PAN fibers (Torayca) with a tensile strength of 2.74 GPa, modulus of 392 GPa and failure strain 0.7%, as stated by the manufacturer, were used in this study. The fiber diameter was 6.6 μm as determined by density measurements. The matrix employed for the production of the fragmentation test specimens was the two part MY-750/HY-951 epoxy system (Huntsman), with a tensile strength of 75–90 MPa, an elongation at break of 3–4% and a modulus of 3.5–4.0 GPa.

2.1. Methods

Growth of CNTs on the CF surface via CVD: A FeCo bimetallic catalyst was used for the CNT growth in this study. The CNT growth process was conducted in a horizontal tubular furnace (Carbolite). Details on the catalyst preparation and the CVD procedure can be found elsewhere [25]. Acetylene was used as the gaseous hydrocarbon source for the CNT growth. Two different growth temperatures have been selected for CNT growth on CF tows, after a preliminary study on single CFs, 750 °C and 850 °C, for 10 min or 30 min in each temperature.

Microstructural and Chemical characterization of CNTs: Field-emission scanning electron microscopy (FE-SEM) was performed with an ESEM Quanta 250 FEG (FEI, The Netherlands) operating at an accelerating voltage of 3.0–5.0 kV. The fibers were placed on a double-sided copper adhesive tape to be stabilized and coated with a thin layer of platinum (5 nm) prior to the SEM analysis to avoid charging effects. FE-SEM was also used for the microstructure analysis of the cross sections of the fragmentation specimens. Additionally, the diameter distribution of the grown CNTs was measured from the acquired SEM images of a population of 60 CNTs for each growth condition. Transmission electron microscopy (TEM) with a HR-TEM 2100, Jeol Co was performed in order to measure the CNT diameters in specific samples. For the preparation of the samples for TEM investigations a quantity of CNT coated CFs were sonicated in acetone and then drop casted onto carbon coated copper grids (CF300-CV-UL). An accelerating voltage of 200 kV was used for the microscope operation. The thermal behavior of CF and CF-CNT hierarchical structures after CVD-growth were investigated by thermogravimetric analysis (TGA) using a Leco TGA701 instrument. Thermal scans were performed under oxygen flow from 30 °C to 800 °C with a heating rate of 10 °C/min. Raman spectra of the produced structures were recorded with a Labram HR – Horiba scientific system. The 514.5 nm line of an argon ion laser operating at 1.5 mW at the focal plane was employed for the Raman excitation. An optical microscope