Acta Materialia 162 (2019) 46–54

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

The formation of highly ordered graphitic interphase around embedded CNTs controls the mechanics of ultra-strong carbonized nanofibers

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ARTICLE INFO

Article history:
Received 30 May 2018
Received in revised form
18 September 2018
Accepted 20 September 2018
Available online 27 September 2018

Keywords:
SWNTs
Carbon nanofibers
Templating effect
Microstructure
Mechanical properties

ABSTRACT

Templating graphitization, *i.e.*, the transformation of certain polymers to highly-ordered graphitic (HOG) domains upon pyrolysis in the vicinity of graphitic nanomaterials, such as carbon nanotubes (CNTs), is known to be an effective approach to modify the microstructure of carbon nanofibers (CNFs). In this work, the microstructure of CNFs subjected to the templating effect of functionalized single-walled CNTs (f-SWNTs) and the effect of templating on mechanical properties of CNF/f-SWNTs hybrid nanofiber are studied. The CNF/f-SWNTs were fabricated via pyrolysis of electrospun polyacrylonitrile precursors with CNT inclusions. Prior to pyrolysis, the precursors were subjected to thermomechanical treatments, known as hot-drawing, to enhance chain and CNT alignment and packing. The study of the microstructure of the precursor and CNFs indicates the crucial role of precursor hot-drawing in enhancing the microstructure of the precursor and CNFs, leading to drastically enhanced templating effect, as evidenced from the thickness of the HOG that forms around CNTs. Mechanical tests on single nanofibers using custom-designed microdevices led to the realization that the templating effect of CNTs on CNFs, when properly implemented via precursor hot-drawing, can considerably increase the strength of CNFs. The average tensile strength and modulus of CNF/f-SWNTs in which HOG domains had clearly formed were measured to be 7.6 and 268 GPa, respectively, which are the highest value reported to date among similar types of materials. The existence and evolution of the HOG around CNTs inside CNFs and mechanical reinforcing of HOG were thoroughly discussed in conjunction with finite element models of building blocks of CNFs, alluding to the stress fields around HOG and CNTs in the CNF. The high-performance 1-D hybrid graphitic nanostructure developed here, CNF/f-SWNTs, can serve as an outstanding reinforcement material for weight sensitive applications.

1. Introduction

Carbon fibers (CFs) and their composite materials are widely used in weight sensitive applications due to their high specific mechanical performance [1,2]. Research and development of high performance carbon strands have received new thrust in the past several years to improve the mechanical properties of carbon fibers by modifying their microstructure, including developing novel precursor fabrication process [3], downsizing precursor fibers [4,5] and introducing functional nano-particles [6–8]. For instance, downsizing precursor polymer fiber from a few tens of micrometers (used to synthesize CFs) to hundreds of nanometers has been both theoretically [9] and experimentally [10–12] demonstrated to lead to carbon nanofibers (CNFs) with strength surpassing those of commercial CFs. These efforts often rely on electrospinning polyacrylonitrile (PAN) precursor nanofibers, followed by post-processing such as hot-drawing to induce chain alignment and carbonization [5,13]. Apart from remarkable mechanical properties [10], electrospun CNFs have also been shown to exhibit other properties which are highly sought for in developing multifunctional nanocomposites, such as high electrical conductivity [14–16], piezoresistivity [17–19] and thermal conductivity [20,21].

Recent studies have demonstrated that applying a small amount of highly graphitic nanomaterials, such as CNTs [6,22–25], graphene nanoribbon [26,27] and graphene oxide [28], into PAN

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https://doi.org/10.1016/j.actamat.2018.09.047
1359-6454/

precursor during electrospinning process may assist with the growth of the graphitic domains in CNFs. Due to strong interaction between CNTs surface and PAN chains, highly ordered polymer interphase with mechanical properties superior to bulk PAN forms around the surface of CNTs in the PAN/CNTs nanofiber [23,28–32]. This extended chain structure of PAN chains around CNTs can serve as a precursor for highly ordered graphitic (HOG) phase in CNFs [22,29,33]. In other words, the CNTs act as a template for the growth of HOG upon carbonization [33].

The regions of CNF outside HOG is often a combination of turbostratic domains and amorphous carbon matrix [11], similar to the microstructure of CNFs obtained from PAN-only precursors. The atomic order in HOG is often higher than turbostratic domains which are formed at the same carbonization temperature, and the defect density in HOG is reported to be comparable to that of turbostratic domains formed at much higher carbonization/graphitization temperature [22]. Thus, there have been efforts to develop hybrid CNFs with graphitic inclusions as a means to effectively improve the performance metrics of the obtained hybrid CNF, such as mechanical strength, or lower its fabrication cost without sacrificing performance through employing reduced carbonization process. However, these efforts are not conclusive yet. For instance, despite the measured increase in the average strength of CNFs from 2.44 GPa to 3.52 GPa by adding only 2 wt% graphene nanoribbons (GNRs), the addition of GNRs significantly increased the scatter in the measured strength values [27]. The variations in the measured strength values can partly be addressed by considering the pros and cons of the HOG on mechanics of CNFs. While the lower defect density of HOG can in principle translate into stronger CNFs, the elastic mismatch between the HOG and rest of the CNFs may induce complex local stress fields and promote failure. This is partly driven by the observation of protruded CNTs from the fractured surfaces of hybrid CNFs as a potential initiator of failure [22].

In this work, we have addressed the above ambivalence in the effect of templated graphitization and the formation of HOG on mechanics of CNFs through a combined nanoscale experimentation and continuum modeling. The templating effect was implemented via the inclusion of functionalized single-walled carbon nanotubes (f-SWNTs) into electrospun PAN precursor nanofibers. The evolution of the microstructures of electrospun PAN nanofibers and CNFs with f-SWNTs inclusions (respectively PAN/f-SWNTs and CNFs/f-SWNTs) was studied, demonstrating strong correlation between precursor microstructure and the microstructure of obtained CNF/f-SWNTs. The MEMS based nano-mechanical testing of individual CNF/f-SWNTs showed a considerable improvement in mechanical performances through engineering microstructure of precursor polymeric nanofiber. The obtained tensile strength and modulus of CNF/f-SWNTs are 7.6 ± 1.7 GPa and 268 ± 29 GPa, respectively, which are the highest value reported to date. Continuum models of hybrid CNFs were also developed to further shed light on the reinforcing effect of HOG interphase and the stress field around SWNTs in CNF. The results demonstrate the superior mechanical properties of HOG over the rest of CNF and its outstanding contribution to the overall mechanical properties improvement in CNF/f-SWNTs.

2. Experimental

2.1. Fabrication of hot-drawn CNF/f-SWNTs nanofiber

Ribbons of polyacrylonitrile (PAN) precursor nanofibers with functionalized single-walled carbon nanotubes (f-SWNTs) were fabricated via electrospinning on a rotary target as discussed in previous publication [23]. The precursor nanofibers were referred to as PAN/f-SWNTs in contrast to PAN nanofibers with no inclusions. Templated graphitization was pursued by adding f-SWNTs to precursor nanofibers. The f-SWNTs, from Carbon Solutions Inc., with length of ~1 μm, contained 1–3 atomic % carboxylic acid groups on the surface to facilitate the dispersion of CNTs within PAN nanofibers. To process CNF precursors, f-SWNTs were first dispersed in dimethylformamide (DMF) solvent (from Sigma–Aldrich) via ultrasonication for 4 h to achieve visually homogeneous solution. Then, PAN powder ($M_w = 150{,}000$ g/mol, from Sigma–Aldrich) was dissolved in f-SWNTs/DMF solution to obtain 10 wt% PAN/f-SWNTs/DMF solution. The concentration of f-SWNTs was controlled to be 0.5 wt% of PAN, which roughly corresponds to 1 wt% of CNTs in CNFs. Electrospinning was performed at a voltage and distance of 16 kV and 20 cm, and flow rate of polymer solution was set to ~0.5 ml/h to obtain a stable jet with a rotating target at ~5.7 m/s peak-up velocity. The PAN/f-SWNTs nanofiber ribbons then were drawn to $\lambda = 3$ (λ, hot-drawing ratio = final length/initial length of ribbon) by applying an engineering stress of ~19 MPa in an oven at a temperature of 135 °C to induce chain alignment [13]. The hot-drawn nanofiber ribbons were stabilized at 290 °C for 2 h in air with 5 MPa constraint stress. Carbonization of stabilized PAN/f-SWNTs nanofibers was carried out in tube furnace (MTI, GSL-1700x) at 1400 °C for 2 h under inert gas (N_2) environment. The carbonized PAN/f-SWNTs nanofibers were referred to as CNF/f-SWNTs. In addition, CNFs without CNTs and/or without precursor hot-drawing were synthesized as benchmarks.

2.2. Microstructural characterization and mechanical testing of nanofibers

FEI Quanta 600 FE-SEM was used to study the surface of PAN nanofibers and CNFs. The semi-crystalline structure of PAN nanofibers and CNFs were studied by collecting X-ray diffraction spectra of nanofiber ribbons via GADDS BRUKER-AXS MWPC 3-thircle X-ray Diffractometer (CuKα, wavelength of 0.154 nm). Scherrer's equation ($K = 0.89$) was used to estimate the crystallite size within PAN and CNFs nanofiber [34]. The PAN nanofiber crystallinity was calculated by dividing the area under deconvoluted crystalline peaks by the total area, including both crystalline and amorphous peaks by using Lorentzian fitting in Origin 9.0 [35]. The PAN crystallite orientation within the nanofiber was obtained based on the wide-angle X-ray diffraction (WAXD) pattern and azimuthal scan of the diffraction peak at $2\theta \sim 17°$ [24]. Graphitic crystallite orientation of CNFs was obtained from the azimuthal scan at $2\theta = 25°$ [3]. Herman's orientation factor was also calculated as described elsewhere [36]. Horiba Jobin-Yvon LabRam Raman confocal microscope with a He–Ne laser (633 nm) was used to analyze the graphitic structure of CNFs. The width (L_a) of the graphitic crystallites (along their basal planes) in CNFs was calculated based on the deconvoluted D- and G-peak area intensity ratio (I_D/I_G) [37,38]. The measurements were repeated a minimum of three times to ensure repeatability, and the average value of the peak ratios was used to calculate the crystallite width. FEI Tecnai G2 F20 transmission electron microscope (TEM) was used to characterize the graphitic structure of CNFs.

MEMS-based nano-mechanical testing platform was used to measure the mechanical performance of individual CNF/f-SWNTs in tension. The MEMS device used in this work and the whole testing process were thoroughly discussed in our previous work [13]. A minimum of six tests were performed for each fabrication condition and the average mechanical properties and standard deviations were reported.

3. Results and discussion

As shown in our previous work [23], adding pristine (*i.e.*,