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The effect of embedded carbon nanotubes on the morphological evolution during the carbonization of poly(acrylonitrile) nanofibers

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Abstract

Hybrid nanofibers with different concentrations of multi-walled carbon nanotubes (MWCNTs) in polycrylonitrile (PAN) were fabricated using the electrospinning technique and subsequently carbonized. The morphology of the fabricated carbon nanofibers (CNFs) at different stages of the carbonization process was characterized by transmission electron microscopy and Raman spectroscopy. The polycrystalline nature of the CNFs was shown, with increasing content of ordered crystalline regions having enhanced orientation with increasing content of MWCNTs. The results indicate that embedded MWCNTs in the PAN nanofibers nucleate the growth of carbon crystals during PAN carbonization.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon fibers (CFs) are one of the most successful carbon products to be commercialized in the past years, due to their high strength and stiffness, combined with their light weight [1]. Almost all CFs are produced from precursor fibers. Polycrylonitrile (PAN) is a commonly used precursor fiber. The initial fiber formation step has a strong influence on the properties of the final CF morphology and properties. The next step is stabilization of the fiber, which is done in most commercial processes by exposure to air at temperatures ranging from 230 to 280 °C. Tension is applied during this step to limit relaxation of the polymer structure. Finally, the precursor fibers are carbonized at 1200–3000 °C. The mechanism of CF formation is a complex process for which various reaction schemes have been proposed [1, 2].

Past studies have shown the fibrillar structure of PAN-based CF which follows from the structure of the precursor fiber [1]. Furthermore, distinct skin–core structure was found in these fibers, whereby the crystallinity at the fiber core is much lower than near its surface. This induces differences in the mechanical, thermal and other properties of those regions [3]. Precursor fibers can be fabricated by the electrospinning (ES) technique, in which a high difference of electrical potential is applied between a polymer solution droplet and a collector, resulting in an electrohydrodynamic instability that produces a jet stream in the form of a Taylor cone [4, 5]. The strong elongation forces that occur during this process result in the formation of thin polymer nanofibers that are expected to exhibit high degrees of molecular orientation and crystallinity. As a result, CFs derived from electrospun precursor nanofibers may exhibit desirable elastic strength and modulus [6]. As the diameter of the electrospun fibers is in the nanometer range, ES carbon fiber mats should have a large surface area compared to traditional CF. Thus, it is expected to elevate the rate of adsorption/desorption, which is a desirable property in applications such as electrodes for double-layer supercapacitors [7–10].

Carbon nanotubes (CNTs), discovered by Iijima [11], are an interesting class of materials with unique properties,
such as high tensile modulus, good heat and electrical conduction, unique optical and electronic properties, etc [12]. Various CNTs containing nanocomposite materials have been prepared with the hope of translating their superior properties to macroscale structures [13, 14]. CNTs have been incorporated into electrosyn polymer nanofibers [15–17] and were shown to reinforce their mechanical properties as well as enhance thermal stability, electric conductivity and other functional properties [18–22]. Incorporation of CNT into PAN fibers by extrusion and electrosynspinning has shown significant interactions between PAN and CNT, which lead to higher orientation of PAN chains during the heating process [23, 24]. Previous studies on carbonized hybrid PAN/CNT films and gel spun fibers have shown the increment of PAN crystallinity, and corresponding improvement of tensile strength and modulus [20, 22]. Chae et al [25] showed that the degree of crystallinity and crystal orientation of carbonized gel spun PAN/single-walled CNT hybrid fibers were higher than those of the pure PAN fibers. Electrosyn PAN nanocomposite fibers containing multi- and single-walled CNTs (MWCNTs/SWCNTs) were also prepared [26, 27]. Incorporation of SWCNTs resulted in an enhanced modulus of the carbonized nanofibers even beyond theoretical predictions based on the rule of mixtures [27].

Our hypothesis is that embedded CNTs in electrosyn hybrid PAN/CNT nanofibers may serve as nucleating centers in the PAN carbonization process, so as to provide for a more ordered graphitic texture with enhanced crystallinity in the regions adjacent to the CNT surface. Furthermore, as the embedded CNTs are usually well oriented along the fiber axis in electrosyn nanofibers, we expect this process to result in enhanced orientation and crystallinity in the fabricated carbon nanofibers (CNFs). In this work hybrid nanofibers with different concentrations of MWCNTs in PAN were fabricated by ES and subsequently carbonized. Morphology characterization of the CNFs at different stages of the carbonization process was done by transmission electron microscopy (TEM) and Raman spectroscopy. Enhanced crystallinity and orientation is expected to improve the properties and functions of the fabricated carbon nanofibers.

2. Experimental details

Multi-walled carbon nanotubes (MWCNTs) were purchased from Nanostructured & Amorphous Materials Inc. (95%, OD 20–30 nm, length 0.5–200 μm). Poly(acrylonitrile) (PAN, \(M_w \sim 150,000\)) was received from Scientific Polymer Products, Inc. The solvent used for dissolving PAN and PAN/MWCNTs dispersion was \(N, N\)-dimethylformamide (DMF, AR, Gadot). MWCNTs were added to DMF in various concentrations and sonicated for 30 min in a 43 kHz Delta D2000 sonicator to form a black slurry. PAN was dissolved in DMF (9% w/w) and this solution was added to the MWCNTs slurry in a weight ratio of 1:1. The fluid was magnetically stirred for 15 min and then further sonicated for 9–17 h depending on the MWCNT concentration. In this work the CNTs were of relatively higher purity and length; therefore a longer sonication time was need to obtain good dispersion, as compared to previous work [28, 29]. The resulting dispersion was found to be homogeneous, exhibiting a dark ink-like appearance, and stable for several weeks.

The electrosynspinning (ES) process was conducted at room temperature using a voltage of 12 kV applied to a syringe needle (0.5 mm in inner diameter) situated 15 cm above a rotating grounded disc (the collector) with a linear speed of 20 m s\(^{-1}\) (~1000 rpm). These conditions were found to be optimal for achieving suitable nanofibers of various diameters [28, 29]. The concentration of MWCNTs in PAN nanofibers after the ES was 0, 2.5, 5 and 25% (w/w). The hybrid precursor nanofibers were stabilized and carbonized in a horizontal quartz tubular oven, allowing heating up to 1200 °C. The stabilization process was carried out in air at 250 °C. The temperature was gradually raised to this temperature at 5 °C min\(^{-1}\) and then maintained constant for an hour. The carbonization process was done in nitrogen atmosphere. The heating rate was 3 °C min\(^{-1}\). Two different types of samples were prepared by different carbonization procedures: the first type was carbonized for 1 h at 750 °C and the second was heated to 750 °C, held for 1 h, and then further heated to 1100 °C. After the highest temperature was maintained for 1 h, the heating was turned off and the sample was cooled overnight in a nitrogen atmosphere. We note that the MWCNT concentration in the carbonized nanofibers was higher than in the precursor fibers due to contraction of PAN during its transforming to carbon. It is thus difficult to ascertain the CNT content in the carbonized hybrids. In subsequent discussions the CNT concentration in all nanofibers is defined by their precursor concentration.

Imaging the precursor and carbonized fibers was done by TEM using a Philips CM120 or FEI Tecnai T12 G2 TEM, with low electron dose at an acceleration voltage of 120 kV. Images were recorded with a Gatan MultiScan 791 CCD camera, using the Gatan DigitalMicrograph 3.1 software package. Lattice imaging of 5% w/w MWCNT hybrid nanofibers was done by a Tecnai F20 G2 high-resolution TEM (HR-TEM) with an acceleration voltage of 200 kV. Images were recorded with a Gatan MultiScan 794 YAG CCD camera. Characterization of the dispersion quality and the interaction between PAN and MWCNTs was done by the cryo-TEM technique. Samples were prepared by rapid vitrification of a thin liquid film over a holey carbon film on a copper TEM grid using liquid nitrogen or supercooled liquid ethane in a controlled-environment vitrification system (CEVS) [30]. During this process DMF was dissolved by the liquid ethane, and thus only PAN and MWCNTs were observed. The TEM imaging is done at a temperature of about −170 °C.

Fiber samples for TEM and HR-TEM imaging were fabricated by two different methods. Precursor fibers were directly deposited on the copper grid with a holey carbon film during the ES process. For this purpose a TEM grid was glued to a standard aluminum stub which was attached to the ES rotating disc collector. The carbonized nanofibers were observed by putting a small piece of a nanofibrous mat into ethanol and sonicating it for 5 min, until splitting into individual fibers has occurred. Subsequently, a drop of this nanofiber dispersion was placed on the TEM grid and ethanol was evaporated.
Morphological investigation of different regions within the nanofibers was done by fast Fourier transform (FFT) of areas of interest. The plane orientation coefficient \( k_{(hkl)} \) was calculated for the FFT images according to [31]

\[
k_{(hkl)} = \frac{90^\circ - \delta_{H(hkl)}}{90^\circ}
\]

where \( \delta_{H(hkl)} \) is the half-width at half-height of the diffraction peak. As the FFT is highly affected by objective aberration during TEM imaging, it is difficult to compare the orientation coefficients calculated from different images. Thus, the orientation coefficients of different regions were normalized by that of the MWCNT walls which showed a maximal level in all FFT images, termed the relative orientation coefficient \( k'_{(hkl)} \).

Raman spectroscopy is a useful technique for characterization of carbon morphology [6, 32–36]. In particular, relevant information can be obtained from the two first-order Raman peaks. The G line, at about 1580 cm\(^{-1}\), is associated with sp\(^2\) vibrations of a perfect graphite crystal. Its position shifts up to 1600 cm\(^{-1}\) for amorphous carbon. The D line, at about 1350 cm\(^{-1}\), is associated with vibrations at the crystal ‘edges’. The ratio between the D and G peak intensities is proportional to the sp\(^2\) grain size or the graphite crystal size for polycrystalline graphite \( L_a \). Simultaneously, the G peak width increases with crystal disorder [34]. The crystal size of polycrystalline graphite can be calculated according to [36]

\[
R = \frac{I_D}{I_G} = \frac{C(\lambda)}{L_a}
\]

where \( I_D \) and \( I_G \) are the intensities of the D and G peaks, respectively, and \( C \) is a constant which depends on the laser wavelength. It is important to note that, for amorphous carbon, \( L_a \) is proportional to \( R^{1/2} \) [34]. Thus the morphology of the fiber needs to be determined first from the G peak position, and then the crystal or sp\(^2\) grain size can be determined from the suitable expression.

Raman spectra of carbonized nanofibers were measured by a Dior Raman microspectrometer using Ar laser illumination with 514.5 nm excitation and about 1 \( \mu m \) diameter focus spot. The crystal size was determined according to equation (2), with \( C(514.5 \text{ nm}) \) equal to 4.4 nm. \( I_D \) and \( I_G \) were determined as areas of the D and G peaks, respectively, which were calculated by a Lorentzian fitting using the Origin 7.5 software package.

3. Results and discussion

The first step of hybrid nanofiber fabrication was the preparation of stable and spinnable MWCNT dispersions in the PAN/DMF solution. The quality of the dispersion was evaluated by the cryo-TEM technique [30] in which a thin film of the dispersion is vitrified in liquid nitrogen or ethane. The example of a cryo-TEM image of a dispersion vitrified with liquid nitrogen (figure 1) demonstrates good separation between the CNTs within the PAN/DMF solution. It was previously shown [15, 28, 37] that cryo-TEM is a very useful tool for dispersion characterization. The difference between individually dispersed nanotubes and aggregates can be easily seen. Note that individual PAN molecules or any hint of their location cannot be imaged in the vitrified solution due to negligible contrast between DMF and PAN. In other cases, where significant polymer/solvent contrast exists, regions of polymer-rich solutions may be imaged [38, 39]. Figure 2(A) demonstrates cryo-TEM imaging of MWCNT
dispersion in PAN/DMF where the DMF has been partially evaporated during sample preparation. Regions in which PAN is aggregated around the MWCNTs can be easily observed in this image. When vitrification was carried out in supercooled liquid ethane, it dissolved the solidified DMF, leaving behind the MWCNTs which appear to be completely covered by PAN, as seen in figure 2(B). This may be due to strong π–π interactions between the CNT surface and nitrile groups of PAN [23, 24]. These images confirm the good quality of the dispersion, as it is readily seen that the CNTs are not aggregated one to the other but are separated by PAN.

Precursor PAN and PAN/MWCNT nanofibers were then fabricated from the relevant solutions or dispersions by ES. It is assumed that the structure of the CNTs (diameter, irregularities along the length, etc) and their deposition within the polymer nanofibers have a strong influence on the ultimate properties of the carbonized fibers. Figures 3(A) and (B) show nanofibers containing individual MWCNTs which appear to
One of the goals of this work was to determine the morphological evolution during stabilization and carbonization of hybrid nanofibers. An HR-TEM image of PAN/MWCNT nanofibers, containing 5% nanotubes, after the stabilization process is shown in figure 4. It shows the multilayer wall of the carbon nanotube and some initial ordering in the ‘shell’ region near the nanofiber surface, with a relative orientation coefficient \( k'_{(hkl)} \) of about 0.83. This demonstrates the well-known distinction between core and shell regions in PAN nanofibers [3].

Figures 5–7 present images of different hybrid nanofibers after a carbonization process at 750°C. Figure 5 shows an image of a carbonized hybrid nanofiber with 5% MWCNT, but in a region which does not contain CNTs. The same distinction between core and shell regions can be seen with
a relative orientation coefficient of 0.44 and 0.82, respectively. (The relative orientation was calculated based on the MWCNT wall shown in figure 6 that was taken from the same fibers at identical conditions.) These results confirm that the shell regions nearly reach their final order and orientation already by the stabilization process. Figure 6 presents an image of a nanofiber similar to that shown in figure 5, showing the embedded MWCNT. It indicates that carbonized PAN in a core region adjacent to the MWCNT achieves a degree of order and orientation similar to that in the shell region ($k_{(hkl)}' = 0.79$).

Whereas hybrid nanofibers with 5% MWCNTs have many regions which do not contain an embedded nanotube within the nanofiber cross section, those made with 25% MWCNTs exhibit nearly complete coverage of the nanofiber length with at least one nanotube in the cross section, and even many
regions having two or three CNTs within the nanofiber cross section (figure 7). The orientation coefficient of the carbonized PAN in these fibers was found to be about 0.86. Due to the absence of fiber regions without CNTs the total orientation in these nanofibers is higher than in nanofibers of lower CNT concentration.

Previous studies have shown that full pyrolysis of PAN is not achieved at a temperature of 750°C [1, 2], so nanofibers...
were also carbonized at 1100°C. Figure 8 depicts a region of PAN/25% MWCNT hybrid nanofiber carbonized at 1100°C. This image exhibits a nanofiber with several MWCNTs inside it (the borders of CNTs are marked by white lines). The relative orientation coefficient of carbonized PAN in this specific region was found to be about 1. This indicates that carbonization of PAN at 1100°C can achieve order comparable to the MWCNT wall when in its vicinity.

Figure 9 exhibits the Raman spectra of pure and hybrid PAN nanofibers carbonized at 750°C. The evaluated parameters were determined using spectra taken at three different positions in the same fiber mat. Figure 10(A) shows that the G peak position is observed between 1575 and 1586 cm\(^{-1}\) with maximum deviation of about 2 cm\(^{-1}\) (calculated from the standard deviation of the different measurements), indicating that the morphology of the nanofibers is polycrystalline and far from being amorphous. The calculated crystal sizes, obtained according to equation (2), are presented in figure 10(C) for different MWCNT concentrations. It can be seen that the structure of the fibers was found to be more crystalline the higher the MWCNT content was. The width of the G peak (figure 10(B)) decreases with increasing CNT concentration, and the dimension of the ordered crystalline regions increases, as estimated from the \(I_D/I_G\) peak intensity ratio, corroborating this observation.

The measured Raman spectra reflect both the carbonized PAN as well as the embedded MWCNTs. Thus evaluation of enhanced crystal size and orientation with increasing MWCNT content should consider that it may be due to the effect of the CNTs themselves. The contribution of CNTs to the overall spectrum cannot be determined exactly, as the actual CNT concentration in the carbonized fibers is not known precisely. We therefore compare the ratio of the apparent crystal dimensions estimated after carbonization at 1100 and 750°C was found to be about 1.3 for pure PAN, and about 2 for PAN/25% MWCNT hybrid CNFs. This indicates the enhanced growth of graphitic crystals in carbonized PAN due to the presence of embedded CNTs.

4. Conclusions

Hybrid PAN/MWCNT nanofibers were fabricated by electrospinning and subsequently carbonized. TEM images and Raman spectra show the polycrystalline nature of the fabricated CNFs and indicate increasing content of ordered crystalline regions having enhanced orientation with increasing CNT content. The observations show that regions in the CNFs that do not contain CNTs exhibit poor crystallinity, whereas CNTs embedded in the PAN nanofibers nucleate the growth of carbon crystals during PAN carbonization.

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