High Performance Carbon Fibers from Very High Molecular Weight Polyacrylonitrile Precursors

E. Ashley Morris^{a,}, Matthew C. Weisenberger^a, Mohamed G. Abdallah^b, Frederic Vautard^b, Hippolyte Grappe^b, Soydan Ozcan^b, Felix L. Paulauskas^b, Cliff Eberle^b, Dave Jackson^b, Sue J. Mecham^c, Amit K. Naskar^{b,*}*

Dedicated to the memory of Professor James E. McGrath

^a Center for Applied Energy Research, University of Kentucky, Lexington, KY, 40511, USA

^b Carbon & Composites Group, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^c Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA, USA

Abstract

Carbon fibers are unique reinforcing agents for lightweight composite materials due to their outstanding mechanical properties and low density. Current technologies are capable of producing carbon fibers with 90-95% of the modulus of perfect graphite (~1025 GPa). However, these same carbon fibers possess less than 10% of the theoretical carbon fiber strength, estimated to be about 100 GPa. Traditionally, attempts to increase carbon fiber rigidity above a certain level results in lower breaking strength. Therefore, to develop advanced carbon fibers with both very high strength and modulus demands a new manufacturing methodology. Here, we report a method of manufacturing moderate strength, very high modulus carbon fibers from a very high molecular weight (VHMW) polyacrylonitrile (PAN) precursor without the use of nanomaterial additives such as nucleating or structure-templating agents, as have been used by others.

*Corresponding authors. Email: ashley.morris@uky.edu (E.A. Morris), naskarak@ornl.gov (A.K. Naskar).

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1. Introduction

Polyacrylonitrile (PAN) precursor derived carbon fibers consume 90% of the carbon fiber market due to their combination of strength and modulus properties [1]. Precursors for commercial carbon fibers are typically produced from PAN copolymers using a solution spinning process [2]. Following polymer solution extrusion and precursor filament generation, thermal conversion of the precursor through thermo-oxidative crosslinking, followed by carbonization in an inert atmosphere, is completed [3]. Over the last 40 years, the performance of carbon fiber has improved incrementally; intermediate modulus (275-310 MPa) fiber and high strength fibers (>5 GPa) were produced based on improvements in precursor quality, carbon fiber processing conditions, and quality control improvement in operational processing parameters [1]. Indeed, the quality of the precursor fibers has a direct effect on the quality of the resulting carbon fibers [4-6]. In this work, our objective was to improve the carbon fiber performance significantly by utilizing very high molecular weight (VHMW) polymer to produce high quality precursors, followed by deployment of an appropriate carbonization protocol. In this case, VHMW polymer was hypothesized to form highly oriented, small diameter precursor filaments through appreciable extensibility of the high molecular weight precursor and better stabilized and less disordered core structure in the precursor and carbonized filaments, respectively.

2. Experimental

2.1 Polymer synthesis and precursor fiber spinning

Initial formulation of a VHMW copolymer of acrylonitrile and methyl acrylate was achieved on a laboratory scale using emulsion polymerization [7]. Copolymers of weight average molecular weight greater than 1,700,000 g/mole were synthesized, with polydispersity of 1.7. Here, collaboration with a commercial polymer producer allowed scale up of the previous laboratory scale to pilot scale, and subsequently produced multiple kilogram batches.

Precursor fibers were spun utilizing the techniques and equipment described in an earlier report [7].

2.2 SEM imaging of precursor fibers

Imaging of the precursor fiber's surface and cross section morphology was done using a Hitachi S-4800 field emission scanning electron microscope (SEM) with an acceleration voltage of 5 kV. Samples were sputter coated with gold for 120 seconds using a Hummer 6.2 Sputter System. Samples were prepared for imaging of the cross-section by cutting the fiber bundle using surgical scissors after exposure to liquid nitrogen. The resulting specimens were placed vertically in the SEM sample holder. Other samples were fixed on the sample holder with conductive carbon tape.

2.3 Tensile testing of precursor fibers

The tensile properties of precursor fibers were measured by bonding single filaments to 40 mm gauge length aperture cards using Easypoxy K-20. Following curing of the epoxy, the aperture card was mounted in the miniature tensile grips of a MTS Systems Q10 machine fitted with a 150 g load cell. The sides of the aperture card were then cut, leaving the filament intact. The crosshead speed was set at 5 mm/min. Twenty individual filament specimens were tested for each tensile sample.

2.4 Thermal analysis of precursor fiber

A DSC Q2000 (TA Instruments) thermal analyzer was used to perform DSC studies with about 4 mg of precursor fibers at a heating rate of 20 °C/min to 450 °C under an air atmosphere. A TGA Q500 (TA Instruments) thermal analyzer was used to perform TGA studies with about 10 mg of precursors fibers at a heating rate of 20 °C/min to 450 °C under an air atmosphere.

2.5 Thermal conversion

A detailed thermal analysis was carried out to determine fiber stabilization and carbonization protocol and the samples were rendered thermoset using 4-zone oxidation ovens at temperatures in the typical oxidation temperature range (220 – 300 °C) [1, 8]. Stabilized fibers were carbonized in two steps for initial pyrolysis (600 – 800 °C) and subsequent structure development through the formation of graphitic crystalline structures (1000 – 1500 °C).

2.6 Tensile testing of carbon fibers

The tensile strength of single carbon fibers was measured according to ASTM D3379-75(1989)e1 (since withdrawn) – “Standard Test Method for Tensile Strength and Young’s Modulus for High-Modulus Single-Filament Materials”. The fiber was mounted on a slotted testing tab with the fiber aligned along the center of the tab. The fiber was secured at opposite ends of the slot by a cyano-acrylate based adhesive. Special care was taken so that the fiber was not misaligned and not twisted, as recommended by the ASTM standards. After the adhesive was cured, the ends of the tab were grasped in the grips of a MTS Alliance RT/5 twin screw load frame controlled by the software Testworks 4 and equipped with a 5 N load cell. The sides of the aperture card were then burned away, leaving the filament intact. Per type of fiber, 30 samples were tested. System compliance was known to be 99.96%. The diameter of each fiber type was determined by comparison of the linear fiber density and bulk density (via helium pycnometry). The Young's modulus was evaluated from the initial linear proportion of the stress-strain curve, but this procedure should be taken with caution due to the non-linearity of the stress-strain curve of carbon fibers. All carbon fiber tensile properties reported in this manuscript, including those for commercial carbon fibers, were tested according to this method.

2.7 Wide-angle x-ray diffraction

Wide-angle x-ray diffraction (WAXD) was used to measure the crystalline parameters of the fiber microstructure. These parameters include (a) the d-spacing between the graphitic layers; (b) the so-called “stack height” of the graphitic layers, reported as L_c ; (c) the crystal size in the direction parallel to the graphene planes, reported as L_a ; and (d) the orientation of the graphitic layers relative to the fiber axis, reported as the misorientation angle, ϕ . The orientation of the graphene planes relative to the fiber axis was determined directly from the azimuthal distribution of the (002) reflection. Since the distribution is nearly Gaussian in shape, the orientation is described here in terms of the FWHM of the (002) reflection in the azimuthal direction in degrees. This quantity is twice the so-called “misorientation angle,” ϕ , that gives the approximate average inclination of the graphene planes with respect to the fiber axis or the angle relative to the fiber axis within which about 50% of the graphene planes lie [9]. All measurements were made with a fully automated Panalytical Materials Research Diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in transmission geometry. The sample consisted of a parallel array of fibers. The breadth of the (002) reflection was measured on the equator (perpendicular to the fibers), while the breadth of the (100) reflection was measured in the meridian direction (parallel to the fibers).

2.8 Transmission electron microscopy

Transmission electron microscopy (TEM) observations were conducted on a Hitachi HF3300 TEM/STEM operating at 200 kV. Transverse cross-sections of carbon fibers were prepared using a focused ion beam (FIB) with a Hitachi NB5000 FIB-SEM instrument using standard in situ lift-out techniques. EPON G2 epoxy resin was used to attach the carbon fibers to the TEM omniprobe grids. A protective layer of electron-beam-deposited tungsten was centered on the fiber axis. Sections were milled with a 40 keV ion beam to a thickness of about 100–200 nm. The specimens were further thinned with a 5 keV ion beam, which was followed by

multiple polishing with a 2 keV ion beam. Selected area diffraction patterns (SADP) were taken and orientation angles measured from azimuthal full-width at half maximum angles.

2.9 Small-angle x-ray scattering

For small-angle x-ray scattering (SAXS) measurements, samples were made from randomly oriented chopped and crushed fibers. The pore-size parameters of a high modulus fiber are not affected when it is ground into a powder. The SAXS measurements were performed by use of a three-pinhole system. Copper K α radiation was provided by a double focusing mirror, and the patterns were recorded using a two-dimensional wire detector. Two sample-to-detector distances (1.5 m and 0.5 m) allowed the measurements to be performed over a scattering vector range ($q = 4\pi\sin\theta/\lambda$) of 0.01 to 0.45 Å⁻¹. The two-dimensional patterns were corrected for flat field errors and scattering from the sample holder. In the case of the powder patterns, the two-dimensional data were integrated azimuthally to obtain a one-dimensional plot of intensity versus the scattering vector, q , and the intensity was converted to absolute units (cm⁻¹) by use of previously calibrated standards made of polyethylene and glassy carbon. The data were analyzed with Irena software.

Pore size distribution results were obtained from the maximum entropy method. This method was developed for Statistical Analysis Software (SAS) by Potton et al. [10, 11] and further elaborated by Jemian et al [12]. This method compares the M measured intensities, $I(q_j)$, on the SAXS curve to M intensities, $y(q_j)$, calculated from a distribution of scattering particles of given shape and characteristic dimension D_i distributed among N different bins of width ΔD_i

$$y(q_j) = \sum_{i=1}^N G(q_j, D_i) x_T(D_i) \Delta D_i, \quad j=1, 2, \dots, M \quad (1)$$

Here, $G(q_j, D_i)$ is the scattering function of a single particle of characteristic dimension D_i at scattering vector q_j and $x_T(D)$ is the distribution function. The calculated and experimental data are compared using the χ^2 statistic.

$$\chi^2 = \sum_{j=1}^M \left(\frac{I(q_j) - y(q_j)}{\sigma_j} \right)^2 \quad (2)$$

where σ_j is the standard deviation of the measured intensity. The values of $y(q_j)$ are adjusted by varying the distribution until χ^2 is equal to M the number of intensity measurements subject to the constraint that the configurational entropy of the distribution function, $x_T(D)$, be maximized. The configurational entropy is given by

$$S = - \sum_{i=1}^N [x_T(D_i) \Delta D_i] \log \left[\frac{x_T(D_i) \Delta D_i}{b} \right], \quad (3)$$

where b is a small constant. The principle advantages of this method are the avoidance of fitting to preconceived empirical models and guaranteed positivity of the solution everywhere in spite of statistical noise in the data. The final fit returns various measures of the characteristic dimension, the volume fraction of scatters, the total number of scatters, and their surface area. In this case, rational solutions could be obtained for the distribution of voids in carbon fibers by assuming an elongated spheroid shape with aspect ratio of order 5. Other potential shapes were tried such as rods and disks, but with less success.

2.10 SEM imaging of carbon fiber surface morphology

A Jeol 6500 Field Emission Scanning Electron Microscope (FE-SEM) was used with an acceleration voltage of 5 kV and an emission current of 60 μ A in secondary electron mode. All samples were fixed on the sample holder with conductive carbon tape.

3. Results and Discussion

3.1 Polymer scale-up and resulting precursor fiber

Scaled-up batches of VHMW polymers produced by a commercial polymer supplier showed some variation between batches. In some cases a bimodal molecular weight distribution was obtained, with a high fraction of VHMW components. The resulting 6.5 wt.% solution of VHMW PAN polymer in N,N-dimethylacetamide (DMAc) solvent produced a very high

viscosity solution (viscosity of 369 Pa.s at 1 s^{-1} shear rate and $25 \text{ }^{\circ}\text{C}$) which could not be spun into fiber form. VHMW PAN with a relatively broader molecular weight distribution that resulted in solutions with 125 – 232 Pa.s viscosity under identical conditions could be processed using the hybrid dry-jet gel spinning technique described by Morris *et al* [7]. Successful production of hundreds of meters of 333-count continuous tow of VHMW PAN was accomplished. Precursor fibers with extraordinary tensile properties, averaging $826 \pm 129 \text{ MPa}$ in strength and $16.5 \pm 3.4 \text{ GPa}$ in elastic modulus, with small filament diameters ($5.3 \pm 0.5 \text{ }\mu\text{m}$), were produced ($N \geq 230$) (typical commercial PAN precursors are generally no less than $6.3 \text{ }\mu\text{m}$ in diameter, with a tensile strength no greater than 690 MPa) [7]. These results proved the effectiveness of scaled up production of VHMW polymer from that completed in previous work [7]. Thus, successful synthesis and spinning of VHMW precursor enabled a significant improvement in precursor fiber properties. A representative spool and photomicrograph of as-spun fibers are shown in Fig. 1. Although the fibers appeared smooth, occasional surface defects were observed. This was attributed to low inter-filament spacing of the spinnerette, which led to occasional fiber fusion in the coagulation bath.

Fig. 1 - (Left) A spool of more than 500 m of continuous, 333 filament count tow of VHMW precursor fiber. (Right) A scanning electron micrograph of VHMW precursor fibers, showing surface defects due to fiber fusion.

3.2 Thermal oxidation

Thermal conversion of the VHMW PAN fibers was completed despite the small amount of surface defects present on the precursor fiber. During the oxidative stabilization step for PAN fibers, heat is evolved due to an exothermic reaction. The onset temperature of this reaction for our VHMW precursor, determined by differential scanning calorimetry data, was significantly higher ($\Delta T > 25\text{ }^{\circ}\text{C}$) than that of other intermediate modulus high strength precursor fibers (Fig. 2). VHMW PAN polymer chains with few end group fractions offer less defect density (the occurrence of local disturbances to the perfect order of the crystal) and significant impermeability to air. Thus, the VHMW precursor requires a higher temperature for the oxidative reaction to initiate [13]. Similar results were found by Lin, et al [14].

Fig. 2 - DSC performed in air at 20 °C/min. TGA performed in air at 20 °C/min.

3.3 Carbonized fiber tensile properties

Carbonized filaments exhibited 4.3 ± 1.0 GPa tensile strength, 361 ± 45 GPa elastic modulus, and 0.94 ± 0.24 % ultimate elongation ($N = 16$). Thus, these filaments exhibit a significantly high modulus (compared to the single filament tensile tested commercial carbon fibers in Table 1) while retaining high tensile strength. Compared to commercial carbon fibers, which typically have $5 - 7$ μm filament diameter, our processed carbon fibers from VHMW PAN exhibit very small filament diameter ($2.2 - 2.8$ μm). As stated previously, VHMW polymers enabled the production of small diameter precursor filaments through a reduced solids content in the dope and increased extensibility [7]. Here, it is hypothesized that the small diameters of these filaments allowed formation of homogeneous microstructure across the diameter in the resulting carbon fibers.

Table 1. Single filament tensile properties of commercial carbon fiber vs. experimental carbon fiber from VHMW PAN.

Carbon fiber	Tensile modulus (GPa)	Tensile strength (MPa)
Toray T700	220	4848
Hexcel IM7	259	5325
Toray T1000G	287	7623
VHMW PAN-based CF	345	4300

The low tensile strength of the VHMW PAN-based carbon fiber shown in Table 1 is likely due to surface defects. Numerous surface defects (pits) of 100-700 nm size resulting from inter-filament fusion during the spinning of the precursor were evident (Fig. 3). It is known that surface defects negatively influence the value of the tensile strength [15]. Therefore, increasing the inter-filament spacing of the spinnerette during precursor spinning to prevent fiber fusion would likely produce precursors and carbon fibers with even higher tensile strength utilizing the same processing procedure described here.

Fig. 3 - SEM images of surface defects found on the carbon fibers made with VHMW precursors.

3.4 Carbon fiber skin-core structure

Skin-core structure is commonly seen in carbon fibers, as reported in literature [16]. The commercial carbon fiber (T700) possesses the typical skin/core structure that exists in carbon fibers [17]. The skin and core measure about 2.0 μm and 3.0 μm , respectively, for an overall fiber diameter of about 7 μm . This skin-core structure is the result of an oxygen diffusion gradient occurring in the precursor fiber during the stabilization step [18, 19]. The carbon structure in the skin region is usually more ordered, with larger crystallites that have better orientation [20-22]. It was reported that with optimal oxidation conditions (that cannot be always compatible with industrial practice, like a time of oxidation of 10 hours for instance), the skin/core structure of carbon fibers disappeared and that the tensile strength significantly increased [17]. However, no modulus values were reported. It is expected that with a disappearance of the core, the resulting fiber will consist primarily of the more ordered crystallites that comprise the skin, therefore resulting in a higher modulus fiber. Fig. 4 shows the transmission electron micrographs and selected area diffraction patterns of a longitudinal section of T700 fiber with skin/core structure. The area diffraction patterns show the visual orientation angles to be 40° and 54° for the skin and core, respectively, indicating the presence of higher ordered carbon in the skin. This implies that in the T700 fiber with skin/core structure, the c-axis has higher degree of alignment in the skin ($\pm 20^\circ$), compared to the core ($\pm 27^\circ$).

Fig. 4 - Longitudinal TEM image of T700 carbon fiber and corresponding selected area diffraction patterns.

To compare the commercial T700 carbon fiber to the carbon fiber from VHMW precursor, TEM images of the fiber cross sections were analyzed. Fig. 5 shows the TEMs for the T700 and VHMW PAN-based CF. For the VHMW precursor fiber, as hypothesized, the small diameter allowed improved mass and heat transfer, and reduced the occurrence of an oxygen diffusion gradient, resulting in a carbon fiber with very little skin/core structure compared to that of T700.

Fig. 5 - Transmission electron micrographs of the cross section of T700 commercial high strength carbon fibers (left) and carbon fiber from VHMW PAN (right).

Fig. 6 shows high-resolution TEM lattice fringe images of VHMW PAN-based carbon fiber skin and core regions, respectively. TEM images of skin and core regions of CF from VHMW PAN do not exhibit significant differences. Unlike the T700 fiber, our small diameter experimental CF exhibited almost no skin-core structure. Elimination of the skin-core morphology was also observed by Kong *et al.* for a slightly larger diameter carbon fibers ($\sim 4 \mu\text{m}$); however, tensile properties for those filaments have not been reported [18]. Shown in Table 1, the absence of a skin/core structure likely contributed to a significantly higher tensile modulus compared to commercial carbon fibers.

Fig. 6 - High resolution transmission electron micrograph lattice fringe images of VHMW PAN-based carbon fibers. (Left) Skin; (Right) Core

3.5 Carbon fiber crystal lattice structure and orientation

X-ray diffraction was carried out on the carbonized filaments to understand the crystal lattice structure and orientation in the filaments. The crystallographic parameters (d-spacing between the graphitic layers, “stack height” of the graphitic layers (L_c), crystal size in the direction parallel to the graphene planes (L_a) and orientation of the graphitic layers relative to the fiber axis), were determined by x-ray diffraction for commercial carbon fibers and our VHMW PAN-based carbon fiber. It was reported in other studies that the value of the tensile modulus for carbon fiber was dictated by the degree of order in the carbon structure (orientation of the graphitic layers) and the size and crystallite orientation [23-27]. As shown in Table 2, commercial carbon fibers of 220 – 287 GPa tensile modulus and 4.8 – 7.6 GPa tensile strength exhibit L_c of 1.8 nm, L_a of 4.9 – 6.2 nm, and 16.8 – 17.1 ° misorientation angles. Crystallite misorientation angle is not to be confused with the specific TEM visual orientation angle discussed above and in Fig. 4, which served to show the difference between skin and core visual diffraction patterns for that particular fiber. The misorientation angle

discussed here is an average crystallographic parameter collected on an entire bundle of filaments that allows for accurate comparison of fiber crystal orientation.

Table 2. Crystalline parameters for carbon fibers determined by wide-angle x-ray diffraction measurement and their tensile properties.

Carbon fiber reference	d(002) (Å)	L_a (nm)	L_c (nm)	Misorientation angle (°)	Tensile modulus (GPa)	Tensile strength (MPa)
Toray T700	3.49	6.2	1.8	16.8	220	4848
Toray T1000G	3.49	4.9	1.8	17.1	287	7623
VHMW PAN-based CF	3.64	3.9	1.3	21.0	345	4300

Usually, for high modulus fibers, high L_c , L_a and high degrees of orientation (i.e., low misorientation angle) are desired [28, 29]. However, our small diameter carbon fibers have a much higher elastic modulus of 345 GPa, and yet exhibit a smaller L_c of 1.3 nm and L_a of 3.9 nm, with a broad misorientation angle (21°). In addition, the d-spacing increased from 3.49 Å for the commercial carbon fibers to 3.64 Å for our carbon fiber. Kong, et al. found that with decreasing carbon fiber diameter, d_{002} increased, L_c decreased, and L_a increased due to improved heat and mass transfer, as well as increased cross-linking processes to improve the growth of the graphitic layers [18]. Therefore, the crystal lattice structure and orientation in the filaments alone is not enough to explain the high modulus that occurs in our carbon fiber from VHMW PAN. Interestingly, a similar type of carbon fibers of relatively larger diameter (5 μm) has been reported recently [30]. Such fibers exhibit a comparable tensile modulus with slightly larger L_c (1.9 nm) and smaller L_a (2.5 nm), again supporting the claim that crystal lattice structure and orientation are not enough to explain the development of high modulus. To further investigate this occurrence, the pore size distribution was investigated using small angle scattering data, as it has been suggested that an increase in the average nanopore length increases Young's modulus [28].

3.6 Carbon fiber pore size distribution

Numerous researchers have attempted to correlate modulus to fiber porosity, drawing various relationships [31-34]. Sonnenschein, for example, found that the modulus of porous materials shows an inverse exponential dependence on the overall porosity [35]. Indeed, the pore size distributions of different carbon fibers studied are shown in Fig. 7. All commercial carbon fibers show two types of porosity, with the main part of the volume distribution corresponding to pores with an average diameter of 1 nm, and the other part of the volume distribution corresponding to pores with an average diameter of 4 nm. The higher (intermediate) modulus commercial carbon fibers (T1000 and IM10) show a lower volume of porosity, especially for pores having an average diameter of 1 nm. All commercial carbon fibers exhibit an equivalent volume of slightly larger pores (4 nm). Our small diameter VHMW PAN-based carbon fiber contained a negligible number of 4 nm pores, and the volume generated by the pores with a diameter of 1 nm was significantly lower compared to commercial fibers (Fig. 7).

Fig. 7 - Comparison of pore size distributions existing in commercial and experimental carbon fibers

From this data, obtaining very high modulus carbon fibers is clearly influenced by the level of porosity (total volume and size of the biggest pores).

4. Conclusions

The carbon fibers derived here from VHMW PAN were able to achieve high modulus compared to conventional fibers, despite lower L_c , L_a and a higher misorientation angle. This suggests that the fibers can likely be further optimized by improving these parameters, and a further increase in Young's modulus can be expected. In addition, the fiber porosity was much lower than conventional carbon fibers, suggesting fiber processing (during spinning of precursors, stabilization, and/or carbonization) was carefully controlled so as to minimize the formation of pores in the fiber. Further work is necessary to ascertain the exact source of this reduction in pore size diameter and distribution. In addition, it is likely that the tensile

strength of the fibers can also be vastly improved by reducing the number of surface defects on the fiber, in this case caused by insufficient hole spacing of the spinnerette, which led to incidents of fiber fusion during spinning. Finally, it has been shown here that the VHMW PAN allowed for the production of small diameter (~5 μm) white fiber, which produced a corresponding ~2.5 μm diameter carbon fiber. This small fiber diameter facilitated the production of a more homogeneous fiber cross section due to improved oxygen diffusion homogeneity during stabilization, with little skin/core structure when compared to the conventional fibers. All else equal, homogeneous fibers will make more efficient use of their cross sectional area under a tensile load, resulting in higher modulus. It has been hypothesized that this improved homogeneity, coupled with the use of VHMW PAN, allowed the resulting carbon fibers to attain higher modulus values compared to larger diameter conventional fibers.

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