High Strength and High Modulus Carbon Fibers

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Abstract

Carbon fibers have been processed from gel spun polyacrylonitrile copolymer on a continuous carbonization line at Georgia Tech (GT) with a tensile strength in the range of 5.5 to 5.8 GPa, and tensile modulus in the range of 354 to 375 GPa. This combination of strength and modulus is the highest for any continuous fiber reported to date, and the gel spinning route provides a pathway for further improvements in strength and modulus for mass production of carbon fibers. At short gauge length, fiber tensile strength was as high as 12.1 GPa, which is the highest value ever reported for a PAN based carbon fiber. Structure analysis shows random flaws of about 2 nm size, which results in intrinsic tensile strength of higher than 20 GPa. Inter-planar turbostratic graphite shear modulus in high strength carbon fibers is 30 GPa, while in graphite the corresponding value is only 4 GPa.

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1. Introduction

Polyacrylonitrile (PAN) polymer [1] was commercialized by the DuPont Company in 1950 and is the only precursor material from which currently high strength carbon fibers can be processed [2-4]. These PAN based carbon fibers are now being used for significant structural applications in aerospace industry (e.g. in Boeing 787), for power generation (wind mill blades), and are increasingly being used in automobiles. Although carbon filaments were first used in light bulbs in late nineteenth century, the research in modern carbon fibers started in 1959 in Japan and a key processing innovation occurred in England in 1964 resulting in high strength fibers. Following these developments, PAN based commercial T300 carbon fiber was introduced by the Toray Company of Japan in 1971 with a tensile strength of 2.5 GPa. Through material and process optimization, by 1980, the tensile strength of T300 carbon fiber was improved to 3.5 GPa [5]. Currently, a widely used PAN based carbon fiber in aerospace industry, the IM7, has a tensile strength of 5.6 GPa and tensile modulus of 276 GPa [6]. PAN based carbon fiber (T1100G) with a tensile strength of 6.6 GPa and tensile modulus of 324 GPa was recently commercialized [7]. After more than 50 years of development, the tensile strength of high strength PAN based carbon fibers is still less than 10% of the theoretical strength of the carbon-carbon bond [8, 9], and about 30% of the theoretical modulus [10]. On the other hand, continuous pitch based carbon fibers can be manufactured with modulus as high as 965 GPa (>90% of the theoretical modulus). However, these high modulus pitch based carbon fibers have relatively low tensile strength (3.1 GPa), resulting from large graphitic grain boundaries and relatively low inter-planar shear modulus. Although it is possible to process PAN based carbon fibers with tensile modulus approaching 600 GPa (which is 57% of the theoretical value for graphite) via high temperature carbonization, this high tensile modulus is achieved at the expense of tensile strength (Fig. 1). Clearly, there is room and need to increase the strength of carbon fibers while also increasing their modulus.

Man-made polymeric fibers are processed by melt or solution spinning [11]. While PAN can be melt spun, currently all commercial PAN fiber production is based on solution spinning. Gel spinning [12] is used for making high strength and high modulus polymeric fibers and can lead to fewer entanglements in the fiber than in the melt and conventional solution spun fiber of the same molecular weight. Through gel spinning, high molecular weight polymer solutions can be spun with higher molecular alignment than what can be achieved by conventional solution

spinning, resulting in higher modulus of the carbonized fiber. However, to date carbonization of gel spun PAN fibers has been carried out as a batch process [13-15], and there are no reports of gel spun fiber carbonization in a continuous process. It has been hypothesized that the continuous carbonization of gel spun PAN will result in a combination of higher strength and higher modulus carbon fibers compared to the conventional solution spun PAN based carbon fibers.

2. Experimental

2.1 Fiber Processing

The polymer used in the current study was poly(acrylonitrile-co-methacrylic acid) (PAN-co-MAA) copolymer with a viscosity average molecular weight of 513,000 g/mol (Japan Exlan Company, Osaka, Japan). The polymer was dissolved in *N,N*-dimethylformamide (DMF) at 90 °C at a concentration of 10.5 g/dl. The prepared solution was spun using a spinning machine equipped with a 100-hole spinneret (hole diameter of 200 µm). The fiber was spun into a methanol bath maintained at -50 °C using an air gap of about 2 cm. The as-spun draw ratio was 3 and the post-spin draw ratio was 8.2 (total draw ratio was 24.6). Post-spin drawing was conducted via multi-step drawing at the drawing temperature as high as 180 °C. The tensile properties and structural parameters of the precursor fiber are listed in Table 1. It is noted that the tensile modulus of this gel spun PAN precursor is 20.7 GPa. This value is significantly higher than the modulus value achieved in the solution spun PAN fiber, which is typically in the range of 7 to 14 GPa [16, 17]. Higher tensile modulus in the gel spun fiber is a result of significantly higher draw ratios achieved in gel spinning than in solution spinning [13, 16, 18]. The precursor fiber tow was stabilized and carbonized using the laboratory scale continuous carbonization facility at GT (Supplementary Fig. 1). The stabilization and carbonization temperatures were as high as 250 °C and 1450 °C, respectively.

Table 1. Tensile and structural properties of the GT PAN precursor fiber.

		GT PAN precursor fiber
Effective diameter (μm)		11.0 ± 0.8
Density (g/cm^3)		1.207
Tensile properties ^a	Strength (GPa)	1.0 ± 0.1
	Modulus (GPa)	20.7 ± 1.1
	Elongation at break (%)	9.4 ± 1.5
WAXD analysis	d -spacing _(200,110) (nm)	0.527
	Crystallinity (%)	64
	Crystal size $L_{(200,110)}$ (nm)	15.7
	FWHM _{azi, (200,110)} (degrees)	6.7

^aTensile properties were measured for 25.4 mm gauge length at a strain rate of 1 %/s.

2.2 Characterization

Tensile tests of the precursor and the carbon fibers were performed with a single filament tensile testing machine (FAVIMAT+, Measured Solutions Inc.) as described elsewhere [19]. The linear densities of the fibers were measured by a vibroscope prior to tensile testing for a fiber gauge length of 25.4 mm. The measured linear density was converted to an effective diameter using the measured bulk density of the precursor and carbon fibers, respectively. The bulk density of the fibers was measured using a pycnometer (AccuPyc II 1340, Micromeritics, Inc). Tensile fractured cross-sections were imaged using a Zeiss Ultra 60 FE-SEM at an accelerating voltage of 5 kV without Au-Pd coating. Tensile testing was also done at 100 μm gauge length using a custom designed apparatus for microscale tensile testing. At short gauge lengths, the tensile strength for each fiber was determined by measuring the cross-sectional area of the fractured fiber SEM image.

The structural characteristics of the precursor and carbonized fibers were studied using wide-angle x-ray diffraction (WAXD). WAXD patterns were collected on a Rigaku micromax-002 ($\text{CuK}\alpha$, $\lambda=0.1542$ nm) equipped with Rigaku R-axis IV++ detector. The collected 2D patterns were analyzed using Area Max v2 and peak fitting was performed using JADE 9.1.5. Raman spectra were collected on a Horiba Scientific Xplora confocal microRaman system (laser wavelength = 785 nm). For transmission electron microscopy, carbon fiber samples were mounted on a copper 3 post Omniprobe lift-out grid (Electron Microscopy Sciences, Inc.) using Epo-Tek 353ND epoxy (Gatan, Inc.) for transverse cross-sectioning. After curing the epoxy at 60 °C for 2 days, the fiber was thinned using a FEI Nova Nanolab 200 FIB/SEM. The carbon fiber

was first protected with a platinum layer. Then, ion beam milling at 30 keV was done followed by final milling at 5 keV until electron transparency was achieved. TEM imaging was performed on a Tecnai TF30 (FEI, Co.) at an accelerating voltage of 80 keV. The thermal stability was studied on a Q500 TGA (TA Instruments) by heating 0.85 ± 0.08 mg of fiber from 30 °C to 1000 °C at a heating rate of 10 °C/min using an air flow rate of 25 mL/min.

3. Results and Discussion

In this work, carbon fibers have been produced in multiple gel spinning runs of precursor fibers and carbonization with average tensile strength values in the range of 5.5 to 5.8 GPa and tensile modulus in the range of 354 to 375 GPa (Fig. 1 and Table 2). There are no other fibers with this combination of tensile strength and modulus, and their modulus is 25-36% higher than that for the IM7 carbon fiber. Normally, an increase in the carbon fiber tensile modulus is accompanied by a decrease in tensile strength. For example, the tensile strength of current PAN based commercial fiber (M40JB) with a modulus of 377 GPa is only 4.4 GPa (Fig.1). However, the higher tensile modulus in the current gel spun PAN based carbon fiber as compared to the IM7 carbon fiber is without any loss in tensile strength (Fig.1, Table 2).

Fig. 1 - Tensile strength versus tensile modulus of various PAN based carbon fibers. Circles represent the tensile properties of commercial PAN based carbon fibers. Stars represent the tensile strength and modulus of the GT PAN based carbon fibers. Trend lines ① and ② represent trajectory of the developments in the high strength and high modulus solution spun PAN based carbon fibers, respectively over the last 30 years. Trend line ③ represents the development trajectory in gel spun PAN based carbon fiber over the last 3 years.

Table 2. Properties and structural parameters of various carbon fibers.

		PAN based carbon fibers			Pitch-based carbon fiber
		GT carbon fiber	IM7	T300	K-1100
Cross-sectional area (μm^2)		19.6 – 21.2	21.2 [6]	38.5 [5]	113.1 [4]
Density (g/cm^3)		1.77 – 1.79	1.78 [6]	1.76 [5]	2.20 [4]
Tensile properties	Strength (GPa)	5.5 – 5.8	5.6 [6]	3.6 [5]	3.1 [4]
	Modulus (GPa)	354 – 375	276 [6]	230 [5]	965 [4]
Oxidative thermal degradation temperature ($^{\circ}\text{C}$)		815	714	771	877
WAXD analysis*	d_{002} (nm)	0.344	0.348	0.349	0.337
	L_{002} (nm)	1.9	1.6	1.4	26.6
	L_{10} (nm)	2.5	2.1	2.0	21.1
	$\text{FWHM}_{\text{azi},002}$ (degrees)	23.1	30.3	35.0	0.5 – 1.0 [20]
Raman intensity ratio	I_G/I_D	0.46	0.43	0.39	2.00

* d_{002} , L_{002} , and L_{10} are inter-planar graphitic spacing, crystal size perpendicular to (002), and crystal size within graphitic plane along the fiber axis, respectively.

Spools of the gel spun PAN precursor and carbon fibers produced in this study are shown in Fig. 2a. Notably, the high strength and high modulus carbon fiber processed via gel spinning route has a non-circular cross-section (Fig. 2b,c and Supplementary Fig. 2), while the commercial high strength, high modulus carbon fibers (cross-sections of IM7 and T1000 are shown in Fig. 2d,e) have near perfect circular cross-sections. Oxygen diffusion from the fiber surface to the core plays an important role in stabilizing the fiber structure [21]. Due to this oxygen diffusion, a circular fiber would result in a more homogeneous structure than a non-circular fiber. Therefore, it is expected that the tensile strength of the gel spun PAN based carbon fiber will increase further with an increase in fiber circularity, provided that the internal micro- and nano-structure of the fiber is not negatively affected by enhanced circularity.

High resolution transmission electron microscopy (HRTEM) images of carbon fibers derived from gel spun PAN fibers showed well developed turbostratic graphitic structure (Fig.

2f), with inhomogeneity at the level of 0.5 to 2 nm scale (e.g. features within circles in Fig. 2f). The IM7 (Fig. 2g) fiber has significantly more heterogeneous structure than the gel spun PAN carbon fiber. For comparison, among the three fibers, the T300 carbon fiber (Fig. 2h) shows the least developed turbostratic graphitic structure, as well as the most heterogeneity.

Fig. 2 - (a) Photograph of spools of the gel-spun GT PAN precursor fiber and the resulting carbon fiber, (b) SEM image of tensile fracture surface of the GT PAN based carbon fibers with tensile strength of 10.2 GPa at 1 mm gauge length and (c) GT PAN based carbon fiber with a tensile strength of 12.1 GPa at 100 μm gauge length. For comparison, fiber cross-sectional images of (d) IM7 and (e) T1000 carbon fibers are also shown. IM7 fiber shown in (d) was tested at 1 mm gauge length and exhibited a tensile strength of 8.7 GPa. High resolution transmission electron micrographs of the (f) GT PAN based carbon fiber, (g) IM7 carbon fiber and (h) T300 carbon fiber. Regions within circles in (f) show areas of defects or heterogeneities that would decrease the fiber tensile strength.

Tensile strength and tensile modulus data for the GT PAN based carbon fibers and for commercial carbon fibers (T300, IM7 and T1000) at various gauge lengths are given in Fig. 3, Fig. 4, and Supplementary Fig. 3. The highest tensile strength of GT PAN based carbon fibers of 25.4 mm gauge length was 8.5 GPa (Fig. 4.e1), while that of the IM7 fiber was 6.9 GPa (Fig. 4.d1). Tensile fracture cross-sectional images of fibers tested at 1 mm and 100 μm gauge lengths exhibiting tensile strength values of 10.2 and 12.1 GPa are shown in Fig. 2b,c (and Supplementary Fig. 2), respectively. The increase in tensile strength with decreasing gauge length is observed in many materials, as the probability of finding defects decreases with decreasing gauge length. The extrapolated intrinsic strength value for the GT PAN based carbon fiber is 20.3 GPa (Fig. 3a). The intrinsic strength was determined based on extrapolation to 1 nm, as this is the scale (0.5 to ~ 2 nm) at which the smallest size defects are present in the gel spun PAN based carbon fiber. About 0.5 nm size defects arise from the PAN polymer chain ends, while defects on the order of 2 nm can arise from polymer chain entanglements. Chain entanglements can be minimized but not fully eliminated in gel spinning as compared to conventional solution spinning. This is due to the fact that lower polymer concentration is used in gel spinning (10.5 g/dl in current study) as compared to solution spinning (typically 20 g/dl). Similarly, polymer chain ends can also not be fully eliminated, though the number of chain ends per unit volume will decrease with increasing polymer molecular weight. Thus tensile strength extrapolated to nano meter scale can be considered as the intrinsic strength of the PAN based carbon fiber. Using this intrinsic strength value and Griffith's equation [22, 23], a defect size of 2.4 nm is predicted (based on the modulus value of 375 GPa and graphite fracture energy value of 4.2 J/m^2). This defect size is in agreement with the defect or the heterogeneity size observed by TEM (Fig. 2f). Plots of tensile strength as a function of defect size for different moduli carbon fibers are given in Fig. 3b,3c. Structural heterogeneity or defects govern the fiber tensile strength [24], and can arise from many factors including solution inhomogeneity, crystalline and amorphous morphology in the fiber, heterogeneity due to coagulation, and heterogeneity induced during stabilization and carbonization. At the molecular level, each end of the polymer molecule will result in a defect size of about 0.5 nm. Therefore, the defect size of 2 – 3 nm would be created from 4 – 6 entangled polymer molecules that would be responsible for the limiting fiber tensile strength of 20 GPa.

Fig. 3 - (a) Tensile strength of the GT PAN based carbon fibers at different gauge lengths; defect size calculated by Griffith equation [22, 23] for various carbon fibers based on (b) intrinsic strength values obtained by extrapolation to 1 nm gauge length, and (c) strength values tested at 25.4 mm gauge length; (d) tensile modulus of the GT PAN based carbon fiber as a function of inverse gauge length to obtain the compliance corrected tensile modulus; (e) theoretical tensile modulus [10, 25] as a function of full width at half maximum (FWHM) of the (002) azimuthal scans for various inter-planar shear modulus (G_{12}) values. Data points for the selected carbon fibers are also shown.

The slope of the solution rheology plot $\text{Log } G'$ vs $\text{Log } G''$ is an indirect measure of the solution homogeneity [26], as well as polymer molecular entanglements. This slope value is 2 for a homogeneous solution. The plot of the dependence of the carbon fiber tensile strength on the slope of the $\text{Log } G'$ vs $\text{Log } G''$ plots of the corresponding solutions in Supplementary Fig. 4, shows increasing fiber strength with increasing slope of the $\text{Log } G'$ vs $\text{Log } G''$ plot. This is a rheological parameter at the molecular level that can be controlled and monitored to further increase the carbon fiber strength.

Fig. 4 - Tensile strengths of (a) T300, (b) IM7, and (c) T1000 [27] as a function of gauge length, estimating the intrinsic tensile strength of these fibers as 8.2 GPa, 14.1 GPa, and 20.9 GPa, respectively; (d-1) tensile strength of individual testing results of IM7 carbon fiber at 25.4 mm gauge length; (d-2) tensile modulus as a function of inverse gauge length to obtain compliance corrected tensile modulus for the IM7 carbon fiber; (e-1, e-2, f-1, and f-2) are the tensile properties of the GT PAN based carbon fibers from two different fabrication runs under the same testing conditions. Data for a third run are given in Fig. 3a and 3d. The tensile modulus results are the average of about 50 tests. The tensile strength and tensile modulus values of IM7 fibers reported by the manufacturer are 5.6 GPa and 276 GPa, respectively, and are within the experimental error of the values reported here based on single filament tests. Intrinsic strength of a Mitsubishi Rayon carbon fiber with a reported tensile strength of 4.7 GPa and tensile modulus of 235 GPa was determined to be 9.3 GPa [28]. Considering that the reported tensile strength of this Mitsubishi Rayon carbon fiber is in between that of the T300 and IM7, and its intrinsic strength is also in between the values for these two fibers, this experimentally determined intrinsic strength value on the Mitsubishi Rayon carbon fiber provides validity for the extrapolated intrinsic strength values in Fig 3a, Fig. 4a, 4b, and 4c.

A comparison of the structural parameters shows that the GT PAN based carbon fiber has smaller (002) d-spacing and larger crystal size perpendicular to the graphitic planes as well as in the plane along the fiber axis, and higher graphitic plane orientation (as measured by the full width at half maximum of the (002) azimuthal plane – that is $\text{FWHM}_{\text{azi},002}$), as compared to T300 and IM7 fibers (Table 2). Data in Table 2 also show that the GT PAN based carbon fiber has higher Raman I_G/I_D ratio than that for T300 and IM7 fibers, which is consistent with the HRTEM images (Fig. 2f, 2g and 2h). Notably, the GT PAN based carbon fiber exhibited about 100 °C higher thermal degradation temperature in air as compared to IM7 and about 40 °C higher as compared to T300 (Fig. 5). For comparison, the structure and property data for high modulus pitch based carbon fiber K1100 are also given in Table 2.

Fig. 5 - Oxidative thermal degradation behavior of the GT PAN based carbon fiber. The degradation behavior of IM7, T300, and K1100 carbon fibers is also given for comparison. The heating rate was 10 °C/min and the air flow rate was 25 mL/min.

In order to understand the tensile modulus behavior of the GT PAN based carbon fiber, theoretical plots of the carbon fiber elastic modulus as a function of $\text{FWHM}_{\text{azi},002}$ are plotted for various G_{12} values in Fig. 3e [10, 25]. G_{12} is shear modulus between graphitic planes. For perfect graphite, the value of G_{12} is 4 GPa [10]. The modulus value for near perfect graphitic fiber K1100 falls on the line represented by $G_{12} = 4$ GPa as expected, while the data for T300, IM7, and GT PAN carbon fibers fall on the line represented by the G_{12} value of 30 GPa. The higher modulus PAN based carbon fiber M60JB falls in between the lines represented by G_{12} of 10 and 20 GPa. Thus, the inter-planar shear modulus in high strength PAN based carbon fibers is 30

GPa, while in graphite the value is only 4 GPa, and falls between these two values for other carbon fibers.

4. Conclusion

This study showed that gel spinning of PAN can result in carbon fibers with a combination of high tensile strength and tensile modulus that has not been achieved previously. In this context, it should also be noted that the current performance of solution spun PAN based carbon fibers has been achieved after nearly half a century of materials and process optimization. However, very limited material and process optimization studies have been carried out to date on the gel spun PAN fiber. Therefore, the gel spun PAN based carbon fiber properties reported in this paper should be considered as the baseline values for this process. Materials and process optimization, enhanced fiber circularity, and increased solution homogeneity will further increase the strength and modulus beyond those reported in this study.

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6. References

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