Characterization of Fiber Structures Developed During Carbon Fiber Conversion Process

Shao C. Chiu and Edward J. Ryan

Cytec Carbon Fibers, LLC
Greenville, SC 29673

Introduction

Graphite crystalline structure evolves in carbon fiber as a result of the formation and the ordering of basal (graphene) planes during the carbonization process. The crystallites can be viewed as turbostratic stacking of planar structure units. The stacking height and the size (length and width) of the crystallite increase and the orientation of crystallites along the fiber axis improves with increased degree of heat treatment. The 'degree of heat treatment' is the combined effect of carbonization temperature and carbonization time. In addition to heat treatment, the tension force applied to carbon fiber during the carbonization step has a significant impact on resulting carbon fiber structures. When subjected to tension at a favorable temperature, the stressed crystallites will align parallel to the fiber axis and give improved orientation. Wide-angle X-ray diffraction (WAXD) has been widely used to characterize the structures of carbon fibers. Reviews of the WAXD data for Polyacrylonitrile (PAN)-based carbon fibers are given in References 1-3. Those data were generally gathered from studies conducted using commercial carbon fiber samples from different sources or by using lab samples where knowledge of the fiber processing conditions was somewhat limited. Consequently, any in-depth correlation between WAXD data and fiber conversion processing parameters could not be easily done. The purpose of the present study was to conduct a systematic and detailed WAXD characterization of carbon fiber samples derived under broad processing conditions. Establishing a process-structure–property correlation was the ultimate objective.

Experimental

Two types of carbon fiber samples were used in this study: (1) Carbon fibers manufactured on Cytec's commercial-scale facilities and (2) experimental carbon fibers produced on Cytec's pilot-scale equipment. The first type of samples included Cytec's commercial products, Thornel® T300, T650/35 and T40/800 and two experimental products designated as IMA (experimental intermediate modulus) and HMX (experimental high modulus). The second group of samples was produced using experimental polymers produced at laboratory scale. These polymers were converted into white PAN fibers using Cytec's standard spinning process on pilot spin line. The white PAN fibers were then converted into carbon fibers using Cytec's pilot scale oxidation and carbonization equipment. The pilot scale carbonization line has two furnaces, i.e. a low temperature (LT) furnace and a high temperature (HT) furnace. The line speeds and stretch ratios were controlled by drives located before and after each furnace. Cytec's AP200 epoxy compatible sizing was applied to the fiber. Carbon fiber tensile strength and modulus were tested using SACMA (Suppliers of Advanced Composite Materials Association) methods.

For the X-ray diffraction study, paper tabs were used to mount the carbon fiber samples. The tabbed samples were prepared by gluing the fiber sample, (under a 500 gram tension) to paper tabs having a 2 cm x2 cm square window. This method was used to ensure good fiber orientation measurement and to minimize damage to the samples during handling. X-ray measurement was done by using the Rigaku-MSC machine located in Clemson University's Center for Advanced Engineering Fibers and Films (CAEFF). A Cu X-ray source having 1.5406A wavelength was used and the curve fitting software OriginPro 7v7.0383 was used for data analysis. The interplanar spacing, d, was calculated by using Bragg's law. The stacking height, L_c, was calculated by using the Scherer equation and the peak width from the 002 reflection. The preferred orientation was measured as the FWHM (full width of half maximum) of the Azimuthal scan of the 002 reflection. The 100 reflection information was used to calculate crystallite dimension [1]. The meridional width was used to obtain the layer plane length parallel to the fiber axis the $L_{a\parallel}$. The equatorial width was used to obtain the layer plane width perpendicular to the fiber axis, $L_{a\perp}$.

Results and Discussion

The results of the WAXD study of a series of commercial-scale equipment produced Thornel® carbon fiber samples are shown in Table 1. The 2 theta scan curves are shown in Figure 1 for the T300 fiber and the experimental 60 msi HMX fiber.

Table 1: WAXD Data for Thornel® Carbon Fiber Samples

Fiber Type	CF Tensile Modulus (msi)	CF Tensile Strength (ksi)	d 002 Spacing (Å)	L_c (Å)	Azimuthal Scan (002) FWHM (°)	$L_{a\parallel}$ (Å)	$L_{a\perp}$ (Å)
T300	33.0	545	3.5	15.9	34.6	25.4	22.0
T650/35	35.9	659	3.5	16.5	32.0	26.6	23.2
T40/800	40.3	800	3.5	17.6	30.7	27.8	23.4
IMA Experimental Fiber	43.7	755	3.5	19.9	27.9	30.0	25.7
HMX Experimental Fiber	60.0	664	3.4	42.6	17.5	77.3	58.4

* Tensile Modulus measured by SACMA method - using chord between 1000 micro-strain and 6000 micro-strain.

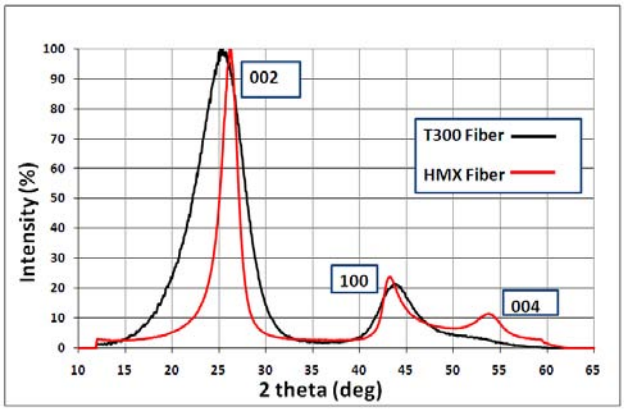

Fig 1. WAXD 2 theta scan curves of T300 fiber and an experimental high modulus (60 msi) fiber

As shown in Figure 1, the 002 peak appears at around 25 degrees for T300 and shifts to a higher value for the high modulus (60 msi) fiber. This shift corresponds to the smaller d-spacing value, 3.4Å, in the high modulus fiber. The widths of the 002 peak and the 100 peak (at around 44 degree) were clearly narrower for the 60 msi fiber than the T300 fiber. Figure 1 also showed that the 004 peak (at around 54 degree) became evident in the high modulus fiber. The data in Table 1 clearly show the stacking height of the graphene planes (L_c) and crystallite's dimension (L_{aII} and $L_a\perp$) increased with fiber modulus as the result of increased heat treatment. The average number of stacking layers was estimated to be 4.5 for the T300 sample and was 12.5 for the 60 msi fiber. The crystallite's length values (L_{aII}) were higher than the width values ($L_a\perp$) for all samples. The preferred orientation was also noticeably improved with fiber modulus, as evidenced by the decreasing FWHM value measured by Azimuthal scan of 002 peak.

To extend this study of the effects of carbonization processing variables on fiber structures and properties, a series of carbonization experiments was conducted at pilot scale. The results are summarized in Table 2. The experimental PAN polymers contained 2.0 wt% co-monomers. The data showed the combination of higher carbonization temperature and longer residence time (doubled) produced samples having higher L_c, L_{aII} and $L_a\perp$ and higher modulus. The effect of fiber tension applied to fiber during carbonization had a significant impact on preferred crystallite orientation and fiber modulus but no clear impact on crystallite dimensions.

Table 2: Effects of Carbonization Parameters on Carbon Fiber Structures and Properties

Carbonization Temperature (°C)	Line Speed (normalized)	Fiber Tension	CF Tensile Modulus (msi)	d 002 Spacing (Å)	L_c (Å)	Azimuthal Scan (002) FWHM (°)	L_{aII} (Å)	$L_a\perp$ (Å)
1200	2	low	37.3	3.5	15.1	30.6	24.8	21.5
1200	2	high	39.4	3.5	15.4	30.2	24.8	21.4
1300	2	low	39.4	3.5	16.2	31.1	26.3	23.2
1300	2	high	42.0	3.5	15.9	29.2	26.5	22.5
1300	1	low	41.1	3.5	16.3	30.7	28.6	22.5
1300	1	high	43.2	3.5	16.6	28.5	27.0	24.4

To further examine the effect of fiber tension during carbonization, another series of experiments was done using PAN polymer containing only 0.7 wt% co-monomer. The experiments were run by using the same line speed and the same carbonization temperature profile, (including the same maximum temperature), but at different tension levels. The experimental results are summarized in Table 3. The data clearly show that the tension applied to fiber has a big impact on the resulting fiber structure and properties. In this case, an increase of about 7 msi in fiber modulus was realized by changing the tension alone. Similar to the results from previous set of experiments, high tensions in carbonization had a significant impact on preferred crystallite orientation, about 4 degrees in the FWHM value, but no clear impact on d-spacing and crystallite sizes (L_c, L_{aII} and $L_a\perp$).

Table 3: Effects of Carbonization Stretch on Carbon Fiber Structures and Properties

Fiber Tension	CF Tensile Modulus (msi)	d 002 Spacing (Å)	L_c (Å)	Azimuthal Scan (002) FWHM (°)	L_{aII} (Å)	$L_a\perp$(Å)
Low	38.8	3.56	15.6	30.6	23.3	20.0
Medium	42.9	3.56	15.7	27.6	23.6	19.0
High	45.3	3.54	14.6	26.8	24.0	20.3

To look for white PAN fiber precursor effects on carbon fiber structures and properties, precursors having different diameters were converted to carbon fibers under same oxidation/carbonization conditions. These white fiber samples were prepared by using different steam stretch ratios on the pilot spin line. The experimental results are summarized in Table 4. The data showed lower denier white fiber produced better oriented carbon fiber and higher modulus. There were no clear impact from white fiber denier on carbon fiber d-spacing and crystallite sizes.

Table 4: Effects of White Fiber Diameters on Carbon Fiber Structures and Properties

White Fiber Diameter (normalized)	CF Tensile Modulus (msi)	d 002 Spacing (Å)	L_c (Å)	Azimuthal Scan (002) FWHM (°)	L_{aII} (Å)	$L_a\perp$(Å)
1.00	36.6	3.48	16.5	32.1	27.1	25.2
0.86	39.0	3.50	16.2	31.3	27.8	24.6
0.71	39.2	3.49	16.2	30.2	26.1	23.7
0.57	39.9	3.49	16.6	30.1	28.8	26.0

Conclusions

The effects of carbonization conditions on carbon fiber structures and properties have been studied. The structural parameters of carbon fiber as measured by wide-angle X-ray diffraction were found to correlate with the heat treatment levels and process tensions applied to the fiber. Using higher carbonization temperature or longer treatment time produced fiber structure with smaller d-spacing, larger crystal sizes (L_c, L_{aII} and $L_a\perp$) and higher preferred orientation. Increasing process tensions had a significant impact on fiber orientation and tensile modulus but did not change crystallite sizes. Reducing white fiber denier had no impact on crystallite size, but resulted in an increase in carbon fiber orientation and carbon fiber modulus.

Acknowledgment. Acknowledgments are made to Mr. Marlon Morales and Dr. Amod Ogale of Clemson University, and Dr. Karla Strong and Dr. Dave Anderson of the Air Force Research Laboratory (AFRL) for their experimental support and valuable advice. Financial support from the AFRL for a portion of this study is gratefully acknowledged.

References

[1] Johnson DJ. "Structure Studies of PAN-Based Carbon Fibers" in Chemistry and Physics of Carbon (ed.) Thrower PA. (1987), Vol. 20, 1-58.
[2] Jain MK, Abhiraman AS. "Conversion of acrylonitrile-based precursor fibers to carbon fibers". Journal of Materials Science (1987), 22, 278-300.
[3] Dresselhaus MS, Dresselhaus G, et al. "Graphite Fibers and Filaments", Springer Series in Materials Science 5, (1988), Chapter 3, 35-84.