MECHANICAL CLASSIFICATION OF CARBON FIBERS FROM RAMAN AND X-RAY SCATTERING

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Introduction

Carbon fibers for application are produced from a wide variety of precursor phases and exhibit a broad range of mechanical characteristics that result from variations in the manufacturing process [1]. Raman spectroscopy, a nondestructive and potentially high-throughput tool, is highly sensitive to a host of phenomena in carbon-based materials [2]. Carbon fibers used in applications are naturally delineated along lines of macroscopic strength properties, and control of the macroscopic strength properties is well understood to be linked to the manufacturing process and ultimate firing temperature of the carbon fibers. Consequently, there are numerous characterizations of spectroscopic observables connected to macroscopic properties of carbon fibers, particularly to optimize production by attempting to quantify signatory changes in fibers [3]. Here we are specifically concerned with the evolution of spectroscopic data collected from carbon fibers as they connect to bulk mechanical properties as a baseline for studying spectral evolution under temperature and strain application. To this end, we present correlative results of experimental studies investigating the ability to connect the macroscopic properties of carbon fibers with microscopic observables across a broad range of macroscopic values.

Materials and Methods

We systematically investigated the Raman spectral responses of 34 commercially available carbon fiber samples derived from polyacrylonitrile precursors that span a wide range of mechanical properties and surface preparations. Fibers are grouped according to manufacturer-specified macropscopic properties into high modulus (HM, bulk modulus between 350 and 600 GPa), intermediate modulus (IM, bulk modulus between 280 and 350 GPa), and high tensile (bulk modulus between 200 and 280 GPa). Samples were prepared for Raman spectroscopy by affixing a small portion of fibers from a larger tow set to an adhesive carbon tab. Individual fibers were scanned with 532, 633, and 785 nm lasers using a Renishaw InVia Raman microscope with a 100× objective having a numerical aperture of 0.85, and lateral spatial resolution of 0.76, 0.91, and 1.13 μm for the 532, 633, and 785 nm lines, respectively. Gratings of 2400, 1800, and 1200 l/mm that offer a spectral resolution of 1.2, 1.8, and 3.1 cm^{-1} were employed for the 532, 633, and 785 nm lines, respectively. The approximate laser power on the samples was 2.5, 1.7, and 30 mW for the 532, 633, and 785 nm lines, respectively. For each fiber sample and spectrometer configuration, 10 separate data sets were taken, where each data set comprised of twelve 30 second exposures. The individual data sets were summed together, and the data were normalized to set the G peak intensity to unity to correct for variations in laser power. Each data set was fit using a Lorentzian to describe the D peak near 1350 cm^{-1} and the T peak near 1150 cm^{-1}. A D' peak near

1620 cm^{-1} was resolved only for fibers in the HM class; in cases where this peak was present, the peak was fit with an additional Lorentzian component. A Breit–Wigner–Fano lineshape [4] was used for the G peak near 1590 cm^{-1}. Background in the region near the T–D–G band was estimated with a linear function and subtracted from the data.

From the Raman sample set, a selection of 17 fibers from the same production batch were used in wide-angle x-ray scattering (WAXS) measurements conducted at the G1 beamline at the Cornell High Energy Synchrotron Source facility. Samples were mounted to an x–y translation stage with custom cell holder. The incident x-ray beam wavelength was 1.258 Å, and x-ray diffraction patterns were collected for ten 200 ms exposures. Data were reduced from the two-dimensional collector by summing data into angular bins of 10 degree width, with data retained from the first detector quadrant. WAXS data analysis focuses on the (002) Bragg reflection following references [5, 6], and data are fit to a Gaussian, producing the average interlayer spacing between graphene sheets (d_{002}), and the average correlation length in-plane (l_ϕ) and out-of-plane (l_c) directions corresponds to the overall graphitic domain size.

Results and Discussion

Results from WAXS demonstrate a clear connection between graphitic domain size and macroscopic properties. Most clearly, there is a robust linear relationship observed between the in-plane correlation and tensile modulus applicable across the entire range of modulus classes studied (Figure 1a, $R^2 = 0.962$). A similar comparison to tensile strength is shown in. Figure 1b, where a weakly linear relationship ($R^2 = 0.631$) for in-plane correlation length is observed for fiber materials in the high tensile and IM class, whereas the HM materials are observed to have longer in-plane correlation lengths. This quantity requires access to the WAXS regime to measure both the equatorial and azimuthal component of the 002 Bragg peak, and is difficult to measure directly in the laboratory; consequently, we sought connections between this parameter and the results from the Raman scattering experiments. Figures 2a and b show the mean value of fit parameters for the D and G peak widths derived from fitting the individual Raman data sets for fiber samples where both x-ray and Raman data sets were acquired plotted against the value of the in-plane correlation length derived from the WAXS fit results. The data shown in Figures 2a and b are derived data acquired with the 532 nm laser, and R^2 values for the linear relationships are 0.906 and 0.918 for the D and G peak, respectively. The position of the D peak is dependent on laser excitation energy [7], but the robustness of the relationship is retained for the 633 nm ($R^2 = 0.906$) and 785 nm ($R^2 = 0.912$) excitations.

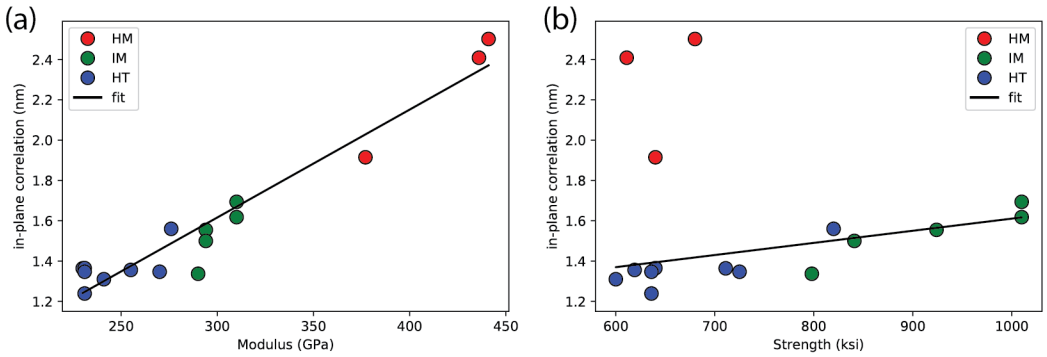

Figure 1. In-plane correlation length determined from WAXS measurements as a function of (a) reported tensile modulus and (b) reported tensile strength. Black lines indicate linear regression model. The HM data are excluded from the fit region for data in Figure 1b.

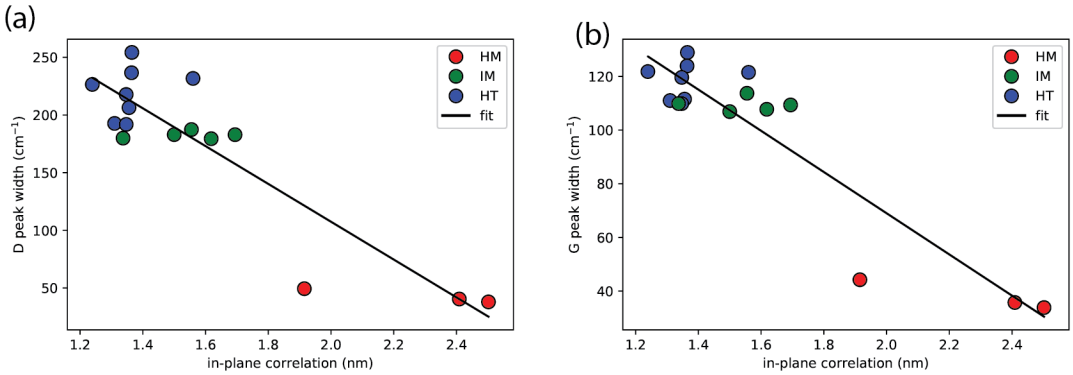

Figure 2. Fitted (a) D and (b) G peak widths derived from fitting of Raman spectra for carbon fibers, cross-references against value of in-plane correlation length derived from WAXS. Data shown derived from 532 nm excitation. Error bars are smaller than marker sizes.

Conclusions

X-ray and Raman scattering measurements combine to indicate significant correlation among several nanoscale observables and macroscopic mechanical properties. In particular, the average size of the in-plane graphitic domains measured by x-ray scattering is strongly correlated with the bulk modulus and well correlated with tensile strength. The in-plane correlation length is directly connected to the Raman spectral features of carbon fibers and is shown in the broadening of peaks known to arise from disorder and strain in the carbon fiber matrix. Further analysis and a physical interpretation of these data will be the subject of future work.

References

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