

# CORRELATION BETWEEN CARBON FIBER RAMAN LINEWIDTH AND CRYSTALLITE SIZE DETERMINED BY X-RAY DIFFRACTION

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## Introduction

X-ray diffraction (XRD) is known to provide a precise measurement of the degree of crystalline order of the hexagonal graphite lattice. The interlayer spacing  $d(002)$ , in-plane coherence length  $L_a$  and the coherence range of planar stacking  $L_c$  can be measured directly from an x-ray diffraction pattern. Raman spectroscopy, on the other hand, has been used extensively to indirectly probe the crystallinity of carbon materials since the vibrational dynamics are closely related to structure. For a carbon-carbon composite, XRD measurements provide the average crystallinity of the composite since the sample volume probed is relatively large. Micro-Raman spectroscopy on the other hand, with its spatial resolution of  $1\mu\text{m}$ , samples a much smaller volume, and allows the crystallinity of the individual carbon fibers and matrix carbons to be measured separately. This information can be used to improve our understanding of how the microstructure of C-C composites affects their final properties.

Using XRD in combination with macro Raman measurements, Tuinstra and Koenig have shown that the ratio of the intensity ( $I$ ) of the disorder-induced line at  $1360\text{ cm}^{-1}$  (referred to as the D band) to that of the intrinsic graphite line at  $1580\text{ cm}^{-1}$  (the G band) is inversely proportional to  $L_a$ [1]. Therefore, it follows that the crystallite size is equivalent to the coherence length of an ordered domain in the graphitic basal plane. In micro-Raman experiments, the orientation of the graphene planes of individual microcrystallites with respect to the optical scattering geometry is not averaged out as it is in a macro-Raman experiment. For this reason, the  $I_D/I_G$  ratio versus crystallite size correlation established from macro-Raman data [1] cannot be accurately used to determine the planar crystallite size  $L_a$ . However, the linewidth of the G band theoretically correlates with crystallite size within the framework of a phonon confinement model to provide a relative measure of  $L_a$ . Since  $L_a$  can be directly obtained by XRD, a correlation established between experimental Raman linewidths and crystallite size  $L_a$  from XRD will allow the use of micro-Raman spectroscopy to probe the ordering of each component in a carbon-carbon composite.

## Experimental

Commercially available pitch and PAN fibers

were heat treated between  $1800^\circ\text{C}$  and  $2200^\circ\text{C}$  under dry nitrogen atmosphere in a graphite furnace. The resulting fibers were ground to powder-like fine fibrils for XRD and micro-Raman measurements. XRD data were collected on a Rigaku Geigerflex D/max horizontal diffractometer mounted on a Rigaku rotating anode. The data were collected from  $10^\circ$  to  $120^\circ$  in a continuous scan mode at  $0.6$  degree/minute using a  $1^\circ$  divergence slit, a  $0.3\text{ mm}$  scatter slit and a  $0.6\text{ mm}$  receiving slit. The data were analyzed using the program CARBON obtained from Prof. J. R. Dahn of Simon Fraser University [2].

The X-ray data were fitted using a single layer model. In this model, the adjacent layers are completely uncorrelated with respect to the position of the basal plane. If  $P_r$  is defined as the probability of finding a random shift between adjacent layers, then  $P_r$  is large for disordered carbons like green-coke and small for graphitic structures, such as synthetic graphite. In a fraction of the layers,  $(1 - P_r)$ , the layers are in registry as in hexagonal graphite. The crystallite size ( $L_a$ ) of the pitch and PAN fibers was obtained from profile fitting the experimental diffraction data using parameters in the single layer model.  $L_a$  represents the in-plane coherence length of a strain-free, graphitic crystallites measured along the (100) direction.

Micro-Raman spectroscopy was performed on seven randomly chosen microfibrillar domains from each sample using an Instruments SA micro-Raman system coupled to a cooled CCD (charge coupled device) array detector. Ar-ion laser excitation ( $514.5\text{ nm}$ ) was used to obtain the Raman spectrum and provided a total power of  $5\text{-}10\text{ mW}$  at the sample surface. The laser beam was focused to a spot size of  $1\text{ micrometer}$  on the sample surface. At these low laser power densities, no thermal effects were observed on the spectral frequencies and lineshapes. Each Raman spectrum was profile-fitted to a sum of modified Lorentzian curves. The linewidths reported here represent the average of the widths obtained from the seven spectra for each sample.

## Results and Discussion

XRD Measurements. Figure 1 shows a typical X-ray diffraction spectrum for the pitch (1a) and PAN fiber (1b) heat-treated to  $2200^\circ\text{C}$ . Table 1 shows the measured  $L_a$  and Raman widths for fibers heat treated to  $1800^\circ\text{C}$  and  $2200^\circ\text{C}$ . The results confirm that the crystallinity of pitch

fibers is more sensitive to heat-treatment as compared with PAN fibers. The crystallite size of the pitch fibers increases from 4.3 nm to 8.2 nm as compared with 2.4 to 3.6 for the PAN fibers following heat-treatment from 1800 to 2200 °C.

**Micro-Raman Measurements.** Raman measurements in the 1000 to 1800  $\text{cm}^{-1}$  frequency region were performed for each fiber. Spectra from pitch and PAN fibers heat-treated to 2200°C are shown in Figures 2a and 2b. The Raman spectrum of crystalline graphite has a resonance-enhanced first-order line at 1580  $\text{cm}^{-1}$  (the G band) which is due to the in-plane  $E_{2g}$  stretching mode of the graphite layer. For disordered carbons with limited long-range order, there are additional broad bands found at 1360  $\text{cm}^{-1}$  (the D band) and at 1620  $\text{cm}^{-1}$  (the D' band [3]), which is attributed to a disorder-induced relaxation of the wave-vector selection rules for finite-size crystallites [1]. As can be seen in Figure 2, both the graphitic (G) and the defect (D) lines are observed in both types of fibers. The linewidths of the G lines were obtained from the profile-fitted spectra. Five modified Lorentzian curves were used to fit each Raman spectrum. The two main Raman peaks (solid curves) are the G band at 1580  $\text{cm}^{-1}$  and the D band at 1360  $\text{cm}^{-1}$ . Two broad peaks (dotted curves) were used to fit the amorphous background. Analysis of the Raman spectrum (Figure 2) for pitch and PAN fibers heat-treated to 2200°C shows that the width of the G and the D bands is larger for PAN fibers as compared with pitch fibers. The Raman results show that for the two heat treatment temperatures used, the PAN fiber has the lowest crystallite size and widest line width at 1800°C while pitch fiber has the largest crystallite size and narrowest line width at 2200°C. In fact the crystallite size of PAN fiber at 2200°C is smaller than those of the pitch fiber at 1800°C indicating that the PAN fiber has much lower crystallinity as compared with the pitch fiber.

## Conclusions

The microstructure of PAN and pitch fibers were measured in terms of their crystallite size,  $L_a$ , and the width of the Raman line at 1580  $\text{cm}^{-1}$  using XRD and micro-Raman techniques. The data confirms that pitch fibers are more graphitizable than PAN fibers. This study has shown the feasibility of relating Raman linewidths to crystallite size ( $L_a$ ) as measured by XRD to determine the crystallinity of the individual components (fibers and matrix) within a C-C composite. This information can be used to improve our understanding of how the microstructure of C-C composites affects their final properties.

## References

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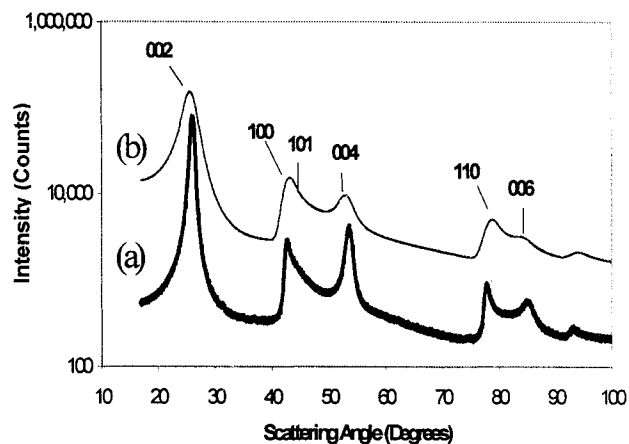


Figure 1. X-ray diffractogram of (a) pitch fiber and (b) PAN fiber heat-treated to 2200°C.

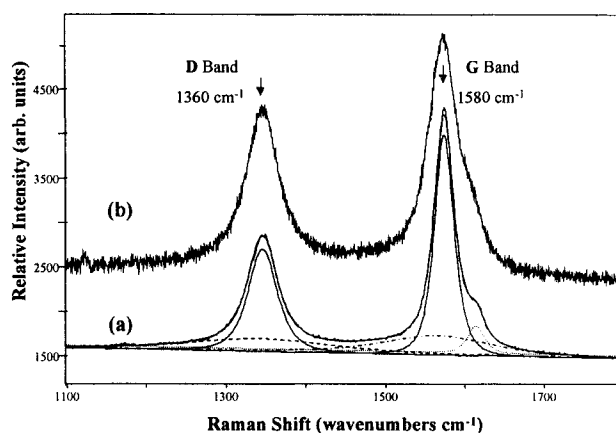


Figure 2. Micro-Raman spectrum of (a) pitch fiber and (b) PAN fiber heat-treated to 2200°C. Solid curves denote the D and G bands.

Table 1. Crystallite Size ( $L_a$ ) and Raman linewidth (G band) for pitch and PAN fibers at 1800°C and 2200°C.

HTT	Pitch Fiber		PAN Fiber	
	Width ( $\text{cm}^{-1}$ )	$L_a$ (nm)	Width ( $\text{cm}^{-1}$ )	$L_a$ (nm)
1800°C	45.6	4.3	60.2	2.4
2200°C	26.2	8.2	42.1	3.6