

# Structural Study of the Oxidized High Modulus Carbon Fiber using Laser Raman Spectroscopy

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## Abstract

This study aims to find a correlation between XRD and Raman result of the oxidized high modulus carbon fibers as a function of its oxidation degrees, and compare with the isotropic carbon fiber reported early.  $L_a$  of the high modulus carbon fiber prepared by oxidation in carbon dioxide gas have been observed using laser Raman spectroscopy. The basic structural parameters of the fibers were evaluated by XRD as well. The  $L_a$  of the original high modulus carbon fibers were measured to be 144 Å from Raman analysis and 135 Å from XRD analysis.  $L_a$  of the 92% oxidized fiber were 168 Å by using Raman and 182 Å by using XRD. There was some correlation between the  $L_a$  value obtained from Raman and XRD. However the  $L_a$  value changes of the high modulus carbon fiber through whole oxidation process showed opposite tendency compare with the isotropic carbon fiber because of the fiber structure basically.

**Keywords :** Raman, XRD,  $L_a$ , Crystallinity, Oxidation

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## 1. Introduction

The high modulus carbon fiber (HM fiber) shows superior mechanical, electrical and chemical properties because of its highly ordered structure. Therefore HM fiber is considered as the best materials in the field of aerospace applications [1-3]. HM fiber has turbostratic structure and the mechanical modulus of fiber is influenced by the degree of orientation along the fiber axis [4].

A fiber consisted of poorly oriented crystallites and/or very tiny crystallites has many crystallite edges. Since the crystallite edges act as an active site the fiber has low oxidation resistivity [5,6].

The oxidation reactions of carbon based materials take place at the active sites preferentially. In addition to the active sites, the other factors affecting characteristics of oxidation reaction include microstructural characteristics related to the inhomogeneity taking place during the manufacture of the carbon materials [7-11]. Also it was reported the homogeneous sheath-core structure of mesophase carbon fiber caused by insufficient carbonization at the middle area of fiber during the manufacture [12].

Many researchers tried to interpret structural parameters of carbon materials via several analyzing techniques such as X-Ray Diffraction(XRD), High Resolution Transmission Electron Microscopy(HRTEM), High Resolution Scanning Electron Microscopy(HRSEM), Scanning Tunneling Microscopy (STEM) and Raman spectroscopy. However it is not easy to find an article using Raman apparatus for structural

analysis of the carbon fiber [13-16].

We reported the results of structural changes of HM fibers due to oxidation using XRD and isotropic carbon fibers using Raman apparatus [17,18]. In this study the structural changes of HM fibers prepared by oxidation in carbon dioxide gas have been observed using laser Raman spectroscopy. The basic structural parameters of the fibers were evaluated by XRD as well, and compared with Raman result.

## 2. Experimental Procedures

### 2.1. Sample preparations and XRD analysis

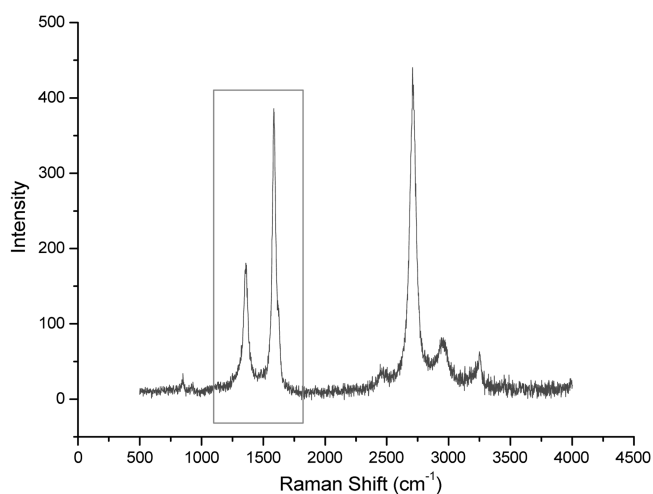
HM fibers were used as raw materials. Based on assortment of carbon fibers according to crystallites orientation, HM fiber is a highly strengthened carbon fiber with modulus 584 GPa.

The original fibers were oxidized by isothermal heating in the horizontal tube reactor using carbon dioxide gas at high temperatures. Burn-off degree was calculated by dividing the weight loss after oxidation by initial weight of sample.

The detailed physical properties of the fibers, oxidation conditions, and the result of XRD spectra such as 002 interlayer spacing and  $L_a$  value were early reported [17].

### 2.2. Raman Analysis

For the Raman analysis, a microscope was used to focused



**Fig. 1.** Raman spectrum of the original HM fiber.

**Table 1.** Structural Parameters of the HM Fibers Obtained from XRD [13]

Burn-off (%)	$d_{002}$ (Å)	$d_{10l}$ (Å)	$L_c$ (Å)	$L_a$ (Å)	Dc
0	3.44	2.12	146	135	0.965
16	3.4	2.11	138	146	0.973
22	3.4	2.11	142	137	0.980
28	3.4	2.12	150	169	0.976
39	3.4	2.12	145	165	0.981
43	3.4	2.12	144	142	0.976
66	3.4	2.12	151	159	0.972
88	3.4	2.12	150	175	0.955
92	3.4	2.12	148	182	0.942

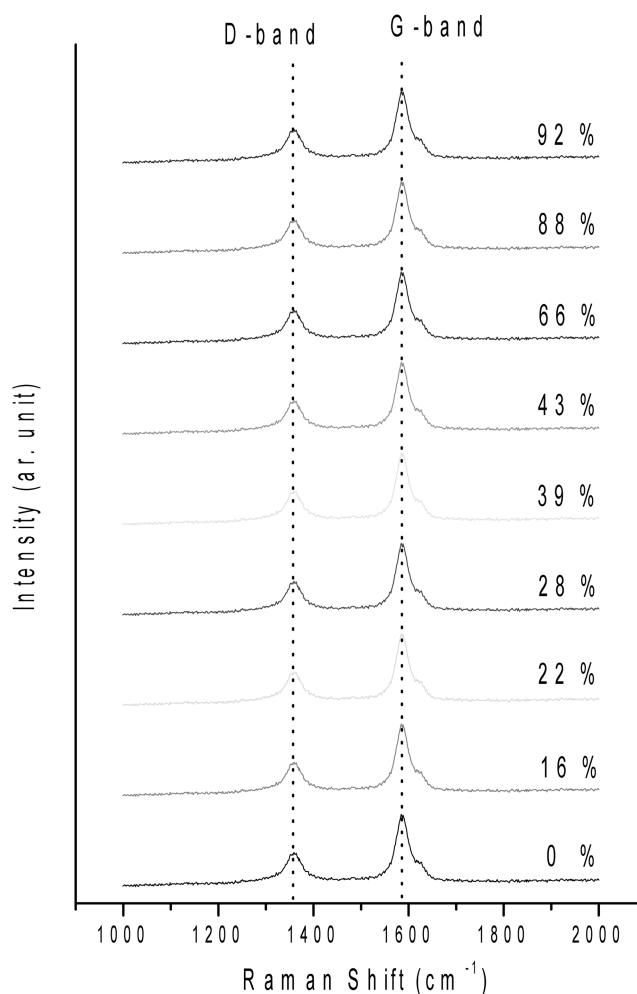
laser beam spot on the fiber surface ( $\times 500$ ). The wavelength and laser beam size of the apparatus were 514.5 nm of argon laser (Green) with  $\sim 2$   $\mu\text{m}$  of diameter.

Extended scans from 500 to 4000  $\text{cm}^{-1}$  were performed to obtain both the 1st- and 2nd-order Raman bands of the HM fibers. The band intensity, and band position were obtained from static scans of the first-order Raman spectra using a Lorentzian curve-fitting procedure[18]. Fig. 1 shows scan result of original HM fiber. We discuss only the 1st-order band in this paper.

### 3. Results and Discussion

#### 3.1. XRD analysis[17]

The structural parameters as a function of burn-off degrees obtained from XRD were summarized in Table 1. 002 and 10/ interlayer spacing show slightly changed after oxidation. The  $L_c$  and  $L_a$  values of the original fibers were 146 Å and 135 Å, respectively. The 002 interlayer spacing of the original fiber



**Fig. 2.** The first-order D and G-bands of the HM fibers shown as a function of burn-off degrees.

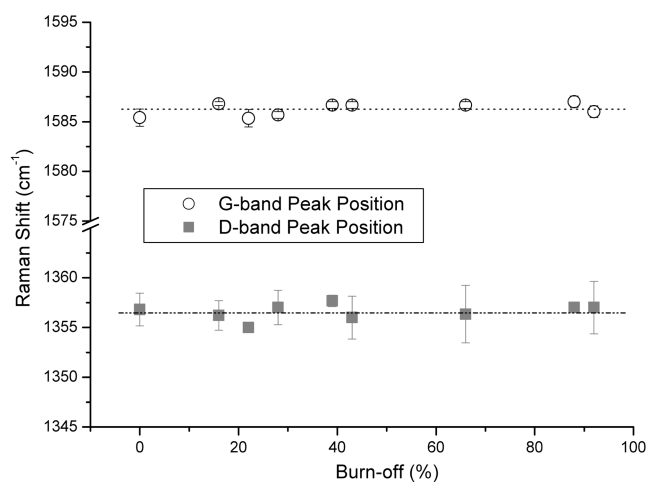
was relatively large as 3.44 Å in comparison with 3.35 Å of graphite. With increasing burn-offs, the  $L_a$  increased up to 182 Å at the burn-off degree of 92%.

It was considered that the increasing of  $L_a$  as the burn-offs increased was caused by removal of atoms located at less ordered area. Therefore, it was assumed that the crystallinity of oxidized fibers became more ordered and the crystallites size of oxidized fibers became smaller than original fiber.

#### 3.2. Raman analysis

Fig. 2 shows the 1st-order Raman bands vary as a function of burn-off degrees of the HM fibers. In all cases the spectra exhibited the same appearance, that is, two well-resolved bands, namely D- ( $\sim 1330$   $\text{cm}^{-1}$ ) and G- ( $\sim 1580$   $\text{cm}^{-1}$ ) band. It seems that the bands of oxidized samples were not shifted from original fiber bands.

In Fig. 3 and Table 2 there were no significant shift exist between the each positions of the D- (1355.0 to 1357.0) and



**Fig. 3.** Peak positions of the HM fibers are not changed significantly as a function of burn-off degrees.

**Table 2.** Mean Values of the Peak Position, Peak Intensity, and  $R(=I_D/I_G)$  Values of the First-order D and G-band of the HM Fibers

Burn-off (%)	Peak Position (Mean)		Peak Intensity (Mean)		$R=I_D/I_G$ (Mean)
	D-band	G-band	D-band	G-band	
0	1356.8	1585.4	260.4	468.6	0.56
16	1356.2	1586.8	337.0	441.4	0.77
22	1355.0	1585.3	332.7	637.3	0.52
28	1357.0	1585.7	255.3	480.7	0.57
39	1357.7	1586.7	257.3	462.7	0.57
43	1356.0	1586.7	362.7	622.7	0.59
66	1356.3	1586.7	339.3	602.3	0.56
88	1357.0	1587.0	265.0	596.0	0.44
92	1357.0	1586.0	281.0	575.7	0.49

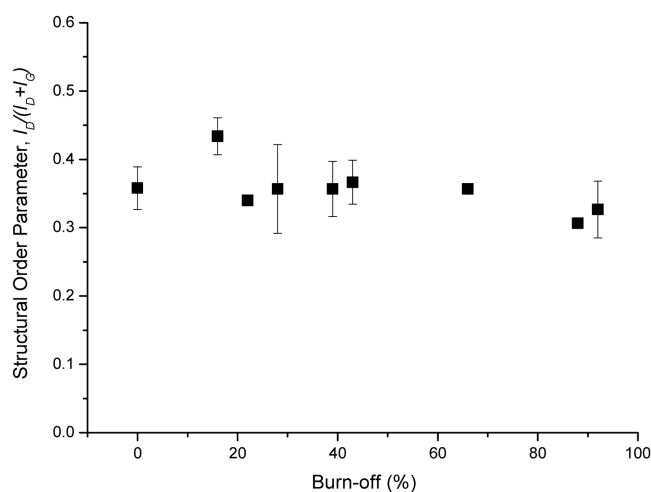
G-bands (1585.4 to 1587.0). The oxidation processes almost have no effect on the band positions and the intensities of the bands.

These results are quite different with results of isotropic fibers as shown in Table 3 [18]. The D-bands of isotropic fibers shifted from 1341.1 to 1358.7. These shifts indicate variation of ordering degrees. Especially it is explained that shifting toward lower wavelength number means the fiber goes to more disordering [19, 20].

Even the intensity ratios ( $R=I_D/I_G$ ) of D- and G-band of the HM fibers were varying in the range of 0.44 to 0.77, these were always lower values of isotropic fibers (0.86 to 0.93) as a function of burn-offs is not significant up to 66% burn-off with exception of 16% burn-off. The variation of R values of HM fibers as a function of burn-offs until 66% burn-off excepting 16%. However the R values slightly decrease at very high burn-offs, 88% and 92%. It could be explained that the reason of non-shifting of Raman bands of HM fibers are caused by well ordered structure of HM fiber.

**Table 3.** Structural Data of the Isotropic Fibers [18]

Burn-off (%)	Peak Position		Peak Intensity		$R=I_D/I_G$	$La(\text{\AA})$	
	D-band	G-band	D-band	G-band		Raman	XRD
0	1358.7	1590.1	216.7	251.5	0.86	23.2	23.6
39	1352.2	1594.0	234.8	270.9	0.87	23.1	-
59	1343.8	1590.2	659.7	721.6	0.91	21.9	22.7
79	1341.1	1597.1	829.3	888.1	0.93	21.4	20.4



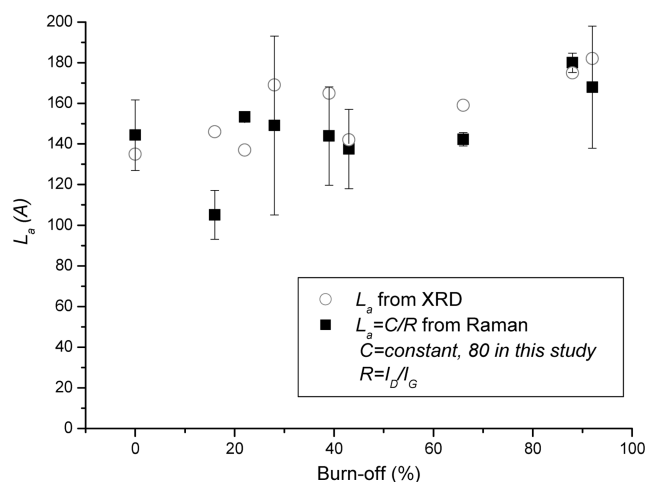
**Fig. 4.** Plots of the structural order parameter  $I_D/(I_D+I_G)$  of the HM fibers.

Since it has crystalline area, non-crystalline area, and mixed area the structure could be changed during oxidation process [21, 22].

In Fig. 4 structural order parameter of HM fibers oxidized more than 66% burn-off decreased slightly, which means fiber has changed to more ordering. In Table 1 La values obtained from XRD show that La increased over 66% burn-off. Therefore it could be suggested that the initial oxidation take place at less ordered area, the ordered area remains until final oxidation stage.

La values from Raman and XRD summarized in Table 4. The structural parameter La of the HM fibers obtained from Raman agrees well also with the structural parameters obtained from X-ray diffraction. Even though absolute values from Raman are usually lower than XRD, the La values from Raman analysis were calculated by using  $L_a=C/R$ , here  $R=I_D/I_G$  and constant C was 80 in this study.

For the isotropic fibers from previous study, it was suggested that each layer consisting of fibers became more disordered as the burn-off proceeded, and the layer stacking became imperfect [18]. From the Raman and the XRD result, it was considered that the decreasing of La as the burn-off increased, was caused by removal of carbon atoms at the edge of crystallites. The Lc and La values of the original fibers were 6.2 Å and 23.6 Å, representing stacks of less than two layer planes. With increasing burn-off, the interlayer spacing increased up to 4.76 Å and Lc increased



**Fig. 5.** Correlation of  $L_a$  values of the HM fiber between Raman and XRD result.

**Table 4.**  $L_a$  Values(mean) of the HM Fibers Obtained from Raman and XRD

Burn-off (%)	$L_a$ (Å)	
	Raman result ( $L_a = C/R$ , $C = 80$ )	XRD result (by Scherrer eq.)
0	144	135
16	105	146
22	153	137
28	149	169
39	143	165
43	137	142
66	142	159
88	179	175
92	167	182

up to 6.7 Å. So, the increasing of  $L_c$  caused merely widening of interlayer spacing. Therefore, it was cleared that the crystallites of activated fibers became more disordered and the size of crystallites of ACFs became smaller than original fibers. Isotropic fiber has the opened structure originally and could be an ACFs.

For the HM fibers, 002 interlayer spacing and  $L_a$  increased as burn-off increased. This results possibly explained by the oxidation process causing effect of heat treatment to the fiber. The effect of heat treatment during activation for the carbon materials has been reported by many researchers[24-27]. It is suggested that increase of  $L_a$  is caused by crystalline growth by heat treating effect during long time oxidation at high temperatures. Furthermore if the crystallinity of growth part was formed to be a poorly ordered, 002 interlayer spacing could be much larger.

The structural parameter  $L_a$  of the HM fibers obtained from Raman compares well also with the structural parameters obtained from X-ray diffraction in Table 4 and

Fig. 5. Fig. 5 shows there are some correlations between the  $L_a$  values obtained from Raman and XRD for the HM fiber. Also, for the isotropic fiber, it could be obtained same result between Raman analysis and XRD analysis.

#### 4. Conclusions

The structural changes of high modulus carbon fibers prepared by oxidation in carbon dioxide gas have been observed using laser Raman spectroscopy. The basic structural parameters of the fibers were evaluated by XRD as well, and compared with Raman results.

No significant shifts measured were observed between the each positions of the D-(1355.0 to 1357.0) and G-bands (1585.4 to 1587.0).

Raman analysis shows that R values slightly decreased at very high burn-offs (88% and 92%), and therefore  $L_a$  increased as burn-off increased. These results were possibly explained that the oxidation process affect the heat treatment to the fiber.

The  $L_a$  of the original HM fibers were measured to be 144 Å from Raman analysis and 135 Å from XRD analysis.  $L_a$  of the 92% oxidized fiber were 168 Å by using Raman and 182 Å by using XRD. The structural parameter  $L_a$  of the HM fibers obtained from Raman compares well also with the structural parameters obtained from X-ray diffraction.

However the  $L_a$  value changes of the high modulus carbon fiber through whole oxidation process showed opposite tendency as compared with the isotropic carbon fiber because of the fiber structure difference basically.

It is suggested there was some correlation between the  $L_a$  value obtained from Raman and XRD for the HM fiber. Also, for the isotropic fiber, same results could be obtained between Raman analysis and XRD analysis.

#### References

- [1] Endo, M.; Kim, C.; Kasai, T.; Mathews, M. J.; Brown, S. D. M.; Dresselhaus, M. S.; Tamaki, T.; Nishimura, Y. *Carbon* **1998**, *36*, 1633.
- [2] Hong, S. H.; Korai, Y.; Mochida, I. *Carbon* **2000**, *38*, 805.
- [3] Montes-Moran, M. A.; Young, R. J. *Carbon* **2002**, *40*, 845.
- [4] Donnet, J. B.; Bansal, R. C. "Carbon Fibers" 2nd ed., Marcel Dekker, New York, **1990**, 8.
- [5] Dami, T. L.; Manocha, L. M.; Bahl, O. P. *Carbon* **1999**, *29*, 51.
- [6] Ismail, M. K. *Carbon* **1991**, *29*, 777.
- [7] Mahajan, O. P.; Yarzab R.; Walker Jr. P. L. *Feul* **1978**, *57*, 643.
- [8] Sanchez, A. R.; Elguezabal, A. A.; Torre Saenz, L. L. *Carbon* **2001**, *39*, 1367.
- [9] Kasaoka, S.; Sakata, Y.; Kayano, S.; Masuoka, Y. *Int.*

- Chem. Eng.* **1983**, 23, 477.
- [10] Hu, Y. Q.; Nikzat, H.; Nawata, M.; Kobayashi, N.; Hasatani, M. *Fuel* **2001**, 80, 2111.
- [11] Rafsanjani, H. H.; Jashidi, E.; Rostam-Abadi, M. *Carbon* **2002**, 40, 1167.
- [12] Blanco, S. Lu, C.; Rand, B. *Carbon* **2002**, 40, 2002.
- [13] Sharma, A.; Kyotani, T.; Tomita, A. *Carbon* **2000**, 38, 1977.
- [14] Kovalevski, V. V.; Buseck, P. R.; Cowley, J. M. *Carbon* **2001**, 39, 243.
- [15] Senneca, O.; Salatino, P.; Masi, S. *Fuel* **1998**, 77, 1483.
- [16] Busyin, R. M.; Rouzaud, J. N.; Ross, J. V. *Carbon* **1995**, 33, 679.
- [17] Roh, J. S. *Carbon Science* **2004**, 5, 27
- [18] Roh, J. S. *Carbon Science* **2008**, 9, 127
- [19] Montes-Moran, M. A.; Young, R. J. *Carbon* **2002**, 40, 845.
- [20] Kuo, C. T.; Wu, J. Y.; Lu, T. R. *Materials Chemistry and Physics* **2001**, 72, 251.
- [21] Lespade, P.; Al-Jishi, R.; Dresselhaus, M. S. *Carbon* **1982**, 20, 427.
- [22] Escribano, R.; Sloan, J. J.; Siddique, N.; Sze, N.; Dudev, T. *Vibrational Spectroscopy* **2001**, 26, 179.
- [23] Montes-Moran, Miguel A.; Young, Robert J. *Carbon* **2002**, 40, 845
- [24] Kamegawa, K.; Nishikubo, K.; Yoshida, H. *Carbon* **1998**, 36, 433.
- [25] Sharma, A.; Kyotani, T.; Tomita, A. *Fuel* **1999**, 78, 1203.
- [26] Yoshizawa, N.; Maruyama, K.; Yamada, Y.; Zielinska-Blajet, M. *Fuel* **2000**, 79, 1461.
- [27] Gondy, D.; Ehrburger, P. *Carbon* **1997**, 35, 1745.