

# RAMAN SPECTRUM OF MODIFIED PAN-BASED CARBON FIBERS DURING GRAPHITIZATION

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## Introduction

In the past, we have modified PAN fibers with potassium permanganate, shortened the oxidation time[1-4], enhanced the tensile strength of the carbon fibers[5], and studied the changes in the physical properties and microstructure of fibers during the process of oxidation[6]. In this article, the study is focused on the changes in the microstructure of PAN graphite fibers during the graphitization process. These changes are noted by using wide-angle X-ray diffraction and the Raman spectrum.

## Experimental

A special grade of acrylic fiber, Courtelle fiber (Courtaulds Ltd., UK.), containing 6% methyl acrylate and 1% (itaconic) acid copolymer was used in this work. A single tow of Courtelle fiber contains 6000 strands of 1.1 denier monofilament. A fiber-wound frame was pretreated by immersing it in a 7% potassium permanganate solution at 85 C for 2 min, then washed with distilled water and dried to a constant weight in an oven.

Stabilization of the precursor was carried out in a constant temperature zone furnace with a fixed length method at 230 C for 7h, in a purified air atmosphere. The stabilized fibers were carbonized to 1300 C at a rate of 240 C/h, from 25 to 1300 C, in a ceramic reaction tube and an oxygen-free nitrogen atmosphere. The carbonized fibers were graphitized to 2800 C at a rate of 15 C/min, from 25 C to 2800 C under Ar flow. Neither tension nor load were applied to the fibers during this process. The samples were heated in this way at different temperatures from 1400 C to 2800 C, at 200 C intervals.

A Rigaku X-ray diffractometer, providing Ni-filtered  $\text{Cu K}\alpha$  radiation, was used to measure the crystalline related properties of the sample. The Raman scattering measurement was performed at room temperature under a nitrogen atmosphere using a 514.5 nm line of an argon ion laser as the incident radiation. The scattered light was collected at a right angle to the incident beam, analyzed by a double-grating monochromator and detected by a cooled photomultiplier tube.

## Results and Discussion

In general, carbon materials have two specific

absorption bands in the Raman spectrum---1580~1600  $\text{cm}^{-1}$  and 1350~1380  $\text{cm}^{-1}$ , respectively[7,8], as shown in Figures 1 and 2. As the heat treatment temperature rises, the non-crystalline carbon is gradually stacked on the crystalline region. The absorption peak intensity at 1360  $\text{cm}^{-1}$  gradually reduces while the absorption peak intensity of the former (1580  $\text{cm}^{-1}$ ) conversely increases with the absorption peak rises. Thus, the ratio of the peak intensity at 1360  $\text{cm}^{-1}$  to that at 1580  $\text{cm}^{-1}$  and the widths of both peaks are typical parameters to quantify the degree of disorder in carbon materials, as shown in Figure 3. The value of the degree of disorder in carbon materials decreases, which indicates that the degree of graphitization increases in these materials. The degree of graphitization of the fibers increases as the graphitization temperature rises. Between 1800-2000 C, the ratio of the intensity conversely increases very slightly, due to the fracture of the microcrystals at the edges of the graphite layers. Above 2200 C, the graphite layers are more easily displaced and gradually stack in a parallel fashion. This leads to the sharp increase in the degree of graphitization. It is observed from Figure 2 that the degree of graphitization of the graphite fibers which were developed from pre-treated PAN fibers is higher than that of those developed from the original PAN fibers after 2200 C. This indicated that the catalytic graphitization of carbon by Mn is easily influenced by experimental temperature. After 2200 C, manganese as a catalyst promoted the catalytic graphitization process. This temperature, 2200 C, was defined the structure transitional temperature.

For PAN fibers which have undergone oxidation and carbonization treatments, the composition of the non-carbon elements have been evolved and exhausted. The crux of graphitization engineering is the elimination of the nitrogen element. Prior to the structure transitional temperature (2200 C), the effect of temperature is mainly conducive to the growth of the graphite-like structure. After the structure transitional temperature, the graphite planes produce tremendous heat vibration due to the high temperature, which leads to a denser and a more uniform arrangement of the graphite structure[5]. The stacking height,  $L_c$ , or crystal thickness, in the graphite layers increases along with the rise in temperature, as shown in Figure 4. This figure shows that above the transitional temperature, the stacking rate of the graphite layers is faster than below the transitional temperature. The stacking high of the graphite fibers developed by modified PAN fibers and original PAN fibers are valued at 8.014

nm and 7.431 nm, respectively. When the temperature rises, the high energy promotes parallel self arrangement along the fiber axis. At 2800 C, the preferred orientation of untreated and pre-treated fibers is 97.3% and 97.6%.

The elastic modulus of graphite fibers is primarily related to the preferred orientation of the fibers and the size of the crystals. The elastic modulus of untreated and pre-treated graphite fibers at 2800 C is 753 and 877 GPa, respectively. At the transitional temperature, the fibers have a moderately elastic modulus. As the temperature rises, the elastic modulus sharply increases. Those fibers pre-treated with potassium permanganate have a higher elastic modulus.

### Conclusions

As the graphitization temperature increases, non-crystalline carbon layers gradually stack on to the crystalline region. As the degree of graphitization increases, the fibers gravitate toward graphite crystals. Prior to the structure transitional temperature, the effect of the temperature is primarily conducive to the growth of the graphite-like structure. As shown by the Raman spectrum and the wide-angle X-ray diffraction analysis, manganese has a catalyzing effect in graphitization, thereby enhancing the mechanical properties of the graphite fibers.

### Acknowledgments

This work was supported by National Science Council of Republic of China (NSC83-0405-E-035-011).

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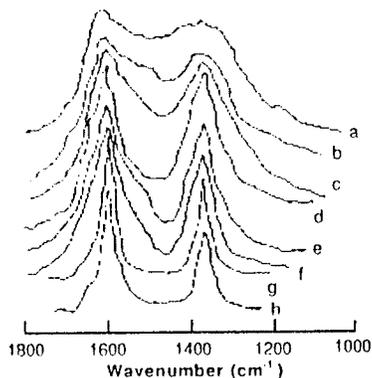


Figure 1 Raman spectra of graphite fibers which were developed from original PAN fibers then carbonized at (a)1400 C; (b) 1600 C; (c) 1800 C; (d) 2000 C; (e) 2200 C; (f) 2400 C; (g) 2600 C; (h) 2800 C.

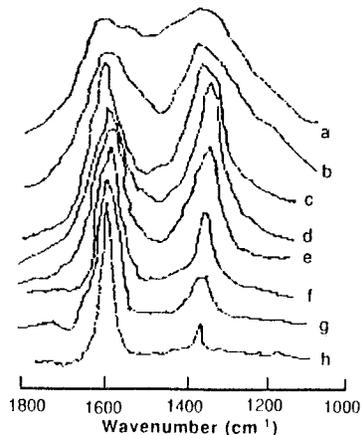


Figure 2 Raman spectra of graphite fibers which were developed from modified PAN fibers then carbonized at (a)1400 C; (b) 1600 C; (c) 1800 C; (d) 2000 C; (e) 2200 C; (f) 2400 C; (g) 2600 C; (h) 2800 C.

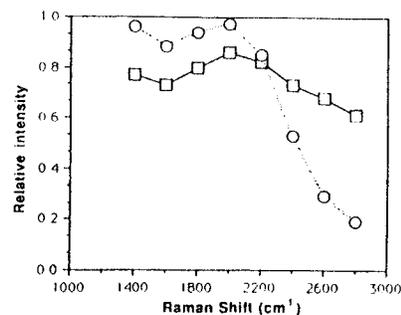


Figure 3 Relation between the ratio  $I_{1360}/I_{1580}$  of graphite fibers and graphitization temperature; graphite fibers developed from: (□) original PAN fibers; (○) modified PAN fibers.

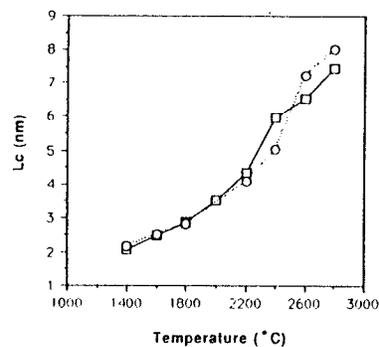


Figure 4 Variation of stacking size ( $L_c$ ) of graphite fibers with different graphitization temperature; graphite fibers developed from: (□) original PAN fibers; (○) modified PAN fibers.