

Raman Spectrum of Modified PAN-Based Carbon Fibers During Graphitization

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SYNOPSIS

Graphite fibers were developed from polyacrylonitrile (PAN) fibers which were modified with potassium permanganate. After the transitional temperature, the formation of graphite structures commenced, the crystals increased in thickness, and the preferred orientation of the fiber crystals increased. The Raman specific absorption peak of noncrystalline carbon layers (1360 cm^{-1}) weakened with the increase in the graphitization temperature, whereas the degree of graphitization rose. The results of this analysis indicate that manganese has the effect of catalyzing graphitization, thus increasing the mechanical properties of the graphite fibers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Carbon fibers are now important industrially and have gained a wide range of applications, from sports products to items used in the aerospace industry. Polyacrylonitrile (PAN) fibers have been found to be the most suitable precursors for making high-performance carbon fiber.¹⁻³ Because of their various technological applications in the industrial and engineering fields, the development of high-strain and high-modulus carbon fibers has become necessary. Bahl and his co-workers pretreated precursors with CuCl to make high-performance carbon fibers.⁴ Cagliostro⁵ modified precursors with benzoic acid to improve the tensile strength of carbon fiber.

EXPERIMENTAL

In the past, we have modified PAN fibers with potassium permanganate, shortened the oxidation time,⁶⁻⁹ enhanced the tensile strength of the carbon fibers,¹⁰ and studied the changes in the physical properties and microstructure of fibers during the process of oxidation.¹¹ 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.

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 immersion in a 7% potassium permanganate solution at 85°C for 2 min, then was washed with distilled water and oven-dried to a constant weight. The manganese content in the resulting carbon fibers was determined using an atomic emission spectrometer. After the modification process,⁶ the content of manganese in the fiber had increased about 60 times over its original content.

Stabilization of the precursor was carried out in a constant-temperature-zone furnace with a fixed-length method at 230°C for 7 h in a purified-air atmosphere. The stabilized fibers were carbonized to 1300°C at a rate of $240^{\circ}\text{C}/\text{h}$, from 25°C 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 $15^{\circ}\text{C}/\text{min}$, 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 step-scan method was used to determine the d spacing and stacking size (L_c , stacking height of layer planes); the step-interval was set at 0.02 degrees. The preferred orientation of the PAN fibers (001) and the carbon fibers $O(002)$ was determined by an X-ray diffractometer with a fiber-specimen attachment. The precursors were located at around 17 degrees (2θ) and the carbon fibers were set at around 25 degrees (2θ) [the (002) plane of carbon fibers is thought to have a hexagonal structure]. The 360-degree azimuthal circle was used to allow the fiber axis to be rotated 360 degrees about the vertical. The d spacing, L_c , and $O(002)$ were calculated by using eqs. (1) (the Bragg equation), (2) (the Scherrer equation), and (3), respectively.

$$n\lambda = 2d \sin \theta \quad (1)$$

$$L(hkl) (\text{in nm unit}) = K\lambda/B \cos \theta \quad (2)$$

$$O(hkl) (\text{in } \%) = [(360 - H)/360]100 \quad (3)$$

in which $\lambda = 0.154 \text{ nm}$, K is the apparatus constant ($= 1.0$), and B is the half-value width in the radian of the X-ray diffraction intensity (I) versus 2θ curve. H is the half-value width in degrees of the curve of (I) versus azimuthal angle.⁶ The preferred orientation, $O(002)$, has a value of 0% if the specimen is completely unoriented. If the crystalline properties are all perfectly parallel to one another, it has a value of 100%.

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 cm^{-1} and 1350–1380 cm^{-1} , respectively, as shown in Figures 1 and 2. The former was observed in single crystals of graphite and assigned to a doubly degenerate deformation vibration of the hexagonal ring corresponding to the E_{2g} mode of graphite with D_{6h}^4 crystal symmetry.^{12,13} The latter is produced by the defect-inducing vibration mode, i.e., the non-crystalline carbon-specific absorption band. As the

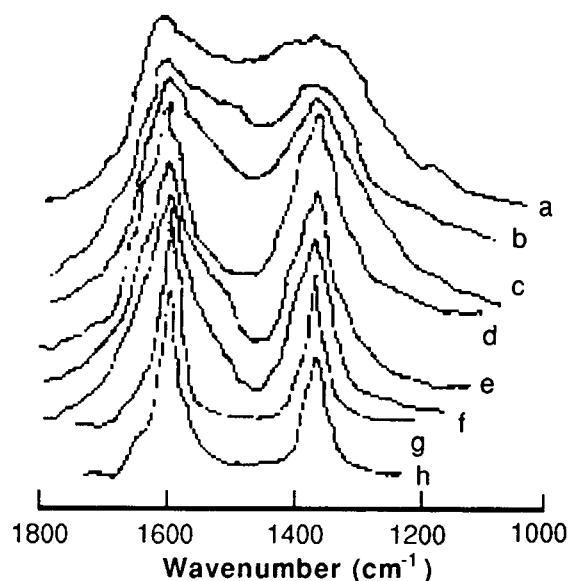


Figure 1 Raman spectra of graphite fibers which were developed from original PAN fibers then carbonized at (a) 1400°C, (b) 1600°C, (c) 1800°C, (d) 2000°C, (e) 2200°C, (f) 2400°C, (g) 2600°C, and (h) 2800°C.

heat-treatment temperature rises, the noncrystalline carbon is gradually stacked on the crystalline region. The absorption peak intensity at 1360 cm^{-1} gradually reduces while the absorption peak intensity of the former (1580 cm^{-1}) conversely increases with the absorption peak rise. Thus, the ratio of the peak intensity at 1360 cm^{-1} to that at 1580 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 pretreated PAN fibers is higher than that of those developed from the original PAN fibers after 2200°C. This indicates that the catalytic graphitization of carbon by manganese is easily influenced by experimental temperature. After 2200°C, manganese as a catalyst promoted the catalytic graphitization process. This

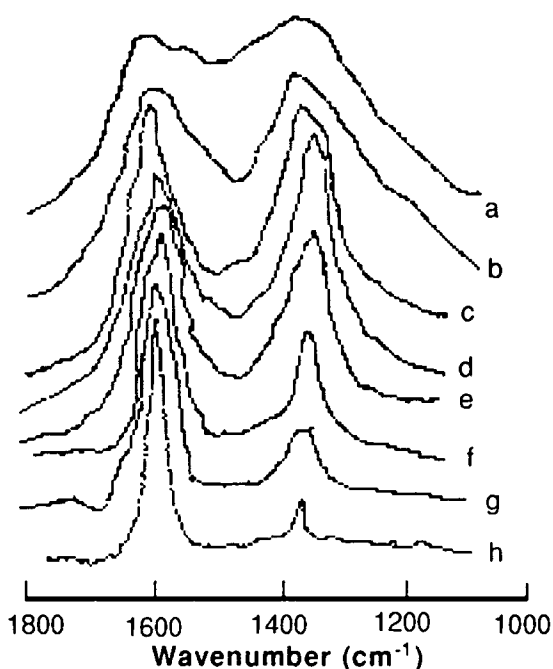


Figure 2 Raman spectra of graphite fibers which were developed from modified PAN fibers then carbonized at (a) 1400°C, (b) 1600°C, (c) 1800°C, (d) 2000°C, (e) 2200°C, (f) 2400°C, (g) 2600°C, and (h) 2800°C.

temperature, 2200°C, was defined as the structure transitional temperature.

For PAN fibers which have undergone oxidation and carbonization treatments, the compositions with noncarbon elements have been evolved and exhausted: the crux of graphitization engineering is the elimination of the nitrogen element. Prior to the

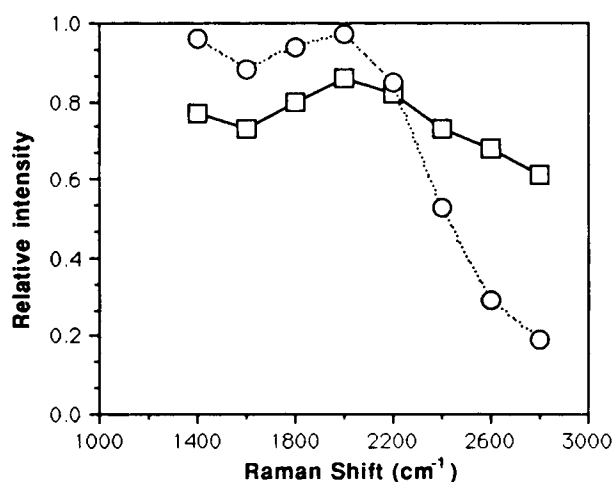


Figure 3 Relation between the ratio I_{1360}/I_{1580} of graphite fibers and graphitization temperature; graphite fibers developed from (□) original PAN fibers and (○) modified PAN fibers.

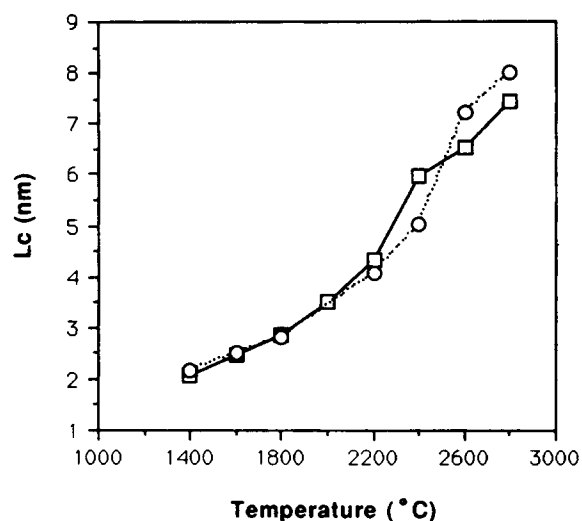


Figure 4 Variation of stacking size (L_c) of graphite fibers with different graphitization temperatures; graphite fibers developed from (□) original PAN fibers and (○) modified PAN fibers.

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.¹⁰ The structural parameters of graphite fibers were studied by wide-angle x-ray diffraction. The graphite layer spacing was measured according to

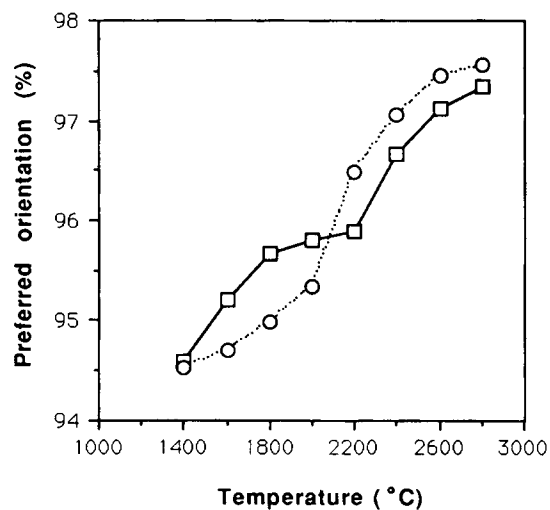


Figure 5 Variation of preferred orientation of graphite fibers with different graphitization temperatures; graphite fibers developed from (□) original PAN fibers and (○) modified PAN fibers.

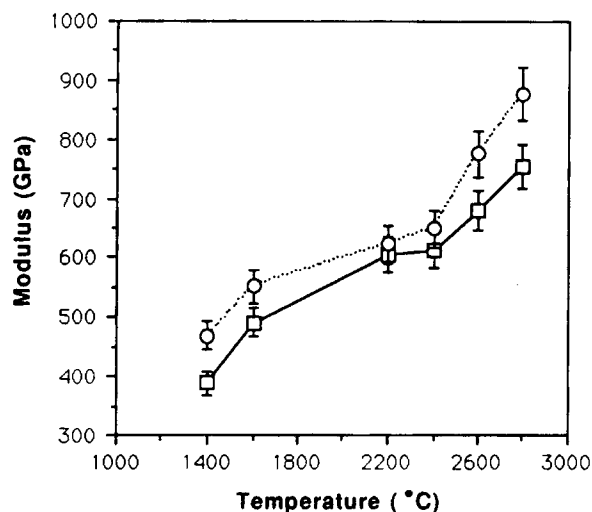


Figure 6 Relation between elastic modulus of graphite fibers and graphitization temperature; graphite fibers developed from (□) original PAN fibers and (○) modified PAN fibers.

the Bragg formula. 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 heights of the graphite fibers developed by modified PAN fibers and the 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, as shown in Figure 5. At 2800°C, the preferred orientation of untreated and pretreated fibers is 97.3% and 97.6%, respectively.

The elastic modulus of graphite fibers is primarily related to the preferred orientation of the fibers and the size of the crystals. Figure 6 shows the changes in the elastic modulus of the fibers during the graphitization process. The elastic moduli of untreated and pretreated graphite fibers at 2800°C are 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 pretreated with potassium permanganate have a higher elastic modulus.

CONCLUSION

As the graphitization temperature increases, non-crystalline carbon layers gradually stack onto the

crystalline region. As the degree of graphitization increases, the fibers gravitate toward graphite crystals. Prior to the structure transitional temperature, the temperature effect is primarily conducive to the growth of the graphitelike structure. After the structure transitional temperature, the graphite plane stacking becomes denser and the arrangement is preferentially parallel. Prior to the transitional temperature, the increases in the crystal thickness, preferred orientation, and elastic modulus of the fibers are moderate. After the transitional temperature, as the formation of the graphite structure commences, the crystal thickness, preferred orientation, and elastic modulus sharply increase. 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.

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