Raman Spectroscopic Study of the Microstructure of Carbon Films Developed from Cobalt Chloride-Modified Polyacrylonitrile

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ABSTRACT: Polyacrylonitrile (PAN) was modified with cobalt chloride at 90°C for 5 min. The carbon films prepared from original and modified PAN films were carbonized up to 1300°C. The structure of the resulting carbon film was studied using X-ray diffraction and Raman spectroscopy. The stacking size obtained from X-ray diffraction approaches the L_c value of the resulting carbon films as the heat treatment temperature increased. The mean average carbon basal planes in crystalline (Lc/d) also increased with increasing pyrolysis temperature. Raman spectra confirmed the progressive structural ordering as treatment temperature increased. During pyrolysis, a substantial decrease in the intensity of the band near the 1350 cm^{-1} region was observed, indicating a decrease in the disordered structure. The crystal size (L_a) of the resulting carbon films also showed a remarkable increase with increased heat treatment temperature. The resulting carbon films developed from the modified PAN films had higher L_c and L_a than those developed from the original PAN film. It was established that cobalt catalyzes graphitization of amorphous carbon during pyrolysis. This modification not only promoted the growth of crystal size but also increased the close packing of the carbon basal planes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2219-2225, 1999

Key words: polyacrylonitrile (PAN); carbon film; Raman spectroscopy

INTRODUCTION

Polyacrylonitrile (PAN) is an attractive material as the precursor of carbon in various forms. It was well known that PAN fibers are good precursors for carbon fibers.^{1–6} Recently, several researchers have prepared carbon films from PAN.^{7–9} Carbon films have interesting physical properties (e.g., high conductivity, optical anisotropy, and high radiation resistance) and, therefore, can be applied as a useful material in the fields of advanced technology.

Before pyrolysis of PAN fibers or films, stabilization is necessary to obtain high-quality carbon. In this process, a lower temperature treatment (200°-300°C) in air (or in an oxygen-containing atmosphere) leads to the formation of ladder polymer.¹⁰ In the study of carbon fibers or films, the step of forming ladder polymers is very important, because it influences the physical properties and microstructure of the final carbon fibers and films.¹¹ We have found that a longer stabilization period promotes an increased number of ladder polymer structures in the stabilized film.⁹ We also found that the carbon films developed using a longer stabilization time have a greater density, greater carbon layer plane stacking height, lower carbon content, higher nitrogen content, and higher electrical conductivity. For greater im-

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provement in performance, carbon films have been developed from cobalt chloride-modified PAN film. In this research, the changes in the microstructure of carbon films during carbonization were studied using Raman spectroscopy and wide-angle X-ray diffraction. Useful information was acquired concerning the interaction of cobalt with carbon and its subsequent promotion of the formation of carbon basal planes in the resulting carbon film.

EXPERIMENTAL

PAN films were solvent cast from dimethylformamide (DMF) solutions with a concentration of 2.5 g/40 mL. PAN was 150,000 MW, obtained from Courtaulds Ltd. (UK). The films were spun on 18 cm \times 20 cm quartz plates. The film thickness was controlled to near 35 μ m. The original films were modified by immersing them in a 5% cobaltous chloride solution at 90°C for 5 min, then washed with distilled water, and dried to a constant weight in an oven. The cobalt content in the resulting films was determined by atomic emission spectrometer analysis. The content of the cobalt in the film had increased to \sim 40 times over its original content after the modification process.

Oxidization of the two PAN films was conducted in a constant temperature zone furnace with a purified air atmosphere at 220°C for 6 h. The resulting stabilized films developed from the original and modified PAN films were named films A and B, respectively. The oxidized films were carbonized up to 1300°C at a rate of increase of 240°C h⁻¹, from 25° to 1300°C, in a ceramic reaction tube and an oxygen-free nitrogen atmosphere. The specimens were cooled immediately.

A Model 8536 Diano X-ray diffractometer, providing Ni-filtered CuK α 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°. The *d* spacing and L_c were calculated using eq. (1) (the Bragg equation) and eq. (2) (the Scherrer equation), respectively:

$$n\lambda = 2d\,\sin\,\theta\tag{1}$$

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

in which $\lambda = 0.1542$ nm, *K* is the apparatus constant (=1.0), and *B* is the half-value width in the

Table I	Properties	of Stabilized	Films
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Sample Code	Developed from	${I_{1600}}/{I_{2400}}_{(\%)}$	AI (%)
Film A Film B	Original PAN film Modified PAN film	$\begin{array}{c} 1.47 \\ 1.77 \end{array}$	$\begin{array}{c} 41.38\\ 46.67\end{array}$

radian of the X-ray diffraction intensity (I) vs. 2θ curve.

The Raman spectrometer used herein was a Renishaw instrument with Raman imaging microscope system 2000, using a 514.5 nm line of an argon ion laser as the incident radiation. Samples were analyzed without any treatment or preparation. The scatted light was analyzed using a double-grating monochromator and detected by a cooled photomultiplier tube.

RESULTS AND DISCUSSION

Properties of Samples

The samples used were original PAN film and modified PAN film, stabilized at 220°C for 6 h. Film A was developed from the original PAN film, and film B was developed from the modified PAN film. The properties of the films before carbonization are given in Table I.

The infrared spectrum for the PAN films contains prominent peaks at 2930 and 2240 cm⁻¹ due to stretch vibration of the methylene (CH_2) and the nitrile (C=N) groups. When PAN films are heat-treated above 180°C, the molecular chains will unfold and move around. The C=N bond originally in the structure will transform into a C=N bond and form the ladder polymer. The peak at 1600 cm^{-1} is due to the C=N group. The strength of the peak of the C=N group (1600 cm^{-1}) increases along with an increase in the degree of stabilization, whereas the peak strength of the C=N group (2400 cm⁻¹) decreases. Thus, the ratio of I_{1600}/I_{2400} can be used as the index of cyclization.¹² In addition, in the X-ray diffraction studies, along with a gradual increase in the degree of stabilization, the diffraction peak at the 2θ $= 17.5^{\circ}$ position in the original PAN film slowly disappears and is replaced by the ladder structures at $2\theta = 26.5^{\circ}$. That is, ladder polymer structures are gradually formed as the stabilization reaction progresses. Therefore, the aromatization index (AI) is used as the reference values for the



Figure 1 Wide-angle X-ray diffraction pattern of carbon films (film A) developed from original PAN.

degree of stabilization.^{6,13} The AI was measured by the following formula¹³:

AI (%) =
$$\frac{I_a}{I_a + I_p}$$
 (3)

in which I_a is the diffraction pattern given by the ladder polymers at $2\theta = 25^{\circ}$, and I_p is the diffraction by the PAN crystal at $2\theta = 17.5^{\circ}$.

Table I shows that film B has a greater I_{1600}/I_{2400} ratio and a greater AI value. It is indicated that film B has more ladder polymer in its film than film A. This is due to the modified PAN films having a lower ordered phase than the original. According to our measurement of the crystal size, the original PAN film is 3.0 nm, and the modified one is 2.7 nm. This indicates that the modified PAN film had a greater disordered phase than the original. Therefore, the diffusion of oxygen became easier in the modified PAN film than the original during stabilization. That is why the modified PAN film had more ladder polymers than the original.

X-ray Diffractometer Studies

Figures 1 and 2 represent the X-ray diffraction profiles of the films carbonized from 300° to 1300°C. At 300°C, both films showed a broader peak at 2θ from 10° to 30°. This peak resulted from the mixing of the original PAN structure and the ladder polymers, which were transformed from the PAN structure. At 500°C the structure at $2\theta \approx 25^{\circ}$ occurred because of the (002)-like reflection of the carbon basal planes in the films. This peak became narrower and intensified with increasing temperature. This was due to the lengthening and broadening of the carbon basal planes from ladder polymers in the stabilized films during carbonization. When both stabilized films were carbonized above 900°C, they exhibited a broad peak at 2θ between 40° and 50° , corresponding to (10L) reflection of the turbostractic carbon structure. The intensity of this peak increased simultaneously with increasing temperature.

The stacking size, L_c , crystal thickness, increases along with the rise in temperature, as shown in Figure 3. The carbon films developed



Figure 2 Wide-angle X-ray diffraction pattern of carbon films (film B) developed from modified PAN.



Figure 3 Variation of stacking height of resulting carbon films as function of carbonization temperature: (\Box) film A; (\bigcirc) film B.

with modified PAN film had a greater stacking size than those developed from the original PAN films during pyrolysis. At the carbonization temperature of 1000°C, the value of L_c for film A is 1.9705 nm, whereas that of film B is 2.0984 nm, as shown in Table II. The carbon film developed from the modified PAN film had a higher stacking size (L_c) and a greater mean number of carbon basal planes (L_c/d) than those developed from the original PAN film. This suggested that cobalt catalyzes the graphitizing of carbon and promotes the packing of carbon basal planes during pyrolysis.

Raman Spectra Analysis

The Raman spectrum of single hexagonal crystal graphite (space group D_{6h}^4) presents a main firstorder E_{2g_2} band at 1582 cm⁻¹ with weaker bands at 42 (E_{2g_1}) and 2724 cm⁻¹ (see refs. 14 and 15). The mode at 1582 cm⁻¹, often referred to as the G mode, is assigned to "in-plane" displacement of the carbon strongly coupled in the hexagonal sheets. Its shifts and line-width variations are indications of the defects of the lattice. It has also been suggested that the spectrum of well-crystallized graphites formed of small grain size (polycrystalline) is present in the band near 1357 cm⁻¹. This mode is usually called the "disorderinduced" or D mode. To improve the accuracy in the determination of spectroscopic parameters, a curve fitting was carried for each spectrum. The best fitting was invariably obtained for the samples with two Lorentzian lines ~ 1357 and 1582 $\rm cm^{-1}$ and a broad Gaussian band at $\sim 1550~\rm cm^{-1}.$ This broad feature was assigned to the amorphous graphitic phase. 14,16,17

All of the Raman spectra of stabilized films during pyrolysis show two strong wide bands near 1582 and 1357 cm $^{-1}$ and a broad band \sim 1500- 1550 cm^{-1} , as shown in Figure 4. The line located near 1582 cm^{-1} is due to the graphitic structure, whereas that near 1357 cm^{-1} is due to a disordered structure in carbon. The intensity of the disordered structure (D mode) decreases during pyrolysis, which indicates that the graphitic structure (G mode) increases in the resulting carbon films. It is also known that an increase of order in carbon is reflected by an increase in the frequency of the G mode, as well as a decrease of its bandwidth.^{17,18} The G mode of the resulting carbon film increases as the carbonization temperature rises. The bandwidth of the G mode of the resulting carbon film developed from the modified PAN film is narrower than that developed from the original. This indicates that the modified PAN-based carbon films have a higher crystalline degree of graphitic carbon than those developed from the original PAN film.

When comparing the intensity of the D band to that of G band, I(D)/I(G), the resulting carbon films developed from the modified PAN films show a lower value than those developed from the original PAN films during pyrolysis, as shown in Figure 5. The resulting carbon films developed from the original PAN film have higher values, indicating that these samples have a higher degree of amorphous phase during pyrolysis. This amorphous contribution may be correlated to interstitial disorder. This indicates that the modification will promote the formation of graphitic carbon in the resulting carbon films.

The chemical reactions of PAN at the carbonization stage will cause the evolution of a large amount of gases. Several authors¹⁰⁻¹² have reported that dehydrogenation will occur at a temperature between 400°–600°C, whereas denitrogenation will occur at a temperature between 600° –1300°C, forming H₂O, HCN, H₂, N₂, CO,

Table IIX-ray Diffraction Parameters ofCarbon Films (Carbonized at 1300°C)

Film	2θ	d (nm)	$L_c~({ m nm})$	L_c/d	$L_a \ ({\rm nm})$
A B	$25.23 \\ 25.19$	$0.3527 \\ 0.3532$	$1.9705 \\ 2.0984$	$5.6 \\ 5.9$	$1.1691 \\ 1.2676$



Figure 4 Raman spectra of carbon films after various pyrolysis; carbon films developed from original PAN (film A) and carbonized at (a) 900°C; (b) 1100°C; (c) 1300°C; these developed from modified PAN (film B) and carbonized at (d) 900°C; (e) 1100°C; (f) 1300°C.

 CO_2 , and NH_3 , which are cracked from the main chain and escape as volatiles. Between the temperatures of 500°–1000°C, HCN and N_2 are formed from the intramolecular interaction and volatilized, which causes the gradual transformation of the ladder structure into carbon basal planes, which lengthen and broaden along with the degree of carbonization. Therefore, the formation of carbon basal planes increases with an increase in the carbonization temperature. In this process, crystalline is lengthened and broadened. This rearrangement of crystalline lead to a decrease in the disordered structure (D mode) and an increase in the graphitic structure (G mode).

The microcrystalline planar crystal size (L_a) can be calculated using eq. 4 (see ref. 19):

$$L_a = 44[I(D)/I(G)]^{-1}$$
(4)

where I(D) and I(G) are the integrated intensities of the D and G bands, respectively.

The crystal size L_a of the resulting carbon films during pyrolysis calculated from eq. (4) is shown in Figure 6. The L_c of both samples increases with an increase in the carbonization temperature. This is due to lengthening and broadening of the carbon basal planes. The samples show a low microcrystalline planar size. The value of L_a is not > 1.5 nm. However, as expected, the resulting carbon films developed from the modified PAN films have a greater crystal size than those developed from the original. When both films were carbonized at 1300°C, the L_a is 1.17 nm and 1.27 nm for films A and B, respectively.

When comparing the values of L_c and L_a for both films heated from 900° to 1300°C, the resulting carbon films developed from the original PAN increase by 18% and 53%, and those developed from the modified PAN film increased 23% and 57% in L_c and L_a , respectively. This study indicated that the resulting carbon films developed from the modified PAN film not only increased the stacking size (L_c) and the mean average carbon basal plane (L_c/d) , but also increased the crystal size (L_a) . According to the findings of several authors,^{19,20} the cobalt ions in the carbon layer will form intercalation compounds. The cobalt acted as catalyst, promoting the crosslinking of the ladder polymer and increasing the lengthening and broadening of the carbon basal planes. These reactions not only promoted the increase in crystal size, but also increased the close packing of the carbon basal planes.



Figure 5 Relationship between the ratio I(D)/I(G) of resulting carbon films and pyrolysis temperature: (\Box) film A; (\bigcirc) film B.



Figure 6 Variation of crystal size of resulting carbon films as function of carbonization temperature: (\Box) film A; (\bigcirc) film B.

CONCLUSIONS

Changes in the microstructure of the carbon films developed from original and modified PAN film were revealed by X-ray diffraction and Raman spectroscopy. We can draw the following conclusions:

- 1. The stacking size and crystal size of the resulting carbon films increase with increasing pyrolysis temperature.
- 2. The disordered structure decreases and the ordered structure increases during pyrolysis. Cobalt catalyzes the graphitization of amorphous carbon during pyrolysis. This reaction not only promotes the increase of crystal size, but also increases the close packing of the carbon basal planes.
- 3. The resulting carbon films developed from the modified PAN films have greater crystal size than those developed from the original. When both films were carbonized at 1300°C, the L_a was 1.17 nm and 1.27 nm for that developed from the original and modified PAN films, respectively.

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