

Improvement in the Properties of PAN-Based Carbon Films by Modification with Cobaltous Chloride

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ABSTRACT: Carbon films were developed from polyacrylonitrile (PAN) modified with cobalt chloride. The modification was carried out by immersing PAN in a 5% cobaltous chloride (CoCl_2) solution at 90°C for 5 min, oven-dried, and then manufactured into films. The original and modified PAN films were oxidized at 220°C for 2 and 6 h in air, respectively, and finally carbonized at 1300°C . The density, microstructure, elemental analyzer, electrical conductivity, and morphology were all studied. According to the results, it was found that films modified with cobalt chloride have a greater stacking height of carbon-layer planes (L_c), density, electrical conductivity, and nitrogen content after carbonization. Moreover, during the carbonization stage, the cobalt ions promote a catalytic action. The carbon films developed from the modified film not only improved electrical conductivity by 12–38%, but also increased tensile strength by 29–36% and the tensile modulus by 69–110%. Therefore, carbon films having better mechanical properties can be obtained after such modification. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1745–1751, 1999

Key words: carbon films; cobaltous chloride; modification; oxidation; carbonization

INTRODUCTION

Carbon films have been designated for use as a shield material for electromagnetic waves, as electrodes in cells, and as a covering material for motors, electrical devices, and other equipment. High polymer carbon films made by thermal pyrolysis of organic polymers have been used extensively.^{1–18} In a study of the polyimide film “Novax” conducted by Li et al.,¹⁷ it was found when that carbon films were carbonized above 800°C the electrical conductivity increased and that this property is enhanced with an increase in temperature. In Kyotani et al.’s study¹⁸ of potassium–graphite intercalation compounds (K-GIC) from

carbon films, it was found that intercalation strongly influences the stacking height (L_c) of carbon basal planes in the carbon films.

This study on PAN-based carbon films was undertaken in view of the research experiments conducted in our laboratories on PAN fibers used as a precursor for producing high-performance carbon fibers.^{19–24} It is also known that the longer the oxidation time the more ladder polymer structures are formed and that carbon films with better mechanical properties can be obtained.²⁴ The previous studies revealed that low-temperature oxidation treatment (200 – 300°C) of PAN fibers in air will produce a cyclization reaction which leads to the formation of ladder polymer structures.^{25,26} In our previous studies on PAN fibers modified with cobaltous chloride,²³ the modified PAN fibers had a higher stacking height (L_c) after oxidation and carbonization. We also found that PAN fibers modified with cobaltous chloride improved the tensile strength of the resulting carbon fibers.

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Table I Ratio of the Bands of the IR Spectra ($I_{1600/2400}$) in Oxidized Films

| Procedure | Films | | | |
|------------------|-------|------|------|------|
| | A | B | C | D |
| Modification | No | No | Yes | Yes |
| Oxidized for (h) | 2 | 6 | 2 | 6 |
| $I_{1600/2400}$ | 1.10 | 1.47 | 1.38 | 1.77 |

In this study, polyacrylonitrile (PAN) was modified with an aqueous solution of cobalt chloride and then manufactured into PAN films, which were then subjected to oxidation and carbonization treatments and subsequently prepared into oxidized films and carbon films. The effect of modification and oxidation on the density, elemental composition, stacking height of carbon layer planes (L_c), electrical conductivity, and mechanical properties of PAN films during carbonization were studied.

EXPERIMENTAL

PAN films were solvent-cast from dimethylformamide (DMF) solutions, with a concentration of 2.5 g/40 mL. PAN was 150,000 g/mol (MW), obtained from Courtaulds Ltd. (U.K.). Films were spun on 18×20 -cm quartz plates. The film thickness was controlled to near $35 \mu\text{m}$. The original films were modified by immersing them in a 5% cobaltous chloride solution at 90°C for 5 min; then they 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 cobalt in the film had increased about 40 times over its original content after the modification process.

The oxidization of the two PAN films was carried out in a constant temperature-zone furnace with a purified air atmosphere, at 220°C for 2 and 6 h, respectively, as shown in Table I. The resulting stabilized films developed from the original and modified PAN films were named films A, B, C, and D, respectively. The oxidized films were carbonized to 1300°C at a rate of $240^\circ\text{C}/\text{h}$, 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 $\text{CuK}\alpha$ 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 the layer planes). The step-interval was set at 0.02° . The d spacing and L_c were calculated using Eqs. (1) (the Bragg equation) and (2) (the Scherrer equation), respectively:

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

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

in which $\lambda = 0.1542 \text{ nm}$, \mathbf{K} is the apparatus constant ($=1.0$), and \mathbf{B} is the half-value width in the radian of the X-ray diffraction intensity (I) versus the 2θ curve.

Elemental analysis was carried out with a Perkin-Elmer Model 240C elemental analyzer. The samples from the carbonization process were analyzed for carbon, hydrogen, and nitrogen. The oxygen content was determined by the difference between these three. The mechanical properties of carbonized films were measured by an Instron 1122 tensile testing machine at a crosshead speed of $0.5 \text{ mm}/\text{min}$ and a load cell of 10 g , with a testing length of 2 cm .

Electrical resistance measurements on the carbon films were made using a GW digital milliohmmeter. The contact resistance at the point of contact between the measuring probe and the film was minimized with silver paint during the measurement. At least 30 films were measured in each experiment and the average measurement of these data was calculated. The cross-section area of all samples was measured under an Olympus BHT microscope with a closed-circuit television camera which magnified the image of the film in order to measure the cross-section area of the film.

RESULTS AND DISCUSSION

Properties of PAN Films and Oxidized Films

PAN undergoes a cyclization reaction at the oxidation stage and the monomeric characteristic of PAN consists of a nitrile group with a dipole-dipole force. When the temperature exceeds 180°C , the molecular chains will unfold and move around. The $\text{C}\equiv\text{N}$ bond originally in the PAN structure is transformed into a $\text{C}=\text{N}$ bond and

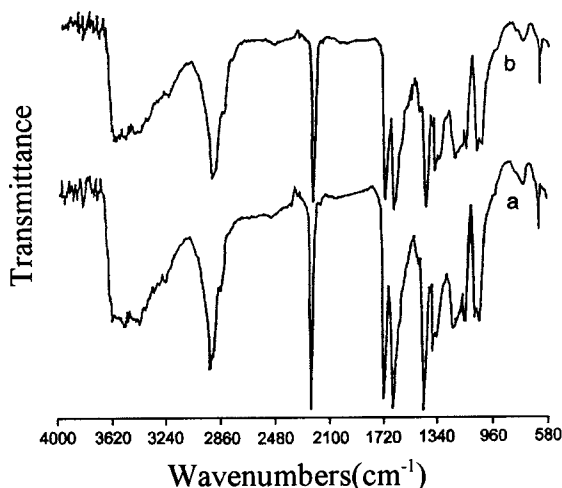


Figure 1 Infrared spectrum of PAN films: (a) original PAN films; (b) modified PAN films.

forms a ladder polymer.¹² This is termed cyclization, as below:

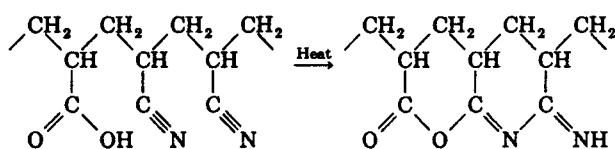


Figure 1 shows the infrared spectra of the original PAN film and the modified PAN film. The infrared spectrum for PAN films contains prominent peaks at 2930 and 2240 cm^{-1} due to the stretch vibration of the methylene (CH_2) and the nitrile ($\text{C}\equiv\text{N}$) groups. No new peaks are found when the film is modified with cobalt chloride. Figure 2 shows the spectrographs of the oxidized films. It can be plainly seen that the peak at 1600 cm^{-1} is attributed to the $\text{C}=\text{N}$ group. The intensity of the peak of the $\text{C}=\text{N}$ group increases with increasing degree of oxidation, whereas the peak strength of the $\text{C}\equiv\text{N}$ group decreases. Thus, the ratio of $I_{1600/2400}$ can be used as the index of cyclization.²⁷ Table I shows that the films, which were oxidized for a longer period of time or had been modified, have a higher $I_{1600/2400}$ ratio. This is indicated by that the oxidized films, which have been modified or subjected to a longer oxidation time, have a more complete cyclized structure.

In addition, in the X-ray diffraction studies, Figure 3 shows the diffraction pattern of the original PAN films. A strong peak is noted at the $2\theta = 17.5^\circ$ position. Warner et al.²⁸ previously reported that the peak at $2\theta = 17^\circ$ of the PAN fibers

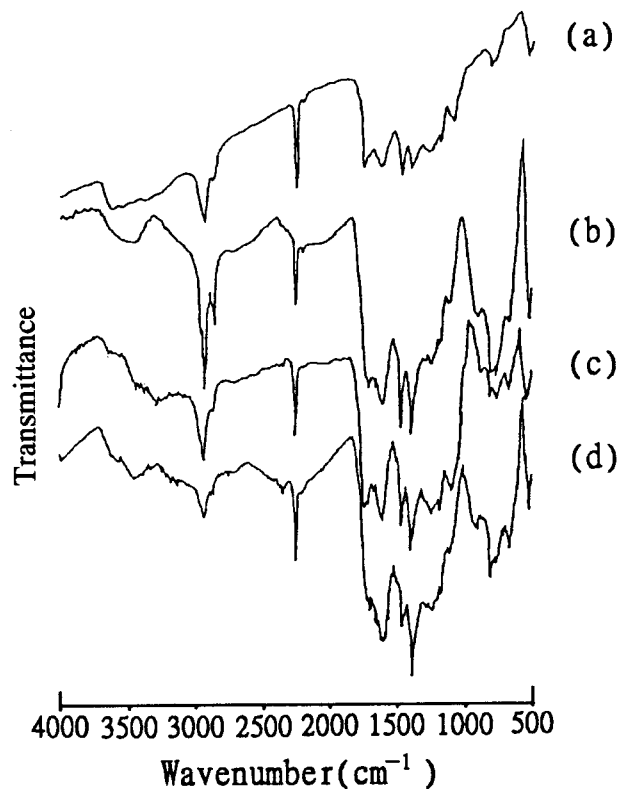


Figure 2 Infrared spectrum of PAN films stabilized at 220°C for (a) 2 h and (b) 6 h and modified PAN films stabilized at 220°C for (c) 2 h and (d) 6 h.

is caused by the ordered phase in the PAN molecular chain and such a structure is termed a laminatelike structure. Further, there is a broad but weak diffraction peak at the $2\theta = 24.3^\circ\text{--}29^\circ$. It is

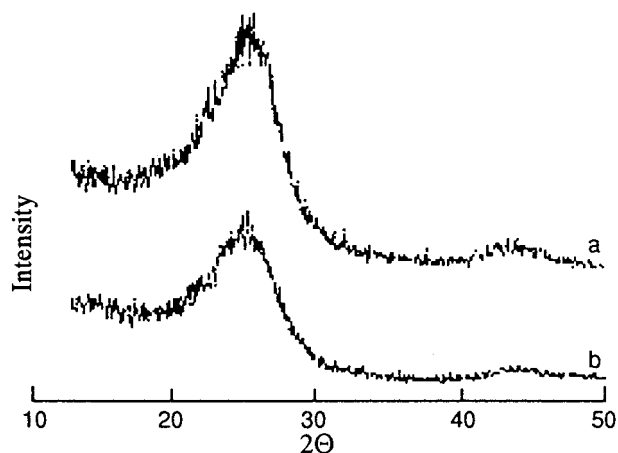


Figure 3 Wide-angle X-ray diffraction patterns of PAN films: (a) original PAN films; (b) modified PAN films.

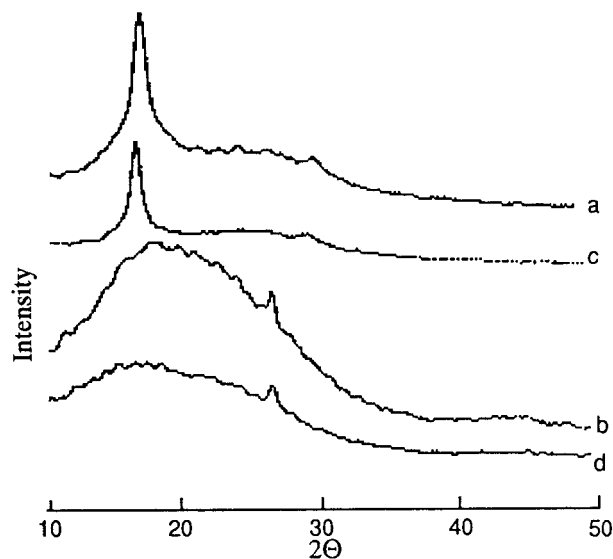


Figure 4 Wide-angle X-ray diffraction patterns of PAN films stabilized at 220°C for (a) 2 h and (b) 6 h and modified PAN films stabilized at 220°C for (c) 2 h and (d) 6 h.

generally believed^{28–30} that this is caused by the disordered phase in the PAN intramolecular chain arrangement. These peaks in the original PAN film were higher than those of the modified film. This indicates that the modified PAN film has a lower ordered phase than that of the original. According to our measurement of the crystal size, the original PAN film was 3.0 nm and the modified film was 2.7 nm. After modification, the crystal size decreased 10%. This indicated that the modified PAN film had a greater disordered phase than that of the original. Because of the more disordered phase, the rate of diffusion of oxygen in the film became easier in the modified PAN film than in the original. In other words, the formation of the ladder polymer is easier in the modified film than in the original PAN. Therefore, the modified PAN film had a greater $I_{1600/2400}$ than that of the original.

The X-ray diffraction pattern of oxidized films is presented in Figure 4. As evident in the figure, along with a gradual increase in the degree of oxidation, the diffraction peak at the $2\theta = 17.5^\circ$ position in the original PAN films slowly disappears and is replaced by the ladder structures at the $2\theta = 26.5^\circ$ position, that is, ladder structures are gradually formed as the oxidation reaction progresses. The formula of Uchida et al.²⁹ and Ko et al.³⁰ is used to analyze the changes in the diffraction peak strength at $2\theta = 17.5^\circ$ and 2θ

$= 26.5^\circ$, that is, the aromatization index (A.I.) is used as the reference values for the degree of oxidation, which are shown in Table II:

$$\text{A.I.} = \frac{I_{26.5}}{I_{17.5} + I_{26.5}} \times 100\%$$

in which $I_{26.5}$ is the peak strength at $2\theta = 26.5^\circ$ and $I_{17.5}$ is the peak strength at $2\theta = 17.5^\circ$ position of the X-ray diffraction pattern.

According to the data in Table II, it is indicated that, with modification or an increase in the degree of oxidation, a higher A.I. value can be obtained. Oxidized films, which have undergone a longer oxidation time or modification, have a more complete cyclization and thus possess more ladder structures. When the films were oxidized for 2 h, the A.I. value was 14.34 and 19.75% for the original and modified films, respectively. After modification, the A.I. value increased 38%. This indicated that the PAN film modified with cobaltous chloride promoted the formation of a ladder polymer during the oxidation process.

Elemental Composition and Mechanical Properties of Carbon Films

The chemical reactions at the carbonization stage will cause the evolution of a large amount of gases. Watt et al.³¹ reported that dehydrogenation will occur at a temperature between 400 and 600°C while denitrogenation will occur at a temperature between 600–1300°C, forming H_2O , HCN , H_2 , N_2 , CO , 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.³² In the process of carbonization, the carbon content increases with increase in the carbonization temperature; however, the nitrogen content conversely decreases.

Table II A.I. Values of Oxidized Films

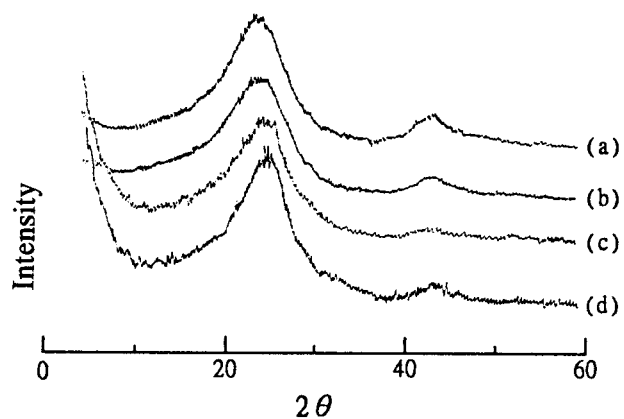
| Measurement | Films | | | |
|-------------|-------|-------|-------|-------|
| | A | B | C | D |
| A.I. (%) | 14.34 | 41.38 | 19.75 | 46.67 |

Table III Elemental Composites (wt %) and Mechanical Properties of Carbon Films (Carbonized at 1300°C)

| Film | N(%) | C(%) | H(%) | O(%) | [N]/[C] | Tensile Strength (MPa) | Tensile Modulus (MPa) |
|------|------|-------|------|------|---------|------------------------|-----------------------|
| A | 2.99 | 96.01 | 0.47 | 0.53 | 0.0267 | 2.45 | 200 |
| B | 3.14 | 96.15 | 0.45 | 0.26 | 0.0280 | 3.04 | 320 |
| C | 3.01 | 96.02 | 0.57 | 0.40 | 0.0287 | 3.15 | 420 |
| D | 3.31 | 96.24 | 0.44 | 0.01 | 0.0295 | 4.12 | 530 |

Table III shows the resulting elemental compositions when all films were carbonized at 1300°C. The carbon films developed using modified PAN films had slightly less carbon content than that of the original. This finding is due to catalysis by Co which promoted the growth and close packing of the carbon basal planes. When PAN films were oxidized for longer periods, it promoted the stable formation of carbon basal planes. The modified PAN films also had a greater nitrogen content and [N]/[C] atom ratio than those of the original PAN film at the same oxidation condition. Guigon and Oberlin³³ reported that the presence of nitrogen causes a soft bonding effect and that the carbon layer spacing of carbon fibers repleted with a high nitrogen content exhibits better toughness and densification.

Therefore, carbon material with a higher nitrogen content is expected to have a greater mechanical properties. The mechanical properties of the resulting carbon films are also in Table III. The tensile strength was 2.45 and 3.15 MPa for the original and modified films, respectively, which were oxidized for 2 h. The tensile modulus was 200 and 420 MPa for the carbon film made from the original and modified PAN films, respectively.

**Figure 5** Wide-angle X-ray diffraction patterns of carbon films: (a) film A; (b) film B; (c) film C; (d) film D.

When the films were oxidized for 2 h, the resulting carbon film made from the modified PAN film improved the tensile strength by 29% and the tensile modulus by 110%. When the PAN films were oxidized for 6 h, the tensile strength and tensile modulus were increased by 36 and 69%, respectively.

Wide-angle X-ray Diffraction

Figure 5 provides the diffraction patterns of two types of films which were carbonized at 1300°C. As shown in this figure, the carbon layer structure at the (002) reflection appears at $2\theta = 25.2^\circ$. Such a structure is the graphitelike laminate structure formed mainly from the ordered stacking of carbon-layer strips.

The carbon-layer stacking height (L_c) is obtained by incorporating the diffraction data on the (002) plane into the Scherrer equation. Table IV shows the variations in the 2θ , L_c , d , and L_c/d of the films after carbonization at 1300°C. The L_c and L_c/d values for film B are higher than for film A. These values for film D are higher than for film B. This finding indicates that oxidized films subjected to a longer oxidation time have greater carbon-layer planes and densification, as do the modified films. In view of these findings, cobalt ions exert a catalytic effect on the formation and stacking of carbon-layer planes.

Electrical Conductivity Analysis

Since the bonding among the carbon layer crystallized plane is weak, it can be regarded as a

Table IV X-ray Diffraction Parameters of Carbon Films (Carbonized at 1300°C)

| Film Code | 2θ | d (nm) | L_c (nm) | L_c/d |
|-----------|-----------|----------|------------|---------|
| A | 25.02 | 0.3556 | 1.845 | 5.2 |
| B | 25.23 | 0.3527 | 1.973 | 5.6 |
| C | 25.05 | 0.3552 | 1.949 | 5.5 |
| D | 25.19 | 0.3533 | 2.101 | 5.9 |

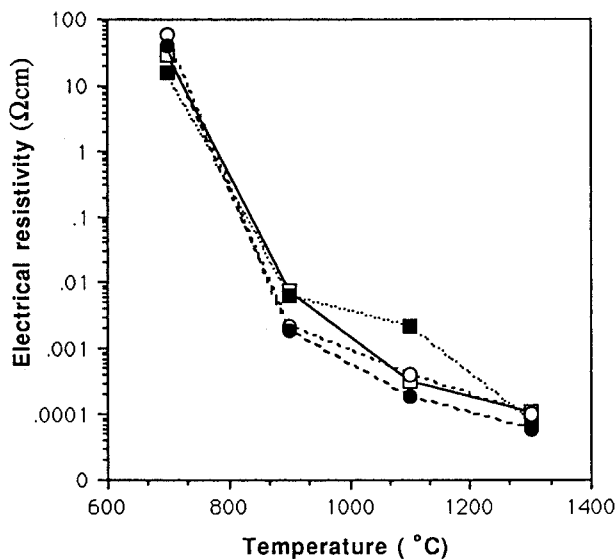


Figure 6 Variation of electrical resistivity of resulting carbon films during pyrolysis: (□) film A; (■) film B; (○) film C; (●) film D.

two-dimensional bonding. Furthermore, carbon atoms are bonded to one another by the π orbital composed of the sp^2 orbital and p orbital. The resonance vibration effect of the π bond of the carbon layer leads to the movement of the π electrons in the carbon layer, thus producing electrical conductivity.

Figure 6 shows the relationship between the carbonization temperature and electrical resistivity (ρ). From the figures, it can be seen that, along with an increase in the carbonization temperature, ρ gradually decreases. Since the carbon-layer stacking increases as the degree of carbonization increases, the π electrons possessed therein will also increase, which leads to a reduction in electrical resistivity and improvement in the conductivity. Film B has a lower electrical resistivity than has film A, and the same case can be noted between films D and C. This point confirms that a longer oxidation time is conducive to carbon layer stacking (L_c), which, in turn, has the effect of improving conductivity.

From Figure 6, it is revealed that the carbon films developed from the modified PAN films have a lower electrical resistivity and higher electrical conductivity than those developed from the original PAN film at 1300°C. When the PAN films were oxidized for 2 h, ρ was $1.1 \times 10^{-4} \Omega\text{cm}$ for the resulting carbon film developed from the original PAN film and $9.8 \times 10^{-5} \Omega\text{cm}$ for the film made from the modified one. When the PAN films

were oxidized for 6 h, ρ was $8.0 \times 10^{-5} \Omega\text{cm}$ for the resulting original-film-based carbon film and $5.8 \times 10^{-5} \Omega\text{cm}$ for the modified-film-based carbon film. The carbon films developed from the modified PAN film improved the electrical conductivity by 12–38%. Wakatsuki^{34,35} classified the reactivity of the transition metals with carbon into three groups through a series of studies on catalysts for diamond synthesis. They indicated that Co metals have a d shell occupied by electrons. The energy level of such a configuration is scarcely changed by accepting additional electrons from carbon. Therefore, Co metals can dissolve carbon. This consideration can be used to explain the catalytic graphitization abilities of Co metals.^{36,37} This study also indicated that Co acted as a catalyst, promoting the growth and close packing of the carbon basal planes. This reaction not only increased the stacking size (L_c) and the mean number of layer planes (L_c/d) but also improved the tensile modulus, tensile strength, and electrical conductivity.

CONCLUSIONS

The effect of PAN film modification with cobaltous chloride on the microstructure of the resulting oxidized and carbon films was investigated. From the above studies and analysis, it is concluded that

1. The modified PAN film has a lower crystal size and ordered phase. After modification, the crystal size of PAN decreases 10% and increases the disordered phase.
2. After modification, the A.I. value for oxidized films developed from modified PAN films increased 38%. The modification process promoted the formation of ladder polymers.
3. Oxidized films subjected to a longer oxidation time will produce higher L_c and L_c/d values, a more abundant nitrogen content, and lower electrical resistivity when subsequently subjected to carbonization treatment.
4. During the carbonization stage, Co promote a catalytic action, and carbon films of better mechanical properties and electrical conductivity can be obtained. The carbon films developed from the modified PAN film improved tensile strength by 29–36%,

tensile modulus by 69–110%, and electrical conductivity by 12–38%.

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