

# STUDY OF THE MICROSTRUCTURE OF CARBON FILM DEVELOPED FROM COBALT CHLORIDE MODIFIED PAN FILMPOLYACRYLONITRILE

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## Introduction

Carbon films have been designated for use as the shield material for electromagnetic waves, the electrodes in cells and as a covering material for motors, electrical devices and other equipment. High polymer carbon films developed from the thermal pyrolysis of organic polymers have been used extensively [1-5]. In this study, 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 properties of PAN films during carbonization were studied.

## Experimental

PAN films were solvent cast from dimethylformamide (DMF) solutions. 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 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 h and 6 h, respectively. 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 °C/hr, from 25 to 1300°C, in a ceramic reaction tube and an oxygen-free nitrogen atmosphere. The specimens were cooled down immediately.

## Results and discussion

Figure 1 shows the spectrographs of the oxidized films. It can be plainly seen that the peak at  $1600\text{cm}^{-1}$  is of the C=N group. The strength of the peak of the C=N group increases along with an increase in the degree of oxidation, whereas the peak strength of the C≡N group decreases.

Figure 2 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 (002)

reflection appears at  $2\theta=25.2^\circ$ . Such a structure is the graphite-like 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.

Figure 3 shows the relationship between carbonization temperature and electrical resistivity. From the figures, it can be seen that, along with an increase in the carbonization temperature, the electrical resistivity ( $\rho$ ) gradually decreases. Film B has a lower electrical resistivity than 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 3, 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. The carbon films developed from the modified PAN film improved the electrical conductivity by 12-38%. This study indicated that cobalt atoms acted as a catalyst, promoting the growth and close packing of the carbon basal planes. This reaction not only increased stacking size ( $L_c$ ) and the mean number of layer planes ( $L_c/d$ ) but also improved tensile modulus, tensile strength and electrical conductivity.

## Conclusions

During the carbonization stage, cobalt ions promote a catalytic action, and carbon films of better mechanical properties and electrical conductivity can be obtained. The carbon films developed from the modified film improved 12-38%, tensile strength by 29-36% and tensile modulus by 69-110%. The carbon films developed from the modified PAN film improved electrical conductivity 12-38%.

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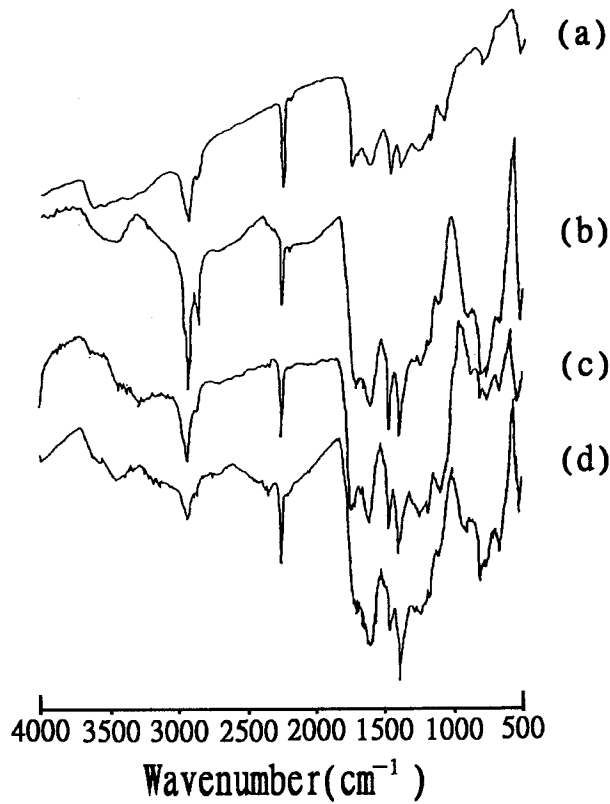


Figure 1 Infrared spectrum of PAN films stabilized at 220°C for; (a) 2 hrs; (b) 6hrs; and modified PAN films stabilized at 220C for; (a) 2 hrs; (b) 6 hrs.

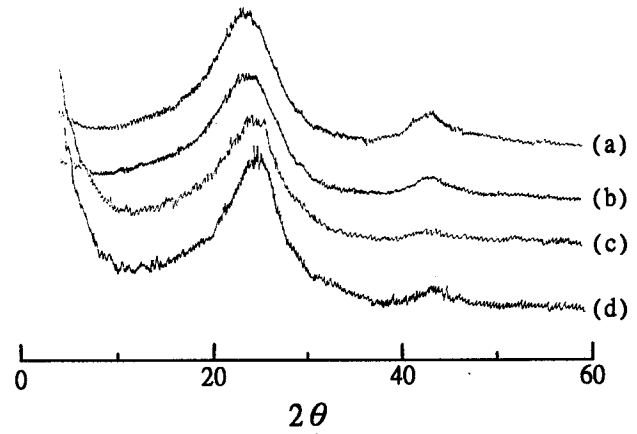


Figure 2 Wide-angle X-ray diffraction patterns of carbon films; (a) film A; (b) film B; (c) film C; (d) film D.

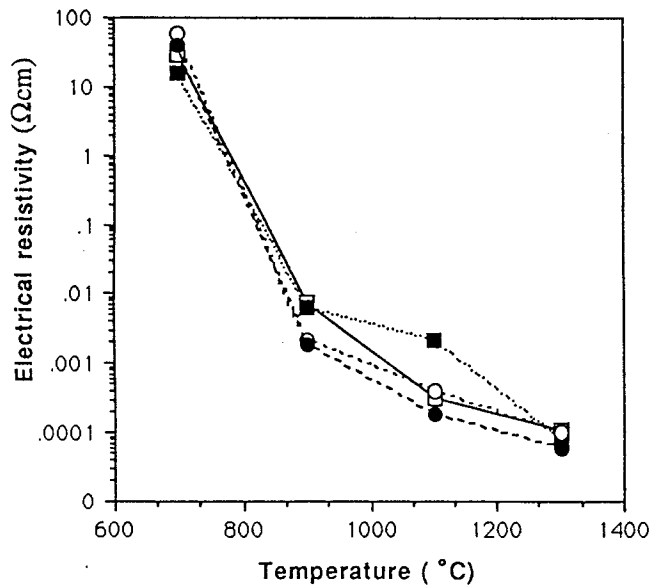


Figure 3 Variation of electrical resistivity of resulting carbon films during pyrolysis; (□) film A; (■) film B; (○) film C; (●) film D.