The Influence of Cobaltous Chloride Modification on Physical Properties and Microstructure of Modified PAN Fiber during Carbonization

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ABSTRACT: Modification of polyacrylonitrile (PAN) fibers with cobaltous chloride has increased crystal size, crystallinity, and density, and also improved tensile strength and modulus of the resulting carbon fibers. In this study, the effect of cobaltous chloride modification on the physical properties, microstructure, and elemental composition of PAN fibers during the carbonization process was examined. The resultant carbon fibers developed from modified PAN fibers had a lower formation temperature of carbon basal planes than those fibers that developed from the original one. The modification process not only improved the tensile strength but also increased the tensile modulus by about 15% of the resulting carbon fibers at carbonization temperature of 1300°C. A higher stacking size (L_c) , or a greater carbon basal plane in crystalline, is one of the reasons to improve the modulus and conductivity of the final carbon fibers. The modification process also increased the electrical conductivity by about 15% at 1300°C and by about 150% at 2500°C. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2409–2415, 1998

Key words: PAN fiber; modification; cobaltous chloride; carbon fiber

INTRODUCTION

Polyacrylonitrile (PAN) fiber has been used as the precursor for making high-performance carbon fibers.¹⁻¹⁵ To broaden the applicability of carbon fibers, many scientists have consistently engaged in research for the improvement of the performance of carbon fibers, such as the enhancement of strength, modulus, and elongation, or the improvement of other functions, such as increased electrical conductivity. Watt and his coworkers² utilized the process of steaming to restretch PAN fibers to improve the mechanical properties of the resultant fibers. Watt¹⁶ further achieved such an

object by applying the tension method during the oxidation engineering. Blakslee et al.¹⁷ utilized the neutron irradiation technique to increase the Young's modulus of carbon fibers. Cooper and Mayer⁵ filled boron into carbon fibers, while Bahl^{8,9} and Ko^{12–15,18} respectively utilized various solvents such as CuCl, SO₂, potassium permanganate, and potassium perchromate to modify PAN fibers so as to promote the mechanical properties of the resultant carbon fibers.

In the carbon industry, artificial graphite has always been prepared with resin as the raw materials. To increase the mechanical properties of artificial graphite, and to reduce the production costs of graphite, many kinds of metal powders are used as a catalyst. Oya and Otani¹⁹ discovered that to promote graphitization, the best results can be obtained with the metal powders of Al, Cr, Mn, Fe, Co, and Ni. Wakatsaki²⁰ indicated that there are still some empty electrons on the d

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orbital of Fe, Co, and Ni that can accommodate the electrons of carbon. The carbon layer structure of the graphite has not been destroyed. Many atoms, molecules, and ions may be interposed between the carbon layers to form a compound, which is the so-called graphite intercalation compounds. Gonsalves et al.²¹ introduced Ti ions into the fibers and the same electroconductive materials and electrode materials. Recently, Ho et al.,²² according to the viewpoint of graphite intercalation compounds, introduced Br₂ into Thornel P-100 carbon fibers so as to improve the electrical conductivity of the resultant carbon fibers.

In our previous study,²³ the effect of modification of the precursor with cobaltous chloride on the properties of the resulting stabilized fibers that were stabilized at 270°C from 1 to 10 h and on the properties of the final carbon fibers has been discussed. This previous study indicated that the modification process would decrease the required stabilization time and improve the tensile strength by 15–40%, and the modulus by 10–20% of the resulting carbon fibers, which were carbonized at 1300°C. In this study, during carbonization the effect of modification of PAN fibers with cobaltous chloride on the microstructure and mechanical properties of the resulting carbonized fibers are reported.

EXPERIMENTAL

A special grade of acrylic fiber, Courtelle fiber (Courtaulds Ltd., UK), containing 6% methyl acrylate and 1% (itaconic) acid copolymer was used to prepare stabilized fibers in this work. A single tow of Courtelle fiber contains 6000 strands of 1.1 denier monofilament. The modification process was carried out by immersing the PAN fibers 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 carbon fibers was determined by an atomic emission spectrometer analysis. The content of cobalt in the fiber had increased about 40 times over its original content after the modification process.²³

Stabilization of the PAN fibers was carried out in a purified air atmosphere in a constant temperature zone furnace with a fixed length method at 270°C for 3 h. The stabilized fibers were carbonized from 400 to 1300°C at a rate of 4°C/min, and samples were taken at 100°C intervals, in a ceramic reaction tube and an oxygen-free nitrogen atmosphere. The specimens were immediately cooled.

The mechanical properties of the carbon fibers were measured by an Instron 1122 tensile-testing machine at a crosshead speed of 0.5 mm/min and a load cell of 10 g, with a testing length of 2.5 cm for carbon fibers. In each sample, at least 25 filaments were tested, and the average value was reported. The diameters of all fibers were measured under an Olympus BHT microscope with a closed circuit television camera that magnified the image of the fibers in order to measure their diameters. Thirty fiber diameters were measured in each experiment, and the average measurement of these 30 fibers was calculated.

A Rigaku X-ray diffractometer, providing Nifiltered Cu k_{α} radiation, was used to measure the crystalline-related properties of the sample. The step-scan method was used to determine the dspacing and stacking size (L_c , stacking height of layer planes). The d spacing and L_c were calculated by using eqs. (1) (the Bragg equation) and (2) (the Scherrer equation):

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

$$Lc(hkl)$$
 (in nm unit) = $K\lambda/B \cos \theta$ (2)

in which $\lambda = 0.154$ 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*) vs. 2 θ curve.

Density was measured at 25° C according to the density gradient column method. The density column was prepared with a mixture of *n*-heptane and carbon tetrachloride, so that a density gradient of about 1.2 to 1.6 g/cm³ extended from top to bottom. For the measurement of densities from 1.6 to 2.0 g/cm³, a density gradient column prepared with a mixture of carbon tetrachloride and 1,3-dibromopropan was adopted.

A Perkin-Elmer model 240C Elemental Analyzer was used to carry out the elemental analysis. The samples from the carbonization process were analyzed for carbon, hydrogen, and nitrogen.

Electrical resistance measurements on the graphite fibers were made using a GW digital milli-ohmmeter. The contact resistance at the point of contact between the measuring probe and the fiber was minimized with the measuring probe, and the fiber was minimized with siliver paint during measuring. At least 30 fibers were

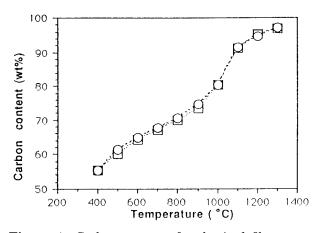


Figure 1 Carbon content of carbonized fibers as a function of carbonization temperature; carbon fibers developed from: (\Box) original PAN fibers; (\bigcirc) modified PAN fibers.

measured in each experiment, and the average measurement of these data was calculated.

RESULTS AND DISCUSSION

The trace elements contained in carbon fibers are partly those originally possessed by the fibers themselves and partly those derived from additives used during the manufacturing process to assist in catalyzing the advancement carbonization and graphitization. Marsh et al.²⁴ reported that the Fe element can generate a reaction at a temperature as low as 600°C to produce turbostratic graphite.

In this article, to investigate the effect of cobalt on carbon fibers during carbonization, there were two stabilized fibers—one developed from original PAN fibers and the other developed from modified PAN fibers—that were used to study the development of the microstructure and physical properties of the fibers at the carbonization stage.

The result of the analysis of the elemental composition of the fibers during the carbonization is shown in Figures 1–3. The carbon content of the fibers increases gradually as the carbonization temperature increases, as shown in Figure 1, whereas the nitrogen and hydrogen elements gradually decrease with a rise in the carbonization temperature, as shown in Figures 2 and 3.

There is a weight loss of the stabilized fibers during carbonization. The noncarbon elements are removed as volatiles, such as HCN, H_2 , NH_3 , CO_2 , CO, and CH_4 , to give carbon fiber with a

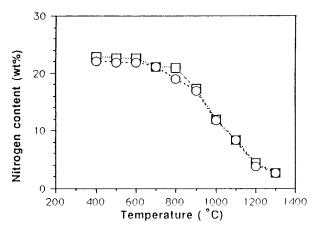


Figure 2 Nitrogen content of carbonized fibers as a function of carbonization temperature; carbon fibers developed from: (\Box) original PAN fibers; (\bigcirc) modified PAN fibers.

yield of about 50% of the mass of original PAN fibers,^{7,16,25} At the early stages of the carbonization, the nitrogen content manifests a slow reduction, as shown in Figure 2. The nitrogen content for both samples decreases when the carbonization temperature is raised. In the early stage of carbonization, the nitrogen content decrease slightly. After the period of the transition temperature, it decreases rapidly as the carbonization temperature rises. The nitrogen content of the carbon fibers that were developed from modified PAN fibers (modified PAN-based carbon fibers) shows a reduction at the transition temperature above 700°C, which is about 100°C lower than that developed from the original PAN fibers (orig-

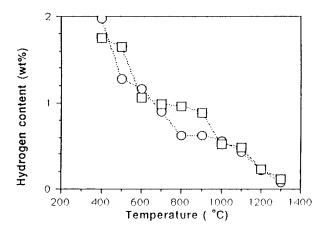


Figure 3 Hydrgen content of carbonized fibers as a function of carbonization temperature; carbon fibers developed from: (\Box) original PAN fibers; (\bigcirc) modified PAN fibers.

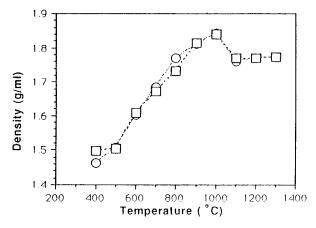


Figure 4 Density of carbonized fibers as a function of carbonization temperature; carbon fibers developed from: (\Box) original PAN fibers; (\bigcirc) modified PAN fibers.

inal PAN-based carbon fibers), which shows a sharp reduction of nitrogen content above 800°C. The transition temperature of the modified PAN fibers is 100°C lower than that of the original PAN fibers. This indicates that PAN fiber modified with cobaltous chloride will promote the formation of the carbon basal planes. As for the variation in the hydrogen content of the fibers, as shown in Figure 3, a more apparent reduction in hydrogen content was noted in modified fibers compared with the unmodified fibers at 700–900°C. These reactions will lead to the crosslinking of the carbon basal planes. This exhibits a trend very similar to the one observed in the variation in the nitrogen content.

It is presumed²⁵ that at 700°C, the ladder polymers are crosslinked together and lead to the evolution of HCN gas. This reaction also causes the lengthening and broadening of the carbon fiber structure. The formation of such a structure, which is earlier in modified PAN-based carbon fibers than in original PAN-based carbon fibers, facilitates the formation of more carbon basal planes, thus enhancing the mechanical properties of the final carbon fibers. Therefore, the modulus of carbon fibers from the modified fibers will be higher than that of carbon fibers from the original PAN fibers.

As for the variation in density of carbon fibers, as shown in Figure 4, an increase in density was noted as the carbonization temperature increased. Density increase very rapidly below carbonization temperature of 1000°C for both fibers. This is because as the carbonization temperature rises, the noncarbon elements in the fibers evolve and the ladder polymer structures interconnect with one another. The aromatization and crosslinking of the heterocyclic rings, as well as the lengthening and broadening of carbon basal planes, led to the repacking of the structure in carbon fibers.²⁵ The modified PAN-based carbon fibers has higher density than the original PANbased carbon fibers at temperature ranging from 700 to 900°C. This is due to higher nitrogen elimination and dehydrogenation for the modified PAN-based carbon fiber, as shown in Figures 2 and 3. The formation of graphite-like ribbons and fibrils in the carbon fibers is due to nitrogen elimination and dehydrogenation.²⁵ Thus, the small nitrogen content and hydrogen content for the modified PAN-based carbon fibers during carbonization between 700 and 900°C shows that carbon basal planes and fibril formations occur rapidly in this temperature range. Therefore, these reactions lead to a higher density for the modified PAN-based carbon fiber. The sudden drop in density at a carbonization temperature from 1000 to 1100°C is caused by the gradual transformation of the open pores in the fibers into closed pores. $^{18,2\bar{6}}$ Because of the formation of the closed pores in fibers, this lead to a decrease in density. However, the density for the modified PAN-based carbon fibers is 1.773 g/cm³, and that of the original PAN-based carbon fibers is 1.772 g/cm³ at the carbonization temperature of 1300°C.

As the carbonization temperature progressively rises, basic carbon layer structures are slowly formed in the fibers. The front-to-rear connection of the ladder polymers causes lengthening of the basic carbon structures, whereas the vertical connection along the fiber's axis causes broadening of the basic carbon structure. The crosslinking of the ladder polymers causes the densification of the structure, so that the tensile strength increases gradually as the carbonization temperature rises, as shown in Figure 5. Tensile strength of the modified PAN-based carbon fibers is 0.2 GPa at 400°C to 3.5 GPa at 1300°C, and that of the original PAN-based carbon fibers is 0.2 GPa to 3.2 GPa from 400 to 1300°C. The tensile strength of the modified PAN-based carbon fibers is greater than the original PAN-based carbon fibers during the heat-treatment process. This is due to the increased microfibril structures and crosslinking generated by the denitrogenation and dehydrogenation reactions.

Above the carbonization temperature of 1100°C, the density of the carbonized fibers gradually increased with a increase in carbonization

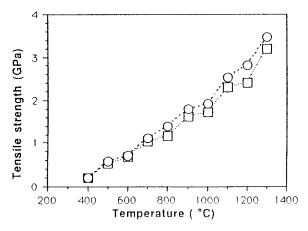


Figure 5 Tensile strength of carbonized fibers as a function of carbonization temperature; carbon fibers developed from: (\Box) original PAN fibers; (\bigcirc) modified PAN fibers.

temperature. The tensile strength and elastic modulus of both carbonized fibers also increased after 1100°C, as shown in Figures 5 and 6. We found that no apparent relationship between the formation of closed pores and the mechanical properties exists at this temperature stage. This is due to the effect of the lengthening and broadening of carbon basal planes being higher than the formation of closed pores.

The results shown in Figure 6 indicate that the elastic modulus of carbon fibers gradually increases along with the temperature. This is caused by the gradual elimination of the noncarbon elements in the fibers, which led to the formation of the carbon basal planes. The modulus of the modified PAN-based carbon fibers is slightly higher than original PAN-based carbon fibers. This is probably caused by the catalytic action of cobalt. This reaction promotes the stacking arrangement of the carbon basal planes, which leads to a denser structure, as shown in Table I.

As manifested in the Figures 5 and 6, the tensile strength and fracture modulus of modified PAN-based carbon fibers are higher than those of

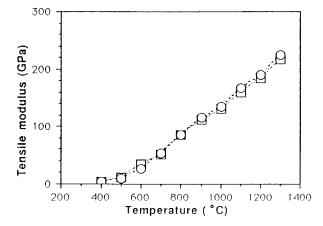


Figure 6 Tensile modulus of carbonized fibers as a function of carbonization temperature; carbon fibers developed from: (\Box) original PAN fibers; (\bigcirc) modified PAN fibers.

the original PAN-based carbon fibers. This is because the cobalt-modified fibers form carbon layer structures earlier and have a higher carbon content that is conducive to the formation of more basic carbon layer structure. The formation of such structures enhances the densification of the fibers and promotes the stacking arrangement of the carbon basal planes. Therefore, there is a greater number of crystalline planes (L_c/d), as shown in Table I, which gives rise to an improved modulus.

During carbonization, elongated strips of aromatic carbon layers are gradually formed. The structures of these aromatic carbon layers are in accord with graphite. The spacing between the layers is generally maintained. However, the orientation of the layers is entirely disorderly. Such a structure is termed turbostratic graphite. These aromatic layers are composed of carbon basal planes. Along the direction of the plane, electrical conductivity may be generated by the movement of the π electrons. The higher the carbonization temperature, the lower the electrical resistivity of the resultant carbon fibers prepared.

Developed from Temperature °C	Modified PAN Fibers			Original PAN Fibers		
	L_c (nm)	<i>d</i> (nm)	L_c/d	L_c (nm)	d (nm)	L_c/d
800	1.067	0.342	3.1	1.066	0.344	3.1
1300	1.237	0.345	3.6	1.173	0.342	3.4

Table I Structure Parameters of Carbon Fibers

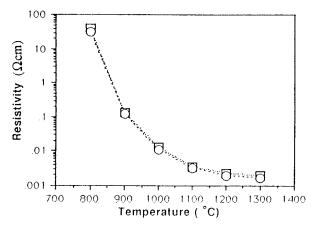


Figure 7 Electrical resistivity of carbonized fibers as a function of carbonization temperature; carbon fibers developed from: (\Box) original PAN fibers; (\bigcirc) modified PAN fibers.

Figure 7 shows the relationship between various carbonization temperatures and electrical resistivity. Along with increase in the carbonization temperature, the electrical resistivity of the carbon fibers gradually falls. The fall in electrical resistivity is considerably marked particularly between the temperatures of 800 and 1100°C. As indicated by the different carbonization temperatures and the resultant variations in the carbon content of the carbon fibers (as shown in Fig. 1), the noncarbon elements are evolved as the carbonization temperature rises, so that the carbon content increases considerably. At this stage, basic carbon structures are gradually formed, and more graphite-like structures are generated, causing a sharp drop in the electrical resistance. Above 1100°C, this trend becomes less severe. For the original PAN-based carbon fibers, the electrical resistivity at a carbonization temperature of 800°C is 3.74 Ω cm, and drops to $3.55 \times 10^{-3} \Omega$ cm at 1100°C. At a carbonization temperature of 1300°C, the electrical resistivity is 1.91×10^{-3} Ω cm for the original PAN-based carbon fibers, and that is 1.64 imes 10⁻³ Ω cm for the modified PAN-based carbon fibers. The carbon fibers developed from the modified PAN fibers have a greater electrical conductivity by 15% than those developed from the original PAN fibers. In our another experiment, both fibers were heat treated to 2500°C. The electrical resistivity is 1.48×10^{-4} Ω cm for the original PAN-based carbon fibers, and that is 6.00×10^{-5} Ωcm for the modified PAN-based carbon fibers. The graphite fibers developed from the modified PAN fibers improve the electrical conductivity by 150%.

As discussed in the foregoing, cobalt exerts an advanced catalytic action on the formation of lattice structure, and simultaneously promotes the stacking arrangement of the crystalline planes. Therefore, the cobalt-modified fibers as opposed to unmodified ones have more carbon layers (higher L_c/d value) making up the basic structure of the carbon fibers, which aids in the movement of π electrons, which in turn, lowers the electrical resistance value and increases the electrical conductivity. Therefore, conductivity of carbon fibers increases with an increase in modulus.

In addition, there are studies that reported that among the carbon layers of the graphite structure, graphite intercalation compounds formed by insertion of atoms or molecules other than those of carbon can synthesize a substance.^{19,22} As long as the graphite structure is not destroyed, many atoms, molecules, ions, etc., may be interposed between the graphite layers to form compounds, which are termed graphite intercalation compounds. Graphite intercalation compounds enable many intercalants to be interposed between the graphite layers. There is electron transfer between the graphite layers and most of the intercalants. One part is ionized, and provides electrons to the graphite layers, and in itself becomes a donor of positive ions, such as Fe, Co, and Ni. Acceptors that take negative ions from the graphite layers to interpose between the layers, such as Co, may have formed graphite intercalation compounds and have a decreased electrical resistance. Because of this, the electrical resistivity of the modified PAN-based carbon fibers is lower than that of the original PANbased carbon fibers, with a value reaching 15% at 1300°C and 150% at 2500°C.

CONCLUSIONS

Carbon fibers prepared from modified PAN fibers have enhanced strength and modulus. During the carbonization stage, the modified PAN-based carbon fibers form a lattice structure at a temperature that is more advanced than that of the original PAN-based carbon fibers by about 100°C, and at the same time have the effect of promoting the stacking arrangement of crystalline planes, leading to an increase in the modulus. The electrical resistivity of carbon fibers decreases as the carbonization temperature increases. A sharp fall is noted between 800–1100°C. The electrical resistivity of the modified PAN-based carbon fibers is lower than that of the original PAN-based carbon fibers, the values being about 15% at 1300° C and 150% at 2500° C.

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