

Manufacture of Carbon Fibers from Polyacrylonitrile Precursors Treated with CoSO_4

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ABSTRACT: Free-radical solution copolymerization of itaconic acid and acrylonitrile was carried out in DMSO using azodiisobutyronitrile as an initiator, changing the feed rate of itaconic acid. The resulting polymerization solution was spun to form polyacrylonitrile (PAN) precursors of carbon fibers. The precursors were treated with a CoSO_4 aqueous solution on-line. The structure and properties of untreated and treated PAN precursors and the resultant carbon fibers were characterized by SEM and TEM, a stabilization process, etc. It is suggested that CoSO_4 acts as a catalyst in the formation of a ladder structure and reduces the temperature of cyclization, and the carbon fibers developed from treated PAN fibers showed improvement in the tensile strength and the Young's modulus. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 153–158, 2002

Key words: PAN precursor; modification and manufacture; structure and properties; carbon fiber

INTRODUCTION

A wide range of precursors, such as polyacrylonitrile (PAN), rayon, pitch, lignin,¹ polyethylene,² and poly(*p*-phenylene benzobisoxazole),³ have been used to prepare carbon fibers. Among these different precursors, only PAN-based carbon fibers have been widely used as reinforcing materials in automobile, aerospace, recreational, and various other industries. Additional use may be attained by further improving the performance, particularly the tensile strength of carbon fibers while keeping the modulus of elasticity at a high level. Thus, there has been a growing demand for a higher quality and better performance of carbon

fibers. Many proposals have been made with a view to coping with such demands. It has been established that the treatment of a PAN precursor under tension load improves the resulting carbon fiber quality.⁴ Bahl et al.⁵ and Mathur and Bahl⁶ modified a PAN precursor with a CuCl aqueous solution to make high-performance carbon fibers. Cagliostro⁷ modified PAN fibers with benzoic acid to improve carbon fiber strength. Ko et al. prepared high-performance carbon fibers using PAN fibers pretreated with KMnO_4 ^{8,9} and CoCl_2 ¹⁰ and discussed the reasons why a modified PAN fiber can reduce the stabilization time and improve the mechanical properties of the resulting carbon fiber. Some patents^{11,12} describe processes for the preparation of carbon fiber from a modified PAN fiber with ammonia and low molecular weight amines. All these items have demonstrated that adding a catalyst to PAN fibers is very useful to improve the structure and the properties of the resultant carbon fibers or to reduce the stabilization time when a PAN fiber is preoxi-

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dized. In addition, physical modification of PAN fiber is also beneficial to improve the properties of carbon fiber.¹³ Rajalingam and Radhakrishnan¹⁴ and Gupta et al.¹⁵ reviewed, in detail, prestabilization treatments which involve the impregnation of PAN precursor fibers with persulfate, cobalt salts, a combination of a salt of iron(II) and hydrogen peroxide, acids, guanidine carbonate,¹⁶ dibutylindimethoxide,¹⁷ and potassium permanganate.¹⁸ These treatments reduce the time required for stabilization by decreasing the energy of activation of the stabilization reactions and result in carbon fibers with improved properties.¹⁹

Most of the previous work has been confined to modification of PAN fiber collected from a special grade of acrylic fiber, especially commercial Cour-telle fiber. According to our present study, in order to not only decrease the manufacture period of carbon fibers but also to improve the qualities of the resulting carbon fibers, the process of treating carbon fiber with PAN fiber treated with a CoSO_4 aqueous solution was introduced. The characteristic feature of this process was that copolymerization, spinning, drawing, treating with CoSO_4 , and setting were carried out on a continuous process line.

EXPERIMENTAL

Materials

Acrylonitrile (AN; Shanghai Reagent Plant, Shanghai, China) was distilled at 76–78°C before use. Azodiisobutyronitrile (AIBN; Shandong Xueyin Chemical Fiber Co., Zibo, China) was recrystallized before use. Dimethyl sulfoxide (DMSO; Shanxi Taigu Chemical General Plant, Taigu, China), itaconic acid (IA; Lucky Co. Ltd., Chuochome Ueda, Japan), and cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$; Tianjin Chemical Reagent Manufacturer, Tianjin, China) were used as received.

Preparation of PAN Precursors

Free-radical solution copolymerization of IA and AN was carried out in a 50-L pilot-scale stainless reactor with DMSO as a solvent and AIBN as an initiator. The resulting 22% (wt/wt) polymerization solution was deaerated, filtered, and then pumped through a spinneret to a coagulating bath. The coagulation bath composition and coagulation bath temperature were 55% DMSO and

20°C, respectively. The coagulated filaments were washed with a 5% CoSO_4 aqueous solution and drawn in three steps in a water bath, followed by lubrication with a heat-resistant amine silicone oil. The resulting filaments were dried to collapse them, further drawn in steam, set, and wound to obtain treated PAN precursors. The jet stretch was 0.7 and the overall draw ratio was 12. For the purpose of comparison, the untreated PAN precursors were manufactured, whereas the coagulated filaments were only washed with pure water instead of the CoSO_4 aqueous solution and all other steps were identical.

Preoxidation and Carbonization

The obtained treated PAN precursors and untreated ones were each heated under a tension of 0.25 g per filament in air, with a temperature gradient in the range of 220–280°C, in order to be converted into oxidized fibers, which were finally heated in high-purity nitrogen up to 1350°C to obtain PAN-based carbon fibers.

Analysis Methods

The conversion was determined gravimetrically. The copolymer compositions were determined from their nitrogen content, as estimated on a PE2400(II)-EA elemental analyzer. In comparison, a Nicolet 750 Magna FTIR was used to record the IR spectra of the copolymers and the copolymer composition was calculated according to the method of Bajaj et al.²⁰ A modified Hardy's thin cross-section sampling device was used to obtain the cross-section samples, which were examined with a scanning electron microscope (SEM), Hitachi Model 8010, at a 25-kV accelerating potential. The specimens were coated with Au to obtain a better image. Tows of PAN precursors and their stabilized fibers were subjected to subsequent examination in a transmission electron microscope (TEM), Hitachi Model 800, at 100 kV. The cobalt content, in the manufactured carbon fibers, was determined by atomic emission spectrometer analysis and it was found that the content of cobalt, in the fiber after treatment, had increased about 360 times over that of the untreated counterpart. The mechanical properties of PAN and the carbon fibers were measured by an XQ-1 tensile-testing machine (made at the China Textile University) at a crosshead speed of 0.5 mm/min with a testing length of 2 cm and load cell of 10 g. In each case, at least 50 sample filaments were

Table I Some Parameters for Solution Copolymerization of AN and IA

Polymer	AN/IA Feed (wt/wt)	M_2 (Mol Fraction)	m_2 (Mol Fraction)		Nitrogen (%)	$m_2/M_2 \times 100$		Conversion (%)
			EA	IR		EA	IA	
PAN	100/0	0	0	0	26.46 ^a	—	—	90.5
P(AN-co-IA) ₁	98/2	0.008	0.0199	0.0211	25.16	248.75	263.75	99.1
P(AN-co-IA) ₂	95/5	0.021	0.0403	0.0510	23.95	191.90	242.86	98.8
P(AN-co-IA) ₃	90/10	0.043	0.0823	0.0907	21.65	191.40	210.93	98.2
P(AN-co-IA) ₄	85/15	0.067	0.0900	0.1026	21.26	134.33	153.13	87.6
P(AN-co-IA) ₅	80/20	0.092	0.1127	0.1277	20.14	122.50	138.80	80.3

^a Theoretical value 26.39.

tested, and the average of 50 filaments was taken for each experiment.

RESULTS AND DISCUSSION

Feed Rate of IA

The comonomer contents in the monomer feed, M_2 , and in the copolymers, m_2 , are listed in Table I. It has been suggested that the copolymer composition changes with the change in the monomer feed. When the IA comonomer was slowly fed into the reactor during copolymerization, the reaction time required for copolymerization was markedly shortened, which accounted for a decrease in the content of the IA comonomer in the reactor by providing a slow rate of feed. Finemann–Ross²¹ and Muller et al.²² gave reactivity ratios of AN and IA, which were $r_1(\text{AN}) = 0.87$ and $r_2(\text{IA}) = 2.52$ and $r_1(\text{AN}) = 0.84$ and $r_2(\text{IA}) = 6.73$, respectively. For AN–IA solution copolymerization in DMSO solvent, we also obtained reactivity ratios for AN and IA of $r_1(\text{AN}) = 0.408$ and $r_2(\text{IA}) = 1.811$,²³ respectively. To obtain an adequate copolymer with a well-distributed sequence, IA should be continuously fed into the reactor. For a given initial monomer mixture, $f_1^0 = 0.998$, $f_2^0 = 0.002$, the instantaneous mol fraction of a comonomer in a monomer mixture, f_2 , and the instantaneous mol fraction of a copolymer in a copolymer, F_2 , at different conversions, C , can be calculated from the following Mayo equations²⁴:

$$F_2 = (r_2 f_2^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2) \quad (1)$$

$$C = 1 - (f_1/f_1^0)^\alpha (f_2/f_2^0)^\beta [(f_1^0 - \delta)/(f_1 - \delta)]^\gamma \quad (2)$$

where

$$\begin{aligned} \alpha &= r_2/(1 - r_2), \quad \beta = r_1/(1 - r_1), \\ \gamma &= (1 - r_1 r_2)/(1 - r_1)(1 - r_2), \\ \delta &= (1 - r_2)/(2 - r_1 - r_2) \quad (3) \end{aligned}$$

Spinning

For the spinning process, wet spinning was employed. The process comprised first extruding a high-conversion spinning solution through a meter pump and through a spinneret (3000 holes, 0.05 mm/hole, $L/d = 2/1$) and then introducing the extrudate into a coagulating bath. The polymer concentration is usually made as high as possible using a low solidifying temperature in the coagulating bath and a low draft ratio for spinning in order to obtain the most ideal fiber structure. The resulting swollen fibers should not contain bubbles or foreign matter. Some different influences, such as impurity and bubbles in the spinning solution and meter pump and poor spinneret quality, may result in abnormal as-spun phenomena.

Stabilization

To obtain high-performance carbon fibers, a stabilization process for PAN fibers is necessary. The stabilization process for PAN precursors, in an oxygen-containing atmosphere at temperatures in the range of 200–300°C, involves (a) an oxidative crosslinking reaction of adjoining molecules and (b) a cyclization reaction of nitrile groups. It is generally accepted that the rate at which the stabilization reaction takes place increases with the stabilization temperature and the stabilization time of the oxygen-containing atmosphere.²⁵

As a result, the low-temperature preoxidation treatment in air leads to the formation of a ladder polymer, due to additional polymerization of the nitrile side groups. Resulting changes in the physical characteristics of fiber during stabilization, such as the viscoelastic properties, which relate to molecular motion in the fiber, have been discussed. It was reported⁸ that pretreating PAN fibers with potassium permanganate, as a catalyst, reduced the time required for stabilization and also improved the mechanical properties of the resultant carbon fibers. In our study, the effect of treating PAN fibers with CoSO_4 on the stabilization was examined. The color variation indicated that chemical reactions did occur during the stabilization process. The temperature at which the fiber color turns brown is about 210°C for untreated PAN precursors and 190°C for ones treated with the CoSO_4 aqueous solution. Cobalt sulfate acts as a catalyst, which can be used to accelerate the formation of a ladder structure, and reduces the temperature of cyclization by about 20°C . This was consistent with reports of some other authors.^{26,27} Co-metal has been found to catalyze the formation of graphitic and turbostratic carbons during the heat-treatment stage, because Co metal has a *d* shell unoccupied by electrons which can accommodate the electrons of carbon. Therefore, the carbon fibers have a higher stacking size and mean number of layer planes, which increases both the tensile strength and modulus of the resulting carbon fibers.

SEM and TEM Study

The observations of the carbon fiber structure by various researchers have been contradictory at

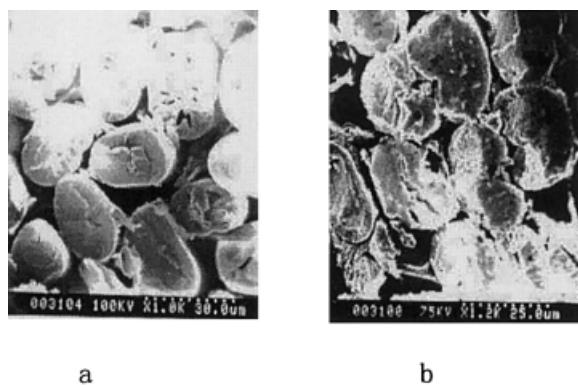


Figure 1 Cross section of (a) treated and (b) untreated PAN precursors.

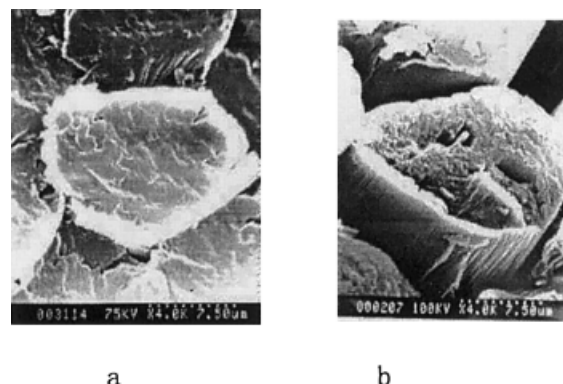


Figure 2 Cross section of stabilized fibers developed from (a) treated and (b) untreated or original PAN precursors.

times. In most cases, the types of precursor fibers, their structures, and conditions for converting them to carbon fibers were not disclosed. It is known that these parameters have substantial influence on the development of the structure in carbon fibers. The concept of basal planes forming ribbons or sheets, arranged parallel to the fiber axis direction in some fashion, has been well substantiated from X-ray and electron microscopic studies by several researchers.²⁸ Morphological features with dimensions much larger than those of the microfibrils have been observed in microtomed sections of carbon fibers of various origins and degrees of graphitization. The morphology of the fiber surfaces was examined under SEM in our work. Figure 1 shows cross sections of PAN precursors; Figure 2 shows the cross sections of stabilized fibers. Under normal conditions for making carbon fiber, the cross section and longitudinal surface of carbon fibers is defined by the cross section and surface of their PAN precursors. It has been suggested that the cross section and

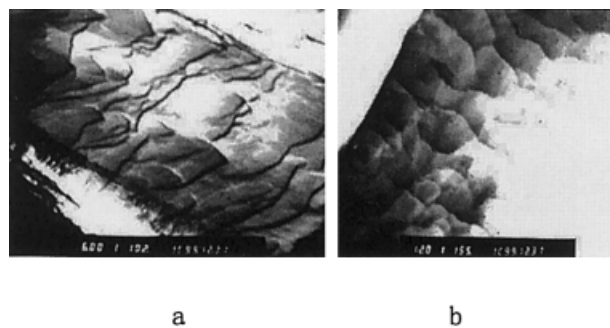


Figure 3 TEM image of (a) treated and (b) untreated PAN precursors.

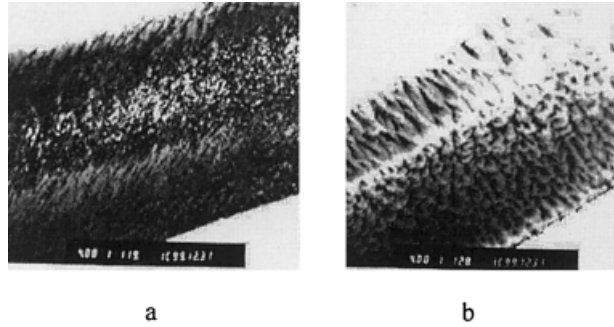


Figure 4 TEM image of stabilized fibers developed from (a) treated and (b) untreated PAN precursors.

longitudinal surface of carbon fibers are similar to their PAN precursors. The surface roughness of carbon fibers can increase the mechanical properties, the interlaminar shear strength (ILSS), of composite material reinforced with carbon fibers. But the cross-section surfaces of both treated and untreated carbonized fibers have a wraparound-based plane structure in the outer zone and a radial structure in the core. This agrees with previous studies,^{29,30} indicating a circumferential crystalline orientation on the circular cross section of those stabilized fibers.

Figures 3 and 4 show TEM images of both PAN precursors and stabilized fibers developed from both treated and untreated PAN precursors. Both fibers gave similar results, showing that stabilized fibers were composed of lamellar platelike structures (LPLS) along the fiber axis, which is consistent with the model provided by Ko.²⁵ The large spacing between two LPLS is one kind of open pore. The lamellar plates, composed of microfibrils, could be packed together during the carbonization stage, narrowing the pores, and the dimensions of the large open pores decrease when the carbonization temperature is increased during the carbonization stage.

Mechanical Properties

The results of the influence of the modification with CoSO_4 on the properties of PAN precursors and their resultant carbon fibers are listed in Table II. It has been shown that the process of preparing PAN precursors and treating them with CoSO_4 on-line does not only decrease the properties of PAN precursors but also improves the tensile strength and modulus of the resultant carbon fibers.

CONCLUSIONS

Free-radical solution copolymerization of IA and AN was carried out in DMSO and the resulting polymerization solution was spun to form PAN precursors of carbon fibers. To obtain an adequate copolymer with a well-distributed sequence, IA should be continuously fed into the reactor. The effect of modification, treated PAN fibers with CoSO_4 and untreated ones, on the stabilization was examined. It seems that the cobalt sulfate acts as a catalyst which can be used to accelerate the formation of a ladder structure and reduces the temperature of cyclization by about 20°C . It was shown that the process of preparing PAN precursors and treating them with CoSO_4 on-line improves the tensile strength and modulus of the resultant carbon fibers. It was demonstrated that the continuous modification method in the spinning process of PAN precursors is effective, and the result is in accordance with the well-known prestabilization treatment which reduces the time required for stabilization and improves the properties of the resulting carbon fibers.¹⁵

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Table II Mechanical Properties of PAN Precursors and Resultant Carbon Fibers

Sample	PAN Precursors		Carbon Fibers	
	Tensile Strength (Gpa)	Young's Modulus (Gpa)	Tensile Strength (Gpa)	Young's Modulus (Gpa)
Untreated	0.87	7.26	2.5	197
Treated	0.89	7.32	3.2	205

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REFERENCES

1. Sudo, K.; Shimizu, K. *J Appl Polym Sci* 1992, 44, 127.
2. Zhang, D.; Sun, Q. *J Appl Polym Sci* 1996, 62, 367.
3. Newell, J. A.; Edie, D. D.; Fuller, L. E. *J Appl Polym Sci* 1996, 60, 825.
4. Watt, W.; Johnson, W. *Appl Polym Symp* 1969, 9, 215.
5. Bahl, O. P.; Mathur, R. B.; Phami T. L. *Mater Sci Eng* 1985, 73, 105.
6. Mathur, R. B.; Bahl, O. P. *Fibre Sci Tech* 1984, 20, 227.
7. Cagliostro, D. E. *Text Res J* 1980, 50, 632.
8. Ko, T. *J Appl Polym Sci* 1989, 37, 541.
9. Ko, T.; Liao, S. *J Mater Sci* 1992, 27, 6071.
10. Ko, T.; Huang, L. *J Appl Polym Sci* 1998, 70, 2409.
11. Wilkinson, K. U.S. Patent 5 804 108, 1998.
12. Wilkinson, K. U.S. Patent 6 054 214, 2000.
13. Wang, P. H.; Liu, J.; Li, R. Y. *J Appl Polym Sci* 1994, 52, 1667-1674.
14. Rajalingam, P.; Radhakrishnan, G. *JMS-Rev Macromol Chem Phys C* 1991, 31(285), 301-310.
15. Gupta, A. K.; Paliwal, D. K.; Bajaj, P. *JMS-Rev Macromol Chem Phys C* 1991, 31, 1-89.
16. McCabe, R.; Michael, J.; U.S. Patent 4 661 336, 1987.
17. Shiedlin, A.; Marom, G.; Zilkha, A. *Polymer*, 1985, 26, 447.
18. Ko, T. H.; Lin, C. H. *J Mater Sci Lett* 1988, 7, 628.
19. Ko, T. H.; Tei, M. L.; Ting, H. Y.; Lin, C. H. *Adv Meter Technol* 1987, 86, 208.
20. Bajaj, P.; Palinal, D. K.; Gupta, A. K. *J Appl Polym Sci* 1993, 49, 823-833.
21. Fineman, M.; Ross, S. D. *J Polym Sci* 1950, 5, 259.
22. Muller, T.; Tudos, F. *J Macromol Sci-Chem A* 1975, 9, 1.
23. Zhang, W.; Jiang, Q. *J Shandong Univ Tech* 1998, 28, 401-408.
24. Zuren, P. *Macromolecule Chemistry; Chemical Industry: Beijing*, 1998; p 199.
25. Ko, T.-H.; Ting, H.-Y.; Lin, C.-H. *J Appl Polym Sci* 1988, 35, 863-874.
26. Ko, T.-H.; Huang, L.-C. *J Mater Sci* 1992, 27, 2429-2436.
27. Weisweiler, W.; Subramanian, N.; Terwiesch, B. *Carbon* 1971, 9, 755.
28. Jain, M. K.; Abhiraman, A. S. *J Mater Sci*, 1987, 22, 278-300.
29. Wicks, B. J.; Coyle, R. A. *J Mater Sci* 1976, 11, 376.
30. Bennett, S. C.; Johnson, D. J. *Carbon* 1979, 17, 25.