

FT-IR Study of Stabilized PAN Fibers for Fabrication of Carbon Fibers

R. Eslami Farsani, S. Raissi, A. Shokuhfar, and A. Sedghi

Abstract—In this investigation, types of commercial and special polyacrylonitrile (PAN) fibers contain sodium 2-methyl-2-acrylamidopropane sulfonate (SAMPS) and itaconic acid (IA) comonomers were studied by fourier transform infrared (FT-IR) spectroscopy. The study of FT-IR spectra of PAN fibers samples with different comonomers shows that during stabilization of PAN fibers, the peaks related to $C\equiv N$ bonds and CH_2 are reduced sharply. These reductions are related to cyclization of nitrile groups and stabilization procedure. This reduction in PAN fibers contain IA comonomer is very intense in comparison with PAN fibers contain SAMPS comonomer. This fact indicates the cycling and stabilization for sample contain IA comonomer have been conducted more completely. Therefore the carbon fibers produced from this material have higher tensile strength due to suitable stabilization.

Keywords—PAN Fibers, Stabilization, Carbon Fibers, FT-IR.

I. INTRODUCTION

PAN fibers are used in weaving (blanket, carpet and clothes) and in engineering- housing (instead of asbestos) and most importantly for producing carbon fibers. In recent decade PAN fibers are considered as main material for production of carbon fibers. PAN fibers manufactured presently are composed of at least 85% by weight of acrylonitrile (AN) units. The remaining 15% consists of neutral and/or ionic comonomers which are added to improve the properties of the fibers. Neutral comonomers like methyl acrylate (MA), vinyl acetate (VA), or methyl methacrylate (MMA) are used to modify the solubility of the PAN copolymers in spinning solvents, to modify the PAN fiber morphology, and to improve the rate of diffusion of dyes into the PAN fiber. Ionic and acidic comonomers including the sulfonate groups like SMS, SAMPS, sodium p-styrene sulfonate (SSS), sodium p- sulfophenyl methallyl ether (SMPE), and IA also can be used to provide dye sites apart from end groups and to increase hydrophilicity [1-3].

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The composition of PAN fiber were used for obtaining precursor fibers usually contains 5-10 % neutral comonomers, 0-5 % acidic and ionic comonomers and the remaining acrylonitrile units. This organic material has an open chain structure with carbon as its backbone. The molecular structure of this fiber is composed of a set of long chain molecules [1].

The manufacture of carbon fibers from PAN precursors is mainly composed of two steps including thermal stabilization and carbonization. The first step (stabilization) involves heating the PAN fibers to approximately 180 to 300 °C in an oxygen-containing atmosphere to further orient and then crosslink the molecules, so that they can survive higher temperature pyrolysis without decomposing. The chemistry of the stabilization process is complex, but consists of cyclization of the nitrile groups ($C\equiv N$) and cross-linking of the chain molecules followed by dehydrogenation and oxidative reactions. This process transforms the linear polymer (or laterally ordered polymer) into a ladder structure which renders the polymer thermally stable and prevents melting during the subsequent carbonization process. The second step involves a carbonizing heat treatment of the stabilized PAN fibers to remove the non-carbon elements in the form of different gases. Carbonization is carried out at temperatures ranging from 700 to 1500 °C in an inert atmosphere. During this process, the fibers shrink in diameter and lose approximately 50% of its weight [3,4].

The main problem of carbon fibers is their high cost. High price of carbon fibers is mainly due to the high cost of the precursor i.e. special grade PAN fibers. To make this wonderful material popular in daily life and civil applications, prices should definitely be lowered. One way of achieving this is using cheap commercial PAN fibers (textile grade PAN). In recent years many attempts have been performed to use commercial PAN fibers as a precursor for fabrication of carbon fibers so that the price of carbon fibers is reduced [5,6]. In this research, chemical structure of commercial and special PAN fibers were studied by FT-IR spectroscopy in order to find the effects of PAN fiber precursor type on the chemical interaction during stabilization and properties of fabricated carbon fibers.

II. EXPERIMENTAL

According to Table I, commercial and special PAN fibers were selected for this study.

TABLE I
 THE SPECIFICATION OF PAN FIBRES PRECURSORS USED

Type of Fibers	Sample Code	Chemical Analysis (%)			
		AN	MA	IA	SAMPS
Commercial PAN Fibers	A	93	6	-	1
Special PAN Fibers	B	94	4.7	1.3	-

The PAN fibers were converted into carbon fibers during two stages as follows:

1- Stabilization in a chamber furnace with the air circulation system at ambient pressure and holding at 200, 210, 220 and 240 °C step by step for 2 hours.

2- Carbonization of the stabilized PAN fibers in a horizontal tubular furnace with a ceramic tube muffle under a high purity nitrogen atmosphere (99.999%) at 1200 °C for 10 minutes.

As received and stabilized PAN fibers were examined in this study by FT-IR. Tablets were made from these samples with KBr, then were studied by FT-IR BRUKER FT-IR spectrometer model IFS48 in oxygen environment and in the range of 400-4000 cm⁻¹. Tensile strength testing was done on carbonized single fiber samples by the ISO 11566 standard procedure. The test apparatus consisted of an Instron 5565 tensile tester equipped with a 2.5 N load cell and a cross head speed of 2 mm/min. The gauge length was kept 25 mm. At least 25 tests were conducted on each sample and the average of results were reported.

III. RESULTS AND DISCUSSION

According to Table I, fibers samples have AN and MA comonomer which are used to facilitate the polymer solubility in structure, increase of flexibility, increase of permeability and dyeability of PAN fibers. The main difference of fibers samples is the second comonomer. Samples A and B have IA and SAMPS comonomers respectively. These comonomers are acidic comonomers which are added to improve the capability of alkaline paint permeability [7].

IR spectra are considered as tool for determination the chemical interaction during heat treatment on PAN fibers. By using of these spectra, it is possible to study the relation between chemical changes and strength, aromatic index and fiber contraction during fabrication process. But analyzing these relations are so difficult because the intensity of bonds used for analysis depends on samples type, form and the way of preparation [8].

In Figs. 1 and 2 of FT-IR spectra of PAN fibers samples before stabilization and in Figs. 3 and 4 FT-IR spectra of stabilized fibers have been shown. In Table II, peaks to these spectra have been extracted and analyzed.

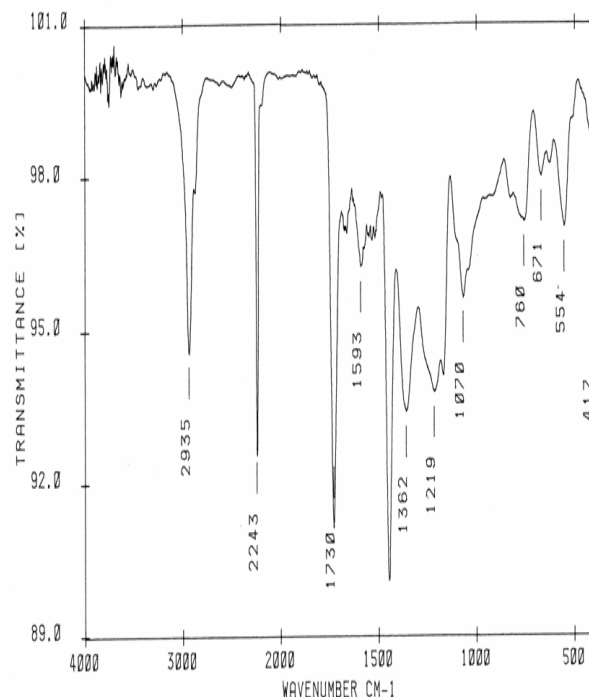


Fig. 1 FT-IR spectra of sample A before stabilization

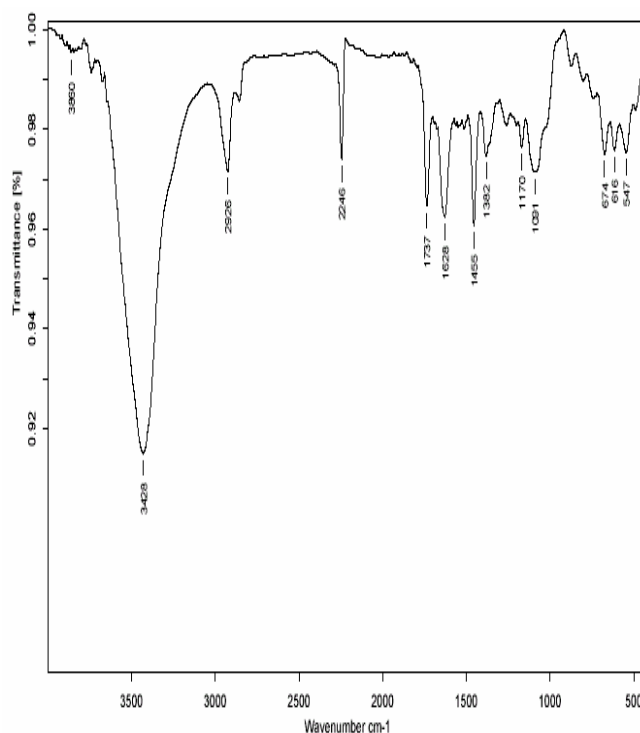


Fig. 2 FT-IR spectra of sample B before stabilization

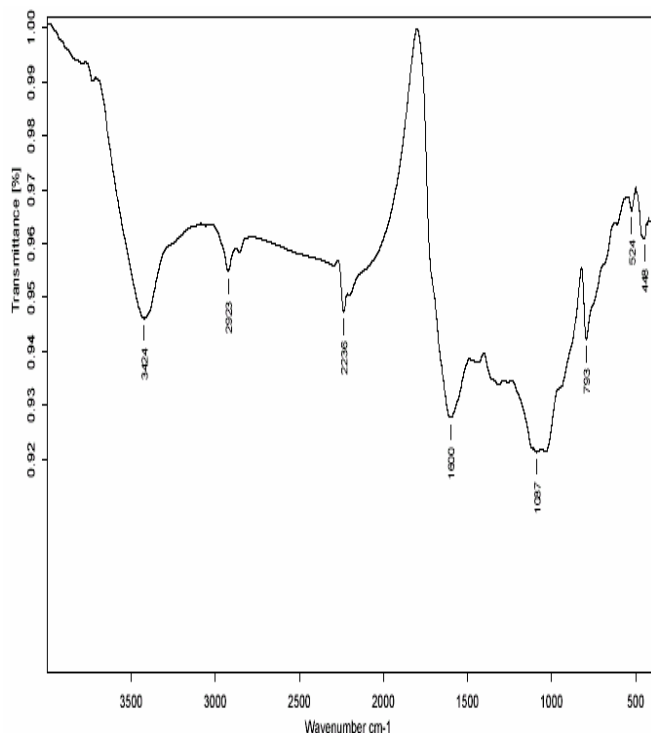


Fig. 3 FT-IR spectra of sample A after stabilization

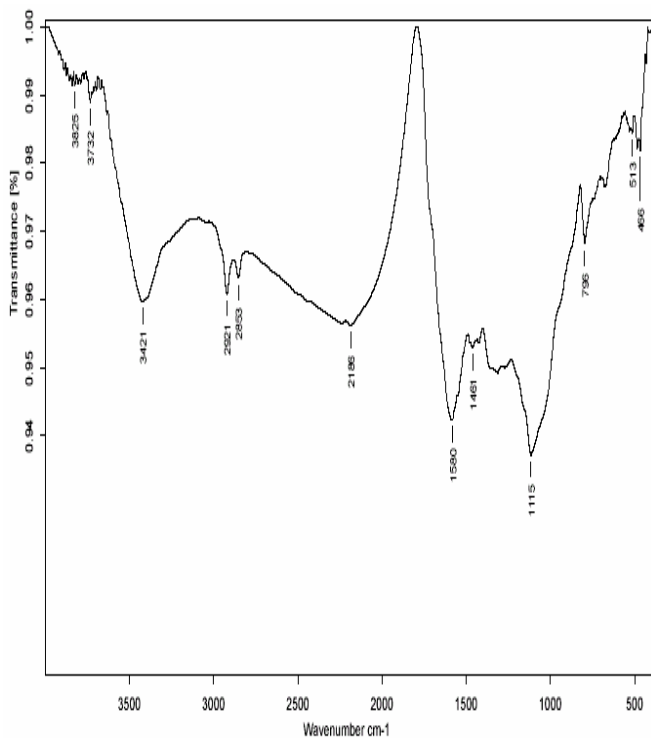


Fig. 4 FT-IR spectra of sample B after stabilization

TABLE II
 MAIN PEAKS OF FT-IR SPECTRA OF PAN FIBERS BEFORE AND AFTER STABILIZATION

Specification of Main peaks (cm ⁻¹)	Sample A stabilization		Sample B stabilization	
	Before	After	Before	After
	-	-	3860	3825
-	-	-	3732	
-	3424	3428	3421	
2935	2923	2926	2921	
2243	2236	2246	-	
-	-	-	2186	
1730	-	1737	-	
1593	-	1628	-	
-	1600	-	1580	
1460	-	1455	1461	
1362	-	1382	-	
1219	-	-	-	
-	-	1170	-	
1070	1087	1091	1115	
760	-	-	-	
-	793	-	796	
671	-	674	-	
554	524	547	513	
417	448	-	466	

FT-IR spectra of PAN fibers have many peaks which related to existence of CH₂, C≡N, C=O, C-O and C-H bonds. The absorption peaks are in range of 2926-2935 cm⁻¹ are related to C-H bonds in CH, CH₂ and CH₃ but in this range the second weak peak is observed which is related to C-H bonds also [9]. Another peak is observed in the range of 2243-2246 cm⁻¹ which is related to presence nitrile (C≡N) bonds and indicates the nitrile group exists in polyacrylonitrile chain. The absorption peaks in the ranges of 1730-1737 cm⁻¹ and 1170 cm⁻¹ are related to C=O or C-O bonds and are resulted from presence of comonomers like MA [10]. Absorbtion in the range of 1593-1628 cm⁻¹ is related to resonance C-O bonds. The peaks in the range of 1455-1460 cm⁻¹ is related to tensile vibration [8] and peaks in the range of 1362-1382 cm⁻¹ and range of 1219 cm⁻¹ are related to vibration in different situation [11].

According to graphs Figs. 1-4 and information of Table II, after heating PAN fibers and its stabilization, changes become visible in peaks. In this situation links in the range of 2926-2935 cm⁻¹ are reduced which are related to CH₂ bond. These links are weakened and with some displacement are observed in the range of 2921-2923 cm⁻¹. Additionally these bonds in the range of 1455-1460 cm⁻¹ are mainly omitted and in the case of sample B have been reduced which is related to CH₂ bonds too. Also, the main reduction is observed in links in the range of 2243-2246 cm⁻¹ which is resulted from the change C≡N bonds and their conversion to C=N. In A sample, C≡N peak is weakened in stabilized samples and are shifted to the

range of 2236 cm⁻¹ but in sample B the C≡N peaks (2246 cm⁻¹) is completely removed. Additionally in sample B the weak peak in 2186 cm⁻¹ is created which is related to C=NH bonds [12,13].

In conclusion, the reduction of peaks in 2243-2246 cm⁻¹ and 2926-2935 cm⁻¹ during stabilization is related to cyclization of nitrile group which is very intense in sample B in comparison with sample A and as it was stated earlier, 2246 cm⁻¹ peak for sample B is removed. This issues show that cycling and stabilization have been conducted more completely in sample B. Regarding this fact that the main difference of samples A and B are in their comonomers, so that in sample B, IA comonomer causes the conversion of C≡N to C=N bonds conducted completely in comparison with sample A contain SAMPS comonomer. A part from remove and reduction intensity of peaks, in some cases new links is observed. For example, in the range of 1580-1600 cm⁻¹ new absorption peaks are observed which are related to C=N or C=C bonds, but peaks in 1580 cm⁻¹ in sample B could be as the result of N-H bond formation. Also new peaks in the range of 793-796 cm⁻¹ are created as the result of =C-H bond formation. Increasing the intensity of =C-H groups and reduction of intensity of CH₂ groups shows that =C-H is created during aromatization of structure in the presence of oxygen [9].

During the stabilization step, the absorption peaks in the ranges of 1730-1737 cm⁻¹ and 1170 cm⁻¹ (related to C=O or C-O bonds) and two groups of peaks in the ranges of 1362-1382 cm⁻¹ and 1219 cm⁻¹ (related to C-H in different situation) mainly are removed in types of fibers. In the range of 670 cm⁻¹, some changes are observed which are not related to chemical changes of PAN fibers during oxidized stabilization. It is believe that this issue is may be related to different modes of CN and C-CN bonds appearance in FT-IR [9,12].

Table III shows the tensile strength of carbon fibers made from samples A and B. Results show that the high tensile strength of carbon fibers is achieved by carbonization of stabilized sample B. These results confirm the FT-IR spectra founding. IA comonomer help to complete stabilization reactions in B sample and increase their carbon fiber tensile strength.

TABLE III
 TENSILE STRENGTH OF CARBON FIBERS PRODUCED FROM TYPES OF PAN FIBERS

Sample Code	Tensile Strength (MPa)
A	1401
B	2710

IV. CONCLUSION

The study of FT-IR spectra of PAN fibers sample with different comonomers shows that during stabilization of PAN fibers, the peaks related to C≡N bonds and CH₂ are reduced sharply. These reductions are related to cyclization of nitrile groups and stabilization procedure. This reduction in PAN fibers having IA comonomer is very intense in comparison with PAN fibers having SAMPS comonomer. This fact indicates the cycling and stabilization for samples having IA comonomer have been conducted more completely. These reactions increase tensile strength of carbon fibers produced from this material in comparison with carbon fibers which are produced from PAN fibers contain SAMPS.

REFERENCES

- [1] J. C. Masson, "Acrylic Fiber Technology and Applications", Marcel & Dekker Inc., 1995.
- [2] K. K. Garg, "Poly-Acrylonitrile and Copolymers", Synthetic Fibers, Apr. / Jun. 1985, 29-35.
- [3] P. Rajalingam and G. Radhakrishnan, "Polyacrylonitrile Precursor for Carbon Fibers", JMS-REV. Macromol. Chem. Phys., C31 (283), 1991, 301-310.
- [4] V. I. Kostikov, "Fibre Science & Technology", Chapman & Hall, 1995.
- [5] O. P. Bahl and L. M. Manocha, "Development of High Performance Carbon Fibers from PAN Fibers", Chemical Age of India, 38, 5, 1987, 181-188.
- [6] H. M. Ezekiel, "Formation of Very High Modulus Graphite Fibers from a Commercial Polyacrylonitrile Yarn", Composite and fibrous Materials Branch, Nonmetallic Materials Divisions, Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio, 184-201.
- [7] D. C. GUPTA, "Acrylic Fibers-Polymerization", Synthetic Fibers, Oct. / Dec., 1984, 14-20.
- [8] O. P. Bahl, et al., "Recent Advances in Carbon Fiber technology", J. of Scientific and Industrial Research, 38, Oct. 1977, 537-554.
- [9] J. Mittal, et al., "IR studies of PAN Fibers Thermally Stabilized at Elevated Temperatures", Carbon, 32, 6, 1994, 1133-1136.
- [10] I. Shimada and T. Takahagi, "FT-IR Study of the Stabilization Reaction of Polyacrylonitrile in the Production of Carbon Fibers", J. of Polymer Science, Part A: Polymer Chemistry, 24, 1986, 1989-1995.
- [11] Z. Wangxi, L. Jie and W. Gang, "Evolution of Structure and Properties of PAN Precursors during Their Conversion to Carbon Fibers", Carbon, 41, 2003, 2805-2812.
- [12] P. Bajaj, D. K. Paliwal and K. Gupta, "Acrylonitrile-Acrylic Copolymers. I. Synthesis and Characterization", J. of Applied Polymer Science, 49, 1993, 823-833.
- [13] M. M. Coleman and R. J. Petcavich, "Fourier Transform Infrared Studies on the Thermal Degradation of Polyacrylonitrile", J. of Polymer Science, 16, 1978, 821-832.