

Conversion of Modified Commercial Polyacrylonitrile Fibers to Carbon Fibers

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

Abstract—Carbon fibers are fabricated from different materials, such as special polyacrylonitrile (PAN) fibers, rayon fibers and pitch. Among these three groups of materials, PAN fibers are the most widely used precursor for the manufacture of carbon fibers. The process of fabrication carbon fibers from special PAN fibers includes two steps; oxidative stabilization at low temperature and carbonization at high temperatures in an inert atmosphere. Due to the high price of raw materials (special PAN fibers), carbon fibers are still expensive.

In the present work the main goal is making carbon fibers from low price commercial PAN fibers with modified chemical compositions. The results show that in case of conducting complete stabilization process, it is possible to produce carbon fibers with desirable tensile strength from this type of PAN fibers. To this matter, thermal characteristics of commercial PAN fibers were investigated and based upon the obtained results, with some changes in conventional procedure of stabilization in terms of temperature and time variables; the desirable conditions of complete stabilization is achieved.

Keywords—Modified Commercial PAN Fibers, Stabilization, Carbonization, Carbon Fibers.

I. INTRODUCTION

CARBON fibers are used in composites with polymer, metal and ceramic matrices. Among the various composites, carbon fiber reinforced plastics have been particularly widely used as high performance materials in view of their light weight and special properties of the reinforcing carbon fibers. Carbon fibers are mainly used in different forms to reinforce lightweight polymer materials such as epoxy resin, polyesters or polyamides. For example, short or continuous yarns, fabrics, etc. can be used to contribute stiffness, strength and reduce the thermal expansion coefficient in the polymer matrix composites. 'Stronger than steel, stiffer than titanium, and lighter than aluminum has become a cliché for carbon fiber composites and is now being realized in practice [1], [2].

At present, three precursors including PAN-based, rayon-based, and pitch-based fibers are mainly used for the

production of carbon fibers. The majority of all carbon fibers used today is made from PAN precursor, which is a form of acrylic fiber. Acrylic 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 acrylic copolymers in spinning solvents, to modify the acrylic fiber morphology, and to improve the rate of diffusion of dyes into the acrylic fiber. Ionic and acidic comonomers including the sulfonate groups like sodium methallyl sulfonate (SMS), sodium 2-methyl-2-acrylamidopropane sulfonate (SAMPS), sodium p-styrene sulfonate (SSS), sodium p-sulfophenyl methallyl ether (SMPE), and itaconic acid (IA) also can be used to provide dye sites apart from end groups and to increase hydrophilicity. The compositions of acrylic 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 [3], [4].

The manufacture of carbon fibers from PAN-based precursors is 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, such 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 like H_2O , NH_3 , CO , HCN , CO_2 and N_2 . Carbonization is carried out at temperatures ranging from 1000 to 1500 °C in an inert atmosphere [1], [2], [5].

The price of carbon fibers is high because of two reasons: 1. The high price of raw materials (PAN fibers). 2. The high cost of production. PAN fibers used in production of carbon

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fibers are special type of these fibers which are different from commercial PAN fibers (used in textile industry) in terms of chemical compositions, type and amount of comonomers, cross section dimension, linear density and tensile strength. Textile PAN fibers (with applications like production of blanket, carpet and cloth) have higher cross section dimension and linear density and lower original tensile strength than special PAN fibers. It is not possible to produce suitable carbon fibers from this type of PAN fibers and final product has very low quality [6].

But in recent years some studies have been done to use textile PAN fibers with low price which led to reduction of price of carbon fibers and these studies almost succeeded in this regard [7], [8]. In previous studies by using some chemical and mechanical treatments before and after stabilization, carbon fibers with suitable mechanical properties were produced. The aim of this article is to examine possibility of carbon fibers fabrication from textile PAN fibers with modified chemical compositions with changes in stabilization parameters. To this matter, thermal characteristics of commercial PAN fibers were investigated and based upon the obtained results, with some changes in conventional procedure of stabilization in terms of temperature and time variables; the desirable conditions of complete stabilization is achieved.

II. EXPERIMENTAL

Commercial PAN fibers used in this study were produced by wet spinning method and have the round formed section. Table I shows the chemical compositions of these fibers (based on factory specifications). The commercial PAN fibers were converted into carbon fibers during two stages as follows:

- 1- Stabilization in a chamber furnace with the air circulation system at temperatures ranging from 180 to 270 °C in the discontinuous working conditions.
- 2- Carbonization of the stabilized PAN fibers in a horizontal tubular furnace with a ceramic tube under a highly pure nitrogen atmosphere (99.999%) at temperatures ranging from 1200-1450 °C for a period of 10 minutes.

TABLE I
THE CHEMICAL COMPOSITIONS OF COMMERCIAL PAN FIBERS USED

Name of Material	Weight (%)
Acrylonitrile (AN)	94
Methyl Acrylate (MA)	4.7
Itaconic Acid (IA)	1.3

To examine the properties of PAN precursor fibers, stabilized PAN fibers and carbon fibers, the following instrument were used:

- 1- Thermal analysis including DSC and TGA carried out by using a STA device (STA-625 from Rheometric Scientific). Samples were heated to 400 °C under an air atmosphere at a heating rate of 2 °C/min.
- 2- Tensile strength testing was done on 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 at 25 mm. At least 25 tensile tests were performed on each fiber types and average of test results were reported here.
- 3- Density was determined on short lengths of the fiber bundles in density gradient columns prepared from ZnCl₂ and H₂O by the ISO 10119 standard procedure. The average density of three tests was taken as the density of each sample.
- 4- Scanning electron microscope (SEM) carried out by using a CAMSCAN MV2300 microscope.

III. RESULTS AND DISCUSSION

In special PAN fibers, in addition of AN polymer, there are comonomers MA, carboxylic acid, vinyl bromide, acrylic acid, methacrylic acid and IA. But in textile PAN fibers, in addition of AN and MA, there are usually VA, SAMPS and SMS comonomers for improving the rate of diffusion of dyes into the acrylic fiber [9], [10]. In this study, according to Table I, commercial PAN fibers with modified chemical compositions have AN polymers and MA and IA comonomers. IA is an acid comonomer and is incorporated in small amounts to improve dyeability of acrylic fibers. Also, IA comonomers cause stabilization to perform in low temperature and high speed and the time of stabilization is reduced [11], [12].

TABLE II
THE PROPERTIES OF COMMERCIAL PAN FIBERS USED

Name of Parameter	Quality
Tensile Strength of Fiber	271 MPa
Elongation-at-Break	28 %
Linear Density	0.33 Tex
Fiber Diameter	21 μ

Special PAN fibers which are commonly used to produce carbon fibers have diameter up to 15 μ and low linear density (up to 0.17 tex) but commercial PAN fibers (which mentioned above) have diameter 21μ and linear density 0.33 tex. High cross section and linear density of PAN fibers cause incomplete stabilization of fibers in ordinary stabilization time-temperature cycles and only surface and middle layers become stabilized. So it is necessary to change conventional procedure of stabilization, by selecting different time and temperature stabilization cycles. Therefore, thermal characteristics of commercial PAN fibers were investigated.

The curves of DSC and TGA of PAN fibers used in this study are shown in Fig. 1. According to the DSC curve, one exothermic process in commercial PAN fibers was observed. This exothermic process is related to thermal stabilizing processes. The evolution of a large amount of heat in this case has been attributed to the cyclization of nitrile groups [11]. The exothermic reaction occurred at the temperature 198 °C.

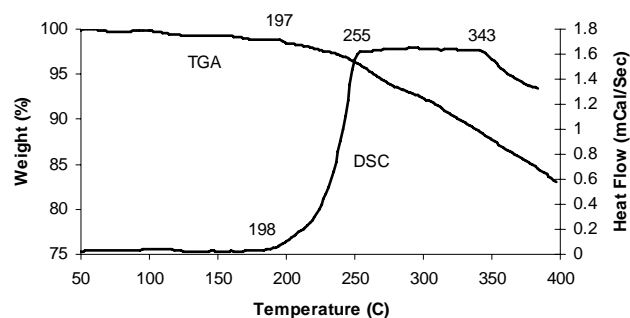


Fig. 1 DSC and TGA curves of commercial PAN fibers used

Based on TGA curve, fibers reactions are carried out with weight loss that the temperature of the initial high weight loss is 197 °C. This behaviour was confirmed by DSC experiments also. Then with comparison of these results, it revealed that weight loss at this stage results of oxidative stabilization, changes in polymer bonds, and remove of some volatile materials (in the form of H₂O, HCN and CO₂). Of course, this weight loss compared weight loss during of carbonization (as a result of the non-carbon elements elimination in the form of various gases) is much lower.

In DSC curves, the temperature of the initial reaction as well as the peak temperature depends largely on the experimental conditions, and especially on the rate of heating [6]. Therefore the resulted temperatures for the above curve are not the exact temperatures of the exothermic reactions and can vary within a thermal range.

On the basis the resulted temperature from the DSC and TGA curves, different thermal cycles were used for stabilization process. Then the density and tensile strength of the stabilized PAN fibers were measured. In Table III various types of stabilization process cycles and in Table IV the results of density and tensile strength of the stabilized PAN fibers have been presented.

TABLE III
STABILIZATION CYCLES OF PAN FIBERS

Cycle Code	Time-Temperature Cycle
S ₁	25-195(°C): 60 min. and hold in 195 °C for 1 hour 195-215(°C): 30 min. and hold in 215 °C for 1 hour 215-230 (°C): 30 min. and hold in 230°C for 1 hour 230-255 (°C): 30 min. and hold in 255°C for 1 hour
S ₂	25-200 (°C): 60 min. and hold in 200°C for 1 hour 200-215 (°C): 30 min. and hold in 215 °C for 1 hour 215-230 (°C): 30 min. and hold in 230 °C for 1 hour 230-255 (°C): 30 min. and hold in 255 °C for 1 hour

S₃ 25-200 (°C): 60 min. and hold in 200 °C for 1 hour
200-215(°C): 30 min. and hold in 215 °C for 1 hour
215-230 (°C): 30 min. and hold in 230 °C for 1 hour
230-255 (°C): 30 min. and hold in 255 °C for 1 hour

S₄ 25-195 (°C): 60 min. and hold in 195 °C for 1 hour
195-215 (°C): 30 min. and hold in 215 °C for 1 hour
215-230 (°C): 30 min. and hold in 230 °C for 1 hour
230-260 (°C): 30 min. and hold in 260 °C for 1 hour

S₅ 25-200 (°C): 60 min. and hold in 200 °C for 1 hour
200-215 (°C): 30 min. and hold in 215 °C for 1 hour
215-230 (°C): 30 min. and hold in 230 °C for 1 hour
230-260 (°C): 30 min. and hold in 260 °C for 1 hour

S₆ 25-205 (°C): 60 min. and hold in 205 °C for 1 hour
205-215 (°C): 30 min. and hold in 215 °C for 1 hour
215-230 (°C): 30 min. and hold in 230 °C for 1 hour
230-260 (°C): 30 min. and hold in 260 °C for 1 hour

S₇ 25-205 (°C): 60 min. and hold in 205 °C for 1 hour
205-215 (°C): 30 min. and hold in 215 °C for 1 hour
215-230 (°C): 30 min. and hold in 230 °C for 1 hour
230-270 (°C): 30 min. and hold in 270 °C for 1 hour

TABLE IV
DENSITY AND TENSILE STRENGTH OF STABILIZED PAN FIBERS

Cycle Code	Density (g/cm ³)	Tensile Strength (MPa)	Ratio of Fiber Tensile Strength Reduction During Stabilization (%)
S ₁	1.347	185	31.9
S ₂	1.351	187	31.1
S ₃	1.358	189	30.2
S ₄	1.339	178	34.3
S ₅	1.339	179	34
S ₆	1.342	180	33.6
S ₇	1.330	169	37.8

As it was stated earlier, the major requirement for producing carbon fibers with desirable mechanical properties from PAN fibers is the fact that PAN fibers become completely stabilized. Different sources expressed different criteria for complete stabilization. Gaining density in ranges between 1.35-1.40 g/cm³ [12], reduction about 30% in tensile strength for stabilized PAN fibers in comparison with PAN fibers [13] and 8-12 % oxygen content in stabilized PAN fibers [14] are among those criteria.

On the basis of the stabilized PAN fibers densities were shown in Table IV, stabilization procedure under cycle S₃ in comparison with other cycles is more complete because the stabilization PAN fibers have high density (1.358 gr/cm³) in comparison with other stabilized PAN fibers produced from other cycles. Also the results of Table IV regarding the ratio of fiber tensile strength reduction during stabilization confirm this fact that stabilization was completed by cycle S₃, because the percentage of the reduction under cycle S₃ is 30.2 %. Stabilized PAN fibers under cycle S₃ were carbonized in higher temperatures from 1200 °C to 1450 °C which the results come in Table V.

TABLE V
TENSILE STRENGTH OF CARBON FIBERS

Code of Carbonization Cycle	Temperature of Carbonization (°C)	Tensile Strength (MPa)
C ₁	1200	2253
C ₂	1250	2270
C ₃	1300	2391
C ₄	1350	2459
C ₅	1400	2541
C ₆	1450	2454

Tensile strength of carbon fibers begins to increase with the increase of temperature of carbonization up to 1400 °C and then begins to decrease. This fact complies with the results of studies on special PAN fibers. Fitzer states that the increase in final heat treatment temperature for producing carbon fibers up to 1600 °C comes along with increase of tensile strength and after that temperature there is sudden reduction of tensile strength [15]. He claims that this reduction is related to nitrogen release from fiber structure [16]. The Fitzer finding are 200 °C more than our results and it's concluded that comonomers as well as fibers fabrication histories change variation of tensile strength with heat treatment temperature also. According to the results of Table V, the highest tensile strength of carbon fibers fabricated from commercial PAN fibers with modified chemical compositions is 2541 MPa and comes with the stabilization cycle S₃ and the carbonization cycle C₅.

IV. CONCLUSION

By applying of stabilization and carbonization process, it is possible to produce desirable carbon fibers from commercial PAN fibers with modified chemical compositions. In order to achieve this, it is necessary to make some changes in conventional stabilization procedure to make sure that the whether stabilization procedure is completely done. The best tensile strength of carbon fibers is gained with stabilization cycle S₃ and the carbonization cycle C₅ and reaches to 2541 MPa.

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