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Conversion of modified commercial polyacrylonitrile fibers to carbon fibers

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Carbon fibres are fabricated from different materials, such as special polyacrylonitrile (PAN) fibres, rayon fibres and pitch. Among these three groups of materials, PAN fibres are the most widely used precursor for the manufacture of carbon fibres. The process of fabrication carbon fibres from special PAN fibres 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 fibres), carbon fibres are still expensive. In the present work the main goal is making carbon fibres from low price commercial PAN fibres with modified chemical compositions. The results show that in case of conducting completes stabilization process, it is possible to produce carbon fibres with desirable tensile strength from this type of PAN fibres. To this matter, thermal characteristics of commercial PAN fibres 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.

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1. Introduction

Carbon fibres are used in composites with polymer, metal and ceramic matrices. Among the various composites, carbon fibre reinforced plastics have been particularly widely used as high performance materials in view of their light weight and special properties of the reinforcing carbon fibres. Carbon fibres 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 aluminium' has become a cliché for carbon fibre composites and is now being realized in practice [5,12].

At present, three precursors including PAN-based, rayon-based, and pitch-based fibres are mainly used for the production of carbon fibres. The majority of all carbon fibres used today is made from PAN precursor, which is a form of acrylic fibre. Acrylic fibres 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 fibres. 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 fibre morphology, and to improve the rate of diffusion of dyes into the acrylic fibre. 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 fibre were used for obtaining precursor fibres 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 fibre is composed of a set of long chain molecules [4,13].

The manufacture of carbon fibres from PAN-based precursors is composed of two steps including thermal stabilization and carbonization. The first step (stabilization) involves heating the PAN fibres to approximately 180 to 300 ºC 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≡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 fibres 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 ºC in an inert atmosphere [5,12,14].

The price of carbon fibres is high because of two reasons: 1. The high price of raw materials (PAN fibres). 2. The high cost of production. PAN fibres used in production of carbon fibres are special type of these fibres which are different from commercial PAN fibres (used in textile industry) in terms of chemical compositions, type and amount of comonomers, cross section dimension, linear density and tensile strength. Textile PAN fibres (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 fibres. It is not possible to produce suitable carbon fibres from this type of PAN fibres and final product has very low quality [2].

But in recent years some studies have been done to use textile PAN fibres with low price which led to reduction of price of carbon fibres and these studies almost succeeded in this regard [6,7]. In previous studies by using some chemical and mechanical treatments before and after stabilization, carbon fibres with suitable mechanical properties were produced. The aim of this article is to examine possibility of carbon fibres fabrication from textile PAN fibres with modified chemical compositions with changes in stabilization parameters. To this matter, thermal characteristics of commercial PAN fibres 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.

2. Experimental

Commercial PAN fibres used in this study were produced by wet spinning method and have the round formed section. Table 1 shows the chemical compositions of these fibres (based on factory specifications). The commercial PAN fibres were converted into carbon fibres during two stages as follows:

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

Table 1. The chemical compositions of commercial PAN fibres 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 fibres, stabilized PAN fibres and carbon fibres, 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 ºC under an air atmosphere at a heating rate of 2 ºC/min.
2- Tensile strength testing was done on single fibre 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 fibre types and average of test results were reported here.
3- Density was determined on short lengths of the fibre bundles in density gradient columns prepared from $ZnCl_2$ and H_2O by the ISO 10119 standard procedure. The average density of three tests was taken as the density of each sample.
4- Scanning electron micrographs (SEM) carried out by using a CAMSCAN MV2300 microscope.

3. Results and discussion

In special PAN fibres, in addition of AN polymer, there are comonomers MA, carboxylic acid, vinyl bromide, acrylic acid, methacrylic acid and IA. But in textile PAN fibres, 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 fibre [10,11]. In this study, according to table 1, commercial PAN fibres 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 fibres. Also, IA comonomers cause stabilization to perform in low temperature and high speed and the time of stabilization is reduced [14,15]. In table 2, the properties of commercial PAN fibres used are given.

Table 2. The properties of commercial PAN fibres used.

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

Special PAN fibres which are commonly used to produce carbon fibres have diameter up to 15 μ and low linear density (up to 0.17 tex) but commercial PAN fibres (which mentioned above) have diameter 21μ and linear density 0.33 tex. High cross section and linear density of

PAN fibres cause incomplete stabilization of fibres 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 fibres were investigated.

The curves of DSC and TGA of PAN fibres used in this study are shown in figure 1. According to the DSC curve, one exothermic process in commercial PAN fibres 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 [15]. The exothermic reaction occurred at the temperature 198 ºC.

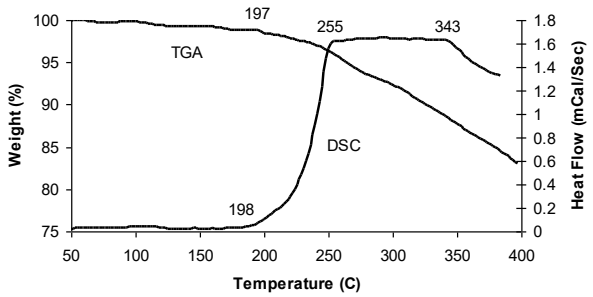

Fig. 1. DSC and TGA curves of commercial PAN fibres used.

Based on TGA curve, fibres reactions are carried out with weight loss that the temperature of the initial high weight loss is 197 ºC. This behaviour was confirmed by DSC experiments also. Then with comparison of these results, its 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 H_2O, HCN and CO_2). 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 [2]. 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 fibres were measured. In table 3 various types of stabilization process cycles and in table 4 the results of density and tensile strength of the stabilized PAN fibres have been presented.

Table 3. Stabilization cycles of PAN fibres.

Cycle Code	Time-Temperature Cycle
S_1	25-195(ºC): 60 min. and hold in 195 ºC for 1 hour 195-215(ºC): 30 min. and hold in 215 ºC for 1 hour 215-230 (ºC): 30 min. and hold in 230ºC for 1 hour 230-255 (ºC): 30 min. and hold in 255ºC for 1 hour
S_2	25-200 (ºC): 60 min. and hold in 200ºC for 1 hour 200-215 (ºC): 30 min. and hold in 215 ºC for 1 hour 215-230 (ºC): 30 min. and hold in 230 ºC for 1 hour 230-255 (ºC): 30 min. and hold in 255 ºC for 1 hour
S_3	25-200 (ºC): 60 min. and hold in 200 ºC for 1 hour 200-215(ºC): 30 min. and hold in 215 ºC for 1 hour 215-230 (ºC): 30 min. and hold in 230 ºC for 1 hour 230-255 (ºC): 30 min. and hold in 255 ºC for 1 hour
S_4	25-195 (ºC): 60 min. and hold in 195 ºC for 1 hour 195-215 (ºC): 30 min. and hold in 215 ºC for 1 hour 215-230 (ºC): 30 min. and hold in 230 ºC for 1 hour 230-260 (ºC): 30 min. and hold in 260 ºC for 1 hour
S_5	25-200 (ºC): 60 min. and hold in 200 ºC for 1 hour 200-215 (ºC): 30 min. and hold in 215 ºC for 1 hour 215-230 (ºC): 30 min. and hold in 230 ºC for 1 hour 230-260 (ºC): 30 min. and hold in 260 ºC for 1 hour
S_6	25-205 (ºC): 60 min. and hold in 205 ºC for 1 hour 205-215 (ºC): 30 min. and hold in 215 ºC for 1 hour 215-230 (ºC): 30 min. and hold in 230 ºC for 1 hour 230-260 (ºC): 30 min. and hold in 260 ºC for 1 hour
S_7	25-205 (ºC): 60 min. and hold in 205 ºC for 1 hour 205-215 (ºC): 30 min. and hold in 215 ºC for 1 hour 215-230 (ºC): 30 min. and hold in 230 ºC for 1 hour 230-270 (ºC): 30 min. and hold in 270 ºC for 1 hour

Table 4. Density and tensile strength of stabilized PAN fibres.

Cycle Code	Density (gr □ cm³)	Tensile Strength (MPa)	Ratio of Fibre 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 fibres with desirable mechanical properties from PAN fibres is the fact that PAN fibres become completely stabilized. Different sources expressed different criteria for complete stabilization. Gaining density in ranges between 1.35-1.40 gr/cm³ [16], reduction about 30 % in tensile strength for stabilized PAN fibres in comparison with PAN fibres [1] and 8-12 % oxygen content in stabilized PAN fibres [3] are among those criteria.

On the basis of the stabilized PAN fibres densities were shown in table 4, stabilization procedure under cycle S_3 in comparison with other cycles is more complete because the stabilization PAN fibres have high density (1.358 gr/cm³) in comparison with other stabilized PAN fibres produced from other cycles. Also the results of table 4 regarding the ratio of fibre tensile strength reduction during stabilization confirm this fact that stabilization was completed by cycle S_3, because the percentage of the reduction under cycle S_3 is 30.2 %. Stabilized PAN fibres under cycle S_3 were carbonized in higher temperatures from 1200 ºC to 1450 ºC which the results come in Table 5.

Table 5. Tensile strength of carbon fibres.

Code of Carbonization Cycle	Temperature of Carbonization (ºC)	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 fibres begins to increase with the increase of temperature of carbonization up to 1400 ºC and then begins to decrease. This fact complies with the results of studies on special PAN fibres. Fitzer states that the increase in final heat treatment temperature for producing carbon fibres up to 1600 ºC comes along with increase of tensile strength and after that temperature there is sudden reduction of tensile strength [9]. He claims that this reduction is related to nitrogen release from fibre structure [8]. The Fitzer finding are 200 ºC more than our results and it's concluded that comonomers as well as fibres fabrication histories change variation of tensile strength with heat treatment temperature also. According to the results of table 5, the highest tensile strength of carbon fibres fabricated from commercial PAN fibres with modified chemical compositions is 2541 MPa and comes with the stabilization cycle S_3 and the carbonization cycle C_5.

4. Conclusion

By applying of stabilization and carbonization process, it is possible to produce desirable carbon fibres from commercial PAN fibres 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 fibres is gained with stabilization cycle S_3 and the carbonization cycle C_5 and reaches to 2541 MPa.

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