**NEW CARBON MATERIALS**
Volume 31, Issue 5, Oct 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

**Cite this article as:** New Carbon Materials, 2016, 31(5): 550-554

NOTE

# The densification mechanism of polyacrylonitrile carbon fibers during carbonization

**Quan-sheng Ma[1], Ai-jun Gao[2]*, Yuan-jian Tong[2], Zuo-guang Zhang[1]**

[1]School of Materials Science and Engineering, Beihang University, Beijing 100191, China;
[2]National Carbon Fiber Engineering Research Center, Beijing University of Chemical Technology, Beijing 100029, China

**Abstract:** The densification mechanism of polyacrylonitrile carbon fibers during carbonization from 900 to 1 400 °C was investigated. The density, elemental composition, microstructure and weight loss of the fibers, as well as the gases released during the process were analyzed to reveal the mechanism. Results indicated that the density of the fibers was strongly dependent on the carbonization temperature and reactions involved indifferent temperature regimes. Condensation, pyrolysis and graphitization reactions were dominant at low (<1 050 °C), medium (1 050-1 250 °C) and high (>1 250 °C) temperatures, respectively. The amount of small molecule gas released and the fiber density both increased rapidly with temperature when condensation reactions dominated. The fiber density decreased as a result of nitrogen release when pyrolysis reactions dominated above 1050 °C while the fiber density increased due to the growth and increase in order of the graphene layers during graphitization. The two fiber density maxima found with increasing carbonization temperature were attributed to the different reactions.

**Key Words:** Carbon fiber; Densification; Carbonization; Condensation; Pyrolysis

## 1 Introduction

Polyacrylonitrile (PAN)-based carbon fibers are the most attractive as reinforcement for advanced composites [1-7], in the aerospace and national defense industry. Carbonization is a necessary step to convert PAN fibers to high-strength carbon fibers [8, 9] and its importance is the same as stabilization [10, 11]. Carbonization is typically carried out in an inert atmosphere at a high temperature (900–1 600 °C). During this process, non-carbon elements are released from the high-molecular-weight polymers to enrich carbon and the density of the fibers increases. In carbonization, stabilized fibers are subjected to heat treatment with an increasing temperature profile within a total residence time of only a few minutes [12-16]. To avoid thermal shock, low-temperature heat treatment usually between 300 and 800 °C is applied prior to carbonization.

Densification of carbon fibers is very important to obtain high performance product. In this work, we prepared PAN pre-carbonized fibers, which were then carbonized in a high temperature carbonization furnace in the temperature range of 900–1 400 °C. Various techniques were used to analyze the densification mechanism in relation to the chemical compositions, structures, and the reaction types. The results of our studies can provide guidelines for choosing more reasonable temperature schemes of carbonization to get highly-densified carbon fibers.

## 2 Experimental

Each tow of PAN fibers used to prepare the fiber samples contained 12 000 strands of monofilament (QF0901, Jilin Qifeng Chemical Fiber Co., LTD, China). Before high temperature heat treatment, PAN fibers were pretreated by passing first through a stabilization furnace and then a pre-carbonization furnace s to get the “pre-carbonized” fibers. The stabilization furnace was divided into six zones (2 m per zone) set at different temperatures (200, 218, 223, 237, 254, and 257 °C). The pre-carbonization furnace was divided into three zones (0.3 m per zone) set at 350, 450, and 680 °C. The pre-carbonized fibers were then heat treated at a high temperature carbonization furnace with two zones (0.3 m per zone). Two temperature schemes denoted as [900, T] and [T, 0] for high-temperature carbonization were used. [900, T] means that the first zone was fixed at 900 °C and the second zone with variable experimental temperatures. [T, 0] means that the temperature of the first zone was variable and the heating device of the second zone was switched off.

Elemental analysis was carried out with an Elementar Vario MICRO CUBE (Germany) elemental analyzer. The carbon, hydrogen, and nitrogen contents were analyzed in the carbonization.

TG-MS was carried out in an Ar atmosphere using a Netzsch STA449C system at a heating rate of 30 °C/min from 30 to 1 400 °C.

**Received date:** 15 August 2016; **Revised date:** 12 October 2016
***Corresponding author.** E-mail: bhgaoaijun@163.com

DOI: 10.1016/S1872-5805(16)60031-8

Changes in crystal structure that occurred during heat treatment were determined by using a Philips X'Pert PRO MDP diffractometer (operated at 40 kV and 40 mA) with Ni-filtered Cu $K\alpha$ radiation. Data were collected over the $2\theta$ range from 10° to 90° at a scan rate of 1(°)/ min. The apparent crystallite size was calculated from the fully corrected and resolved peak profiles. The crystallite size was calculated from the Scherrer equation (Eq.1) using the diffraction peak position and the full widths at half maximum (FWHM):

$$L(nlk) = K\lambda / B\cos\theta \quad (1)$$

where $\theta$ is the diffraction peak position of the (nlk) plane, $\lambda$=0.154 06 nm is the wavelength of the X-rays, $B$ is the FWHM the peak in radians of and $K$ is the Scherer geometric or shape factor. The crystallite correlation length ($L$a) along the fiber axis was determined by the (110) diffraction peak of the meridian scan. The shape factor K is 1.84 for $L$a.

Fiber tension was measured on-line during the high temperature carbonization by a tension meter (Schmidt DTMX-2000, German).

The density was measured at 25 °C in a density-gradient column (LLORD, UK), prepared with a mixture of 1,2-dibromoethane and carbon tetrachloride, which gave a density gradient from about 1.65 to 1.85 g/cm$^3$ from the top to the bottom.

## 3 Results and discussion

### 3.1 TG curves of the pre-carbonized fibers in He atmosphere

The TG curve of the pre-carbonized fibers at a heating rate of 30 °C/min is shown in Fig. 1. The mass of the fibers decreases with temperature. Below 700 °C, only a small amount of weight loss is observed because the fibers had been treated at 680 °C in the pre-carbonization. Between 700 °C and 1050 °C, the amount of weight loss increases appreciably, owing to the release of non-carbon elements from chemical reactions occurring at elevated temperature. Above 1050 °C, the weight loss in the TG curve begins to level off, which is

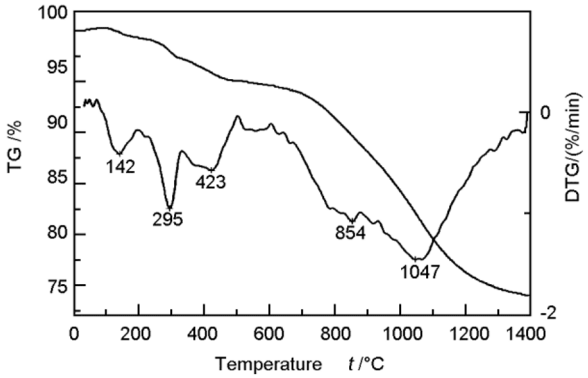


Fig. 1 TG and DTG curves of the pre-carbonized fibers.

indicative of a low content of non-carbon elements. The total weight loss of the fibers during heat treatment was 26.2%. In the derivative the mogravimetric analysis (DTG) curve in Fig. 1, two peaks were detected, which represented two discrete weight-loss temperature regimes: 700–900 °C and 900–1 400 °C, corresponding to weight losses of 6.2% and 14.9% respectively.

### 3.2 Elemental analysis

In the pre-carbonized fibers, there was a large amount of nitrogen, hydrogen, and oxygen, the content of which changed during the high-temperature carbonization, as shown in Fig. 2. Under the [900, T] and [T, 0] temperature schemes, the carbon and nitrogen contents varied in a similar manner, although their changing rate was faster under the [900, T] temperature scheme than the [T, 0] one mainly because the carbonization at low temperature was prolonged. As mentioned in the previous section, there was a mass loss at 700–900 °C. For the [900, T] temperature scheme, there was a significant drop in nitrogen content above 900 °C with a maximum releasing rate occurring at around 1 050 °C. Below 900 °C, the increase in the relative carbon content was slow and the release of nitrogen was insignificant. However, above 900 °C, the relative carbon content in the fibers increased markedly owing to the rapid release of nitrogen.

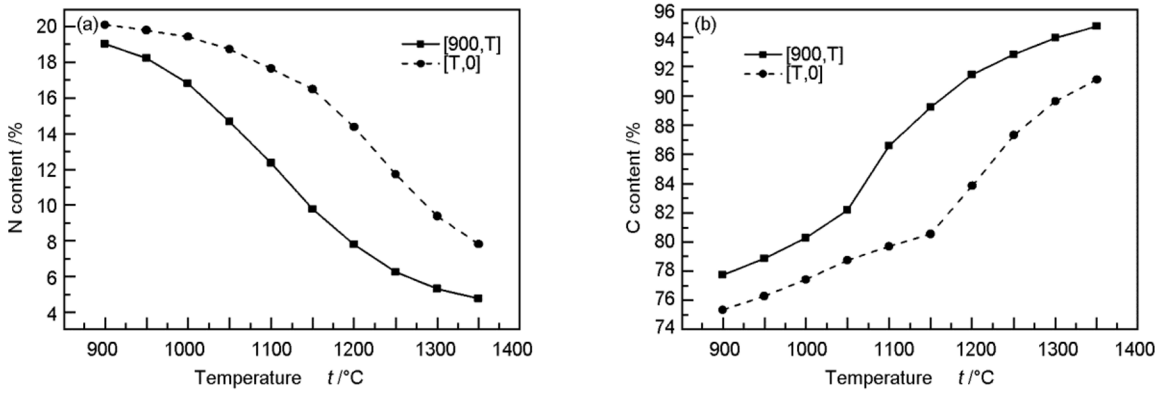


Fig. 2 Relative contents of elemental (a) nitrogen and (b) carbon as a function of temperature.