NEW EVALUATION OF PREOXIDATION EXTENT OF DIFFERENT PAN PRECURSORS USING EVOLUTION OF CORE/SHELL MORPHOLOGICAL STRUCTURE

Jie Liu, Wangxi Zhang, Jieying Liang

Department of carbon fibers and composites, Beijing University of Chemical Technology, Beijing ,100029, China

Corresponding author e-mail address: zhangwx@mail.buct.edu.cn

Introduction

For preparing a high performance carbon fiber, a polyacrylonitrile(PAN) fiber is presently recognized as the most important and promising precursor [1], which is a special acrylic fiber produced from a polymer of high molecular weight, moderate polydispersity, minimum molecular structure defects at the step of polymerization and fine fineness fiber of high tenacity and initial modulus. Then, the preparation of a carbon fiber usually includes three key processes, that is, spinning, preoxidation and carbonization, among which a preoxidation reaction is very important, because of it is a rate-determining or time-consuming step [2] during the conversion of PAN precursors to carbon fibers. It has been known that the preoxidation reaction is extremely complicated, because PAN fibers undergo various physical and chemical modifications, such as formation of an intermolecular crosslink and intramolecular cyclization, uptake and penetration of oxygen, polymerization of nitrile side groups to naphthyridine ring, shrinkage or elongation in a fiber, as a result, transforming a linear molecular structure to yield a ladder structure that can be subjected to the last high-temperature carbonization treatment without fusion. The quality of resultant carbon fibers depends strongly the degree of preoxidation, therefore, some parameters, such as the change of density, stabilization index [3], aromatization index [4], etc., were proposed to be a measure of the preoxidation extent of a PAN precursor which influences the ultimate properties of the end carbon fibers. However, examining the relationship between the morphology changes of the cross section of preoxidized fibers and their stabilization extent is an extremely straightforward approach. In this paper, we concentrate the comparative study of different precursor fibers and the evolution of core/skin of PAN fibers with the increase of heat treatment temperature.

Experimental

The selected PAN precursors were supplied from Asahi Kasei, Courtaulds, Mitsubishi, Beihua and Jihua, respectively. These precursor fibers maybe contain various chemical compositions. The preoxidation was carried out in a batch scale furnace with the fibers keeping a fixed length. The whole temperature pattern was programmed as an elevating 2 •/min rate from ambient temperature to a various desired temperature. When the aim temperature is reached, an individual preoxidized fibers sample was taken out.

The various fiber samples were embedded in an epoxy 618 resin, cured, and then were cut with a special ultra-thin microtome. The cross-section of the fibers was examined in a X5Z-H optical microscope with a camera.

Density of various fibers was obtained at 25 • by the use of density gradient column method. A column was used in which comprises a mixture of n-heptane and carbon tetrachloride with a gradient from 1.00 to 1.60 g/cm^3.

Results and Discussion

Determination of core/shell ratio

Figure 1 shows the schematic diagram of determining the core/shell ration of a fiber, the area of the skin, *AS*, can be calculated according to the following formula:

$$AS(\%) = \frac{\sum \pi (RS - RC)^2}{\sum \pi (RS)^2} \times 100 \qquad (1)$$

Where, *RS* is the radius of a fiber and *RC* is the radius of the core in a fiber.

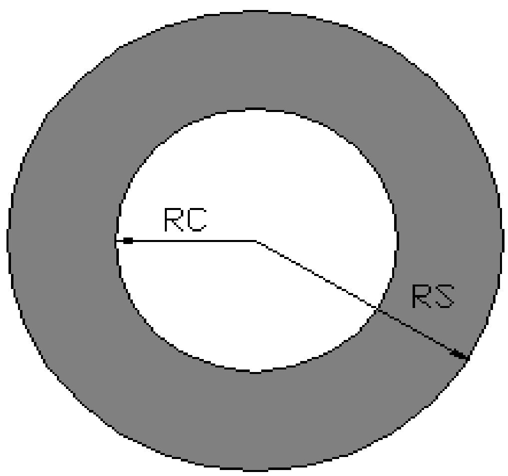
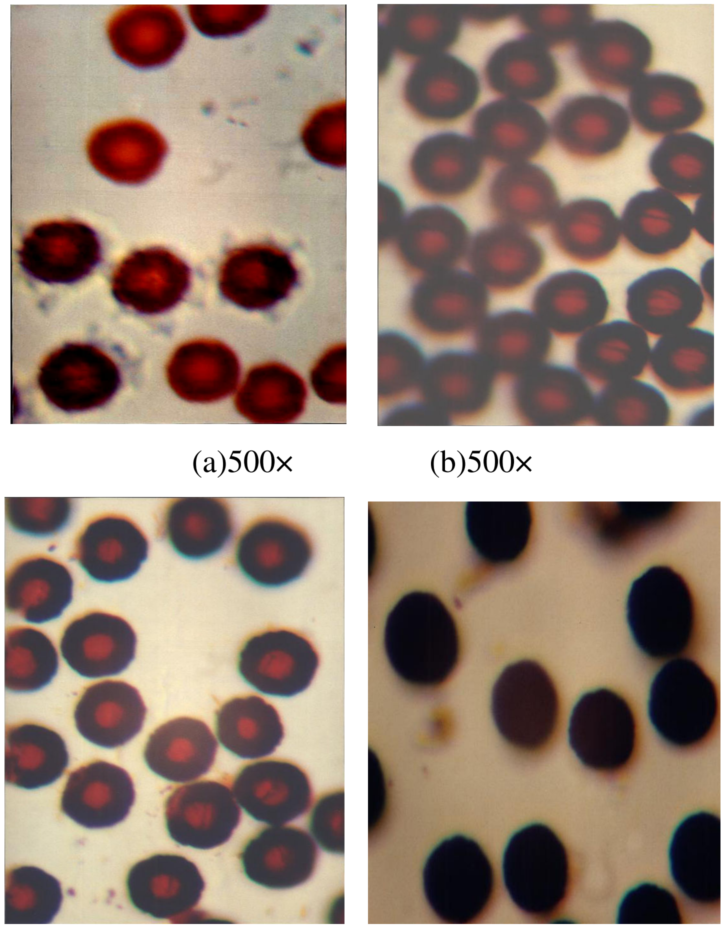


Figure1. The schematic diagram of determining the core/shell ratio of a fiber

The radius of the core and the fiber were measured from a transmission optical micrograph of a cross section of a fiber, as demonstrated in Figure 2. It has been generally found that with the increase of preoxidation extent, the area of the skin has been increased. It is assumed that the area of the skin (*AS*) of an original PAN fiber is regarded as zero. But it is not totally true, because the skin morphology had been formed in case of experiencing a solidification process when a fiber precursor was wet-spun. Here, in order to distinguish from the skin originated from inclusion of oxygen in a preoxidized fiber, this skin resulted from the solidification process is excluded. If the preoxidized fibers are fully thermal stabilized, the *AS* is designated as 100 %.



(a)500× (b)500×

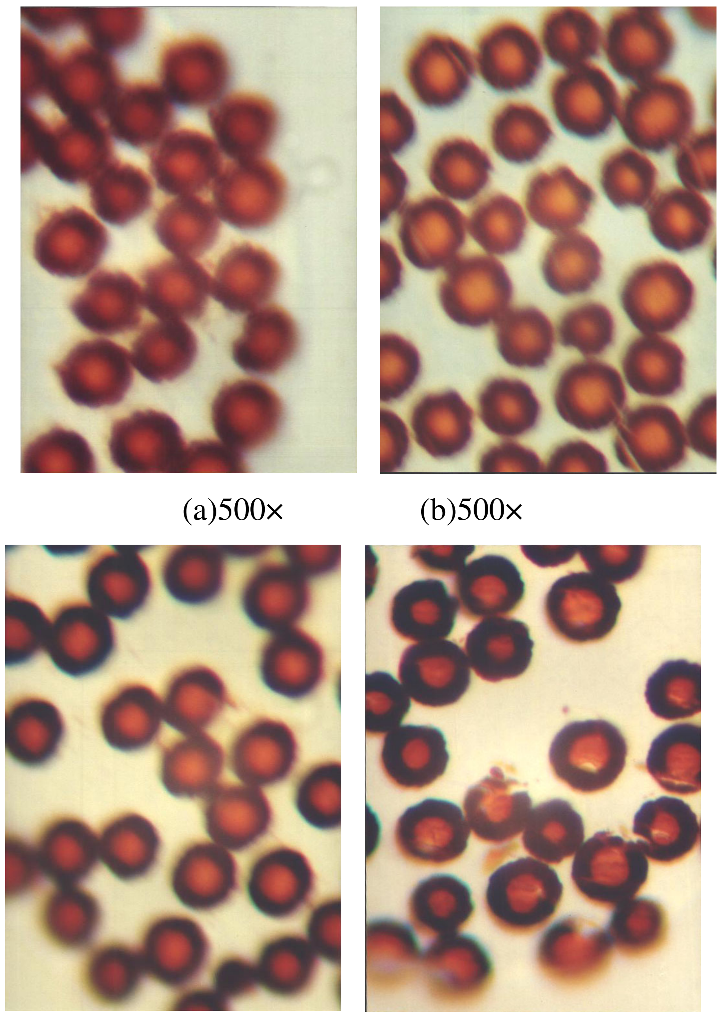
(c)500× (d)500×

Figure 2. The skin/core morphology of preoxidized fibers developed from Asahi Kasei precursors after heat treatment temperature (a)at 260 •;(b)at 280 •;(c)at 300 •;(d)at400 •

Evolution of core/skin morphology

The preoxidation reaction in air results the uptake of oxygen in a fiber, and the penetration of oxygen from the outer to the inner part of a fiber undergoes gradually with the increase of temperature or time. The outer part combined with oxygen which makes the fibers oxidized becomes dark yellow, then brown, dark in the end, whereas the inner part in a fiber which has not been combined with oxygen all the same displays undertone. Therefore, the cross-section morphology between the outer and inner part in the same fiber display discrepant morphological features.

The comparable difference of morphological structure between the outer part and the inner part in one fiber provides a new clue to evaluate the extent of preoxidation. Figure 3 shows the representative changes of cross-section morphology of preoxidized fibers developed from a Courtaulds precursor fiber at different heat treatment temperature. What the obtained changes of AS of some different preoxidized fibers with increase of temperature is shown in Table 1. It has been shown that for all different type PAN precursors with the increase of heat treatment temperature, the AS value increases. However, the formation and development rate of a core/shell displays different type, for example, when the heat treatment temperature is elevated to 240 •, both the *AS* value of preoxidized fibers developed from Asahi Kasei and Mitsubishi precursors are zero, whereas the *AS* of preoxidized fibers developed from Courtaulds and Beihua precursors has reached to 50.21 % and 58.26 %, respectively. This finding indicates that the thermal stabilization reaction of Courtaulds and Beihua precursors starts at a lower temperature compared to that of Asahi Kasei and Mitsubishi ones. As the temperature is up to 400 •, for all preoxidized fibers, the *AS* is 100 %. It should be noted that different PAN precursors should have different corresponding preoxidation program, keeping heating rate and other parameters at adequate values. But it is true that the core/shell morphology can directly tell us whether the extent of preoxidation is enough or not.



(a)500× (b)500×

(c)500× (d)500×

Figure 3 The core/skin morphology of preoxidized fibers developed from Courtaulds precursors after heat treatment temperature (a)at 240 •;(b)at 260 •;(c)at 280 •;(d)at 300 •

Table 1 The relationship between *AS* and temperature

Temperature(•)		210	240	260	280	300	350	400
AS(%)	Asahi Kasei	0	0	52.56	58.78	65.87	82.37	100
	Courtaulds	0	50.21	55.10	61.33	68.60	76.16	100
	Mitsubishi	0	0	54.10	56.89	59.67	80.40	100
	Beihua	0	58.26	60.25	65.05	69.36	76.20	100
	Jihua	0	54.82[a]		57.92	61.58	76.34	100

[a] Developed from 270•

The changes of density

The density of a preoxidized fiber is a usual measurement for estimating the extent of preoxidation [4]. Here, in order to scan some relations between density and abovementioned core/shell morphology, some preoxidized fibers developed from different PAN precursors were selected to comparatively study their changes of density with increase of heat treatment temperature. The density of preoxidized fibers as a function of temperature is shown in Figure 4. The densities of all precursor fibers increase when the heat treatment temperature increases, however, it has been clear that different PAN precursors have various densities with the increase of heat treatment temperature. Furthermore, the temperature, time, reaction medium and thermal stress will influence the changes in the density of a preoxidized fiber. Therefore, it is not very exact to evaluate the preoxidation extent for different PAN precursors using an identical density regime. If the preoxidation extent of all PAN precursors is controlled according to traditional aim, e.g., 1.35～1.38 g/cm^3, some PAN precursors maybe have been over-preoxidized, whereas other type PAN precursors probably have not underwent enough preoxidation reaction, as a result, some potentials for increasing the quality of resultant carbon fibers can not be fully made use of in the preparation process of high performance PAN-based carbon fibers

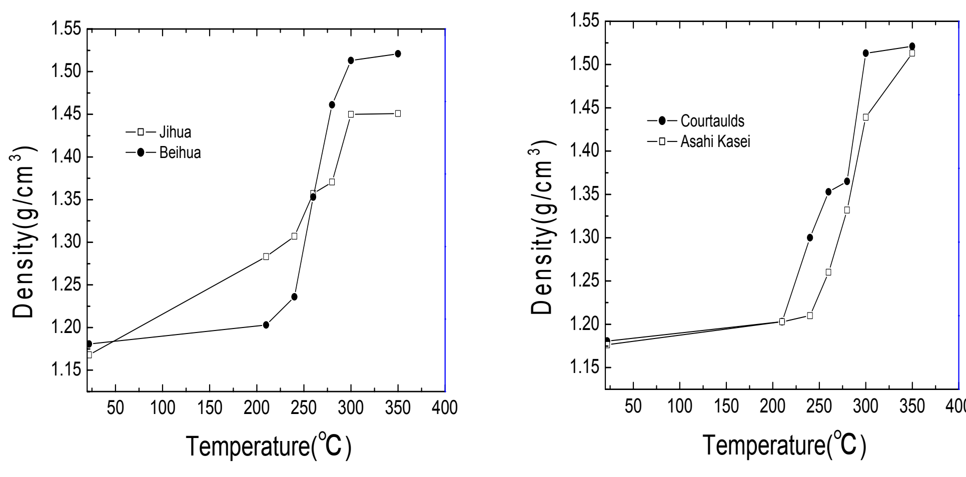


Figure 4. Relationship between density and heat treatment temperature

Conclusions

Conventional approach, e.g., density aim method, to evaluate the preoxidation extent of PAN precursor fiber is not very exact. However, a preoxidation extent, especially from conventional preoxidation temperature up to an elevated temperature in the range of 300～400□ can be followed up the scent by measuring the area of skin in the cross-section morphology, which is a kind of firsthand evidence.

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