Polymer Bulletin 58, 933–940 (2007)
DOI 10.1007/s00289-007-0737-1

Polymer Bulletin

SEM and OM Study on the Microstructure of Oxidative Stabilized Polyacrylonitrile Fibers

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Received: 17 September 2006 / Revised version: 28 November 2006 / Accepted: 19 January 2007
Published online: 26 January 2007 –

Summary

Three polyacrylonitrile fibers were oxidative stabilized by two heat treatment modes. OM and SEM were utilized to analyze the microstructure of oxidative stabilized fibers. In experiment I (by stepwise increasing temperature), no skin-core structure occurs in the polished cross-sections of stabilized fibers from 195°C to 265°C, unless they are subsequently heated by temperature higher than 270°C. In experiment II (by isothermal temperature), the oxidative stabilized fibers heated at 230°C for 120min shows homogeneous microstructure, but those heated at 250°C for only 60min displays distinct skin-core morphology. The shape of the boundary between the skin and the core resembles the cross-section shape of precursor fibers, but the thickness of the skin keeps almost unchanged of about 4μm. With the increasing of temperature, the stiffness of stabilized fibers increases and the evolution of microstructure undergo four steps. It indicated that temperature is the essential factor that affects the skin-core morphology, while the cross-section shape of precursor is irrelevant to that. If fibers are directly heated at high temperature without low temperature treatment, the light colored core will fuse into a hole and deteriorate the properties of carbon fibers.

Introduction

Polyacrylonitrile (PAN)-based carbon fibers are emerging as important reinforcement materials in many applications where light weight and high strength are the prime requirements [1, 2]. It is well known that the properties of carbon fibers are strongly dependent on their microstructure, which is influenced by a series of factors such as the properties of PAN precursor fibers, the conditions of oxidative stabilization and carbonization, and the microstructure of stabilized fiber [3-8]. The former two factors have been investigated in detail in our previous papers [9, 10]. In the present work, the microstructures of oxidative stabilized fibers at different stages were analyzed by scanning electron microscopy (SEM) and optical microscopy (OM) so as to

understand the microstructural evolution during the manufacture of carbon fiber. To our knowledge, the studies that dedicated on the microstructure of stabilized fibers are very few except some incomplete research on the skin-core morphology. Mathur, Mittal and their coworkers [11, 12] ever proposed that $KMnO_4$ was not only as catalyst for cyclization reaction, but also as plasticizer. Liu [13] found that the modification of PAN precursor fibers with $KMnO_4$ improved the skin-core ration during thermal stabilization process. Zhang [14] proposed that measuring the area ratio of skin/core could be used to evaluate the preoxidation extent of stabilized fibers. However, the formation mechanism of skin-core morphology and the microstructural evolution during thermal stabilization of PAN fibers are far from clearly known. In this work, some new aspects were proposed to provide useful directions for producing high property carbon fibers.

Experimental

Materials

PAN fibers were used as precursor in this work. The copolymer was polymerized with acrylonitrile and itaconic acid (99/1 wt.%) in dimethylsulfoxide (DMSO) using 2, 2′-azobisisobutyronitrile (AIBN) as initiator under an inert atmosphere of nitrogen. The polymerization solution was wet spun using a spinneret with 1000 capillaries and was drawn sequentially in DMSO coagulation bath, boiling water and water steam. By using different spinning parameters, three PAN fibers with different cross-sectional shape and different titre were obtained. The properties of precursor fibers are tabulated in Table 1.

Table 1. The properties of precursor fibers

Precursor	Titre (dtex)	Tensile strength (cN/dtex)	Elongation at break (%)	Shape of cross-section
P1	0.82	8.67	11.4	round
P2	1.02	7.40	10.2	round
P3	1.18	7.03	11.3	bean-like

Thermal stabilization and carbonization

Thermal stabilization of PAN fibers was carried out by two heating modes using self-designed equipment, reported in our previous paper [9]. For experiment I, fiber P2 was fed successively through ten furnace zones. The temperatures of the 10 zones were designated in sequence as 195°C, 205°C, 225°C, 235°C, 245°C, 255°C, 265°C, 270°C, 275°C, and 275°C, respectively. The duration for the fibers to pass through each zone was about 6min. For experiment II, the P1, P2 and P3 were heated together in one zone for the same time with two ends fixed to keep constant length, after the temperature was isothermally controlled at 230±2°C. Also they are heated at 250±2°C by the same method. The as-stabilized fibers treated by the two kinds of experiments were subsequently carbonized from 350 to 1400°C in carbonization furnace under the protection of pure nitrogen.

Characterization

The various oxidative stabilized fibers were embedded vertically in epoxy resin, preparing for microstructural characterization. The skin-core morphology was observed from the polished cross-sections on a JXA-840 optical microscope (OM) with a camera. The fracture cross-sections prepared in liquid nitrogen were coated with carbon and were observed using a JXA-40 SEM and a JEOL JSM-7600F cold field emission SEM. The tensile strength of the resulting carbon fiber tows was measured on a RGD-5 tensile testing machine (Shenzhen, China) at a cross-head rate of 5 mm/min and a gauge length of 200 mm.

Results and discussion

OM microstructure of oxidative stabilized fibers in experiment I

When PAN fibers are heat treated, the surface color will change from white to yellow, brown and eventually black with the rising of temperature or the increasing of heating time [15, 16], but the inner color has been observed heterogeneous by some researchers using OM [14, 17, 18]. In the present experiment I, we found that the oxidative stabilized fibers at different stages from 195 to 265°C show homogeneous color distribution, as shown in Figure 1(a), while those heated over 270°C appear uneven color at the radial direction. A dark colored skin and light colored core appears in the polished cross-section of fibers in Figure 1 (b). When temperature is higher than 270°C, the color difference between the skin and the core becomes more distinct. From the results of experiment I, it seems that the formation of skin-core morphology is caused by the combined effect of time and temperature. But in the following experiment, we found that temperature but not time is the essential factor.

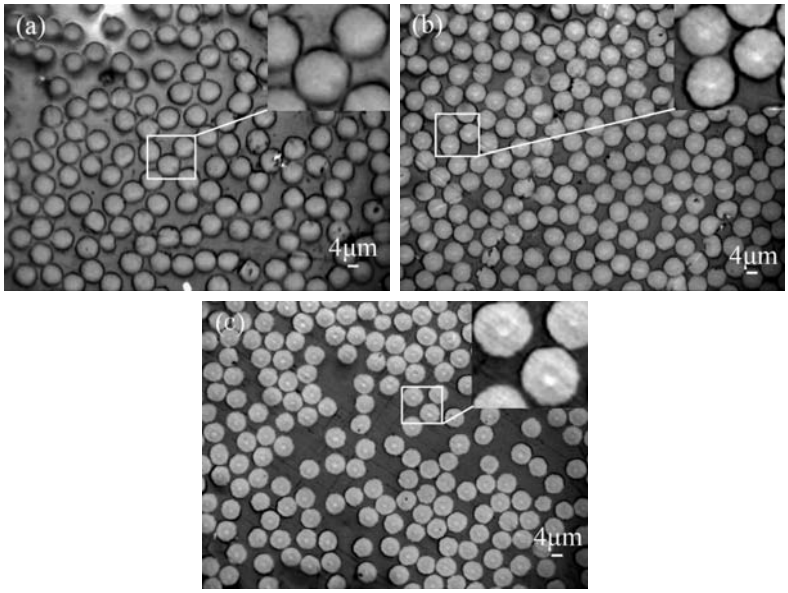

Figure 1. OM microstructure of oxidative stabilized fibers in experiment I. (a) heated from 195 to 250°C; (b) heated from 195 to 270°C; (c) heated from 195 to 275°C. Insets are the magnified images from the white rectangles.

OM microstructure of oxidative stabilized fibers in experiment II

Effect of temperature on the skin-core morphology

Figure 2 shows the OM microstructure of polished cross-section of fiber P1 which has been heated at 230°C for 120min and at 250°C for 60min and 120min, respectively. It can be seen that there is no skin-core morphology in the oxidative stabilized fibers heated at 230°C for 120min, but obvious skin-core morphology occurs in those fibers heated at 250°C for only 60min. With the duration time prolonged for 120min (as shown in Figure 2 (c)), the color of the skin becomes darker and the color of the core is not as bright as those in Figure 2 (b). This result indicates that if precursor fibers are heated at low temperature, uniform structure may present in the oxidative stabilized fibers even for very long duration time; but if they are heated at high temperature, heterogeneous skin-core morphology will come into being at short notice.

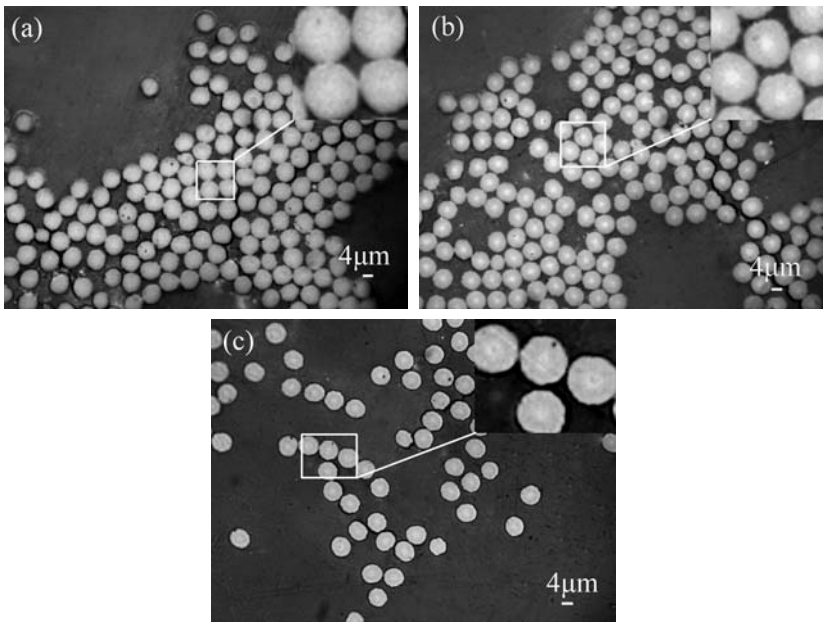

Figure 2. OM microstructure of oxidative stabilized fibers in experiment II. (a) heated at 230°C for 120min; (b) heated at 250°C for 60min; (c) heated at 250°C for 120min. Insets are the magnified images from the white rectangles.

Effect of cross-section shape of precursor fibers on the skin-core morphology

It is well known that some properties of precursor fibers, such as chemical composition, crystallinity and porosity, have much effect on the oxidative stabilization reactions. But no published literature has reported whether the cross-section shape of precursor fibers has influence on the microstructure of stabilized fibers. In the present paper, two precursor fibers (fiber P2 and P3) with different cross-section shape were isothermally treated at 250°C for 120min. The microstructures were shown in Figure 3 (a) and (b), respectively. It is clearly seen that skin-core morphology exists in both fibers, but the shape of the boundary between the skin and the core is not the same. In Figure 3 (a), the shape of the boundary is round, while in Figure 3 (b) the shape of the

boundary is like a bean, just resemble the cross-section shape of the precursor fiber. Therefore, it can be speculated that the formation of skin-core morphology is irrelevant to the cross-section shape of precursor fibers.

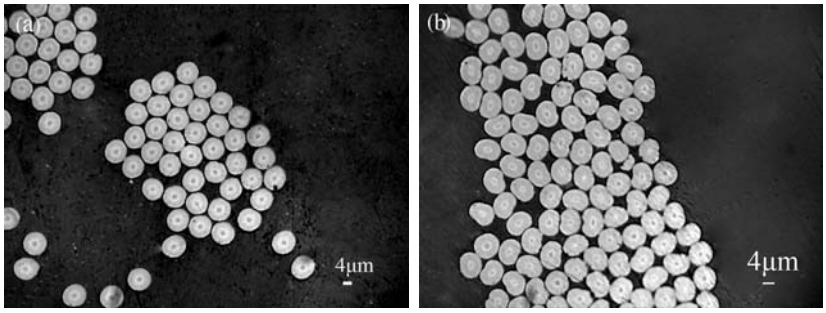

Figure 3. OM microstructure of oxidative stabilized fibers heated at 250°C for 120min from precursor fibers P2 and P3 with different cross-section shape. (a) round cross-section; (b) bean-like cross-section.

Effect of the titre of precursor fibers on the skin-core morphology

So far, it is not clear whether the titre of PAN precusor fibers has effect on the skin-core morphology of oxidative stabilized fibers. But some studies have indicated oxygen distribution in the mesophase pitch fibers is related to the diameter of pitch fibers. I. Mochida et al. [19] proposed that the fiber thinner than 10μm showed no skin-core structure. Figure 2 (c), Figure 3 (a) and (b) show the microstructure of stabilized fiber of PAN fiber P1, P2 and P3, respectively. The titres of the three precursor fibers are listed in Table 1. It can be seen that the skin-core morphology becomes more distinct with the increasing of fiber titre, but the thicknesses of the skin in three images are almost the same, which is about 4μm. Coincidentally, no skin-core morphology was found in individual filament with diameter of about 4μm, as shown in the rectangular frame in Figure 4. While, around it, other filaments with diameter about 10μm have obvious dark colored skin and light colored core. Thus, the present results suggest that 4μm is the critical diameter of PAN precursor fibers to avoid skin-core morphology in oxidative stabilized fibers, at least the experimental conditions in this paper was concerned.

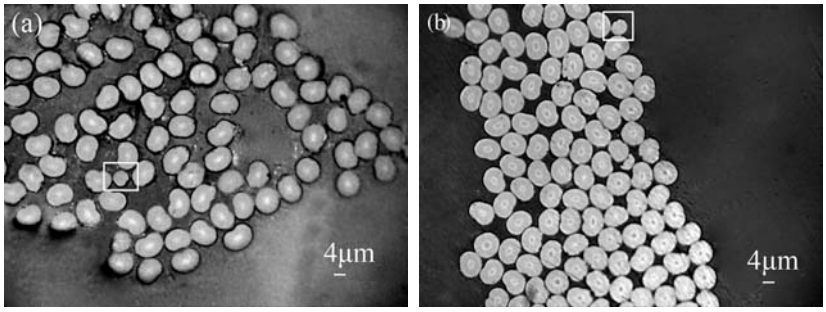

Figure 4. OM microstructure of oxidative stabilized fibers from fiber P3. (a) heated at 250°C for 60min; (b) heated at 250°C for 120min.

SEM microstructure of oxidative stabilized fibers in experiment I

During the process of polishing, we find that the stiffness of oxidative stabilized fibers become higher and higher with the increasing of temperature, because it is difficult to obtain a smooth plane for the fibers stabilized at low temperatures, but easier for those stabilized at higher temperatures. In order to give a better explanation, the oxidative stabilized fibers in experiment I were fractured in liquid nitrogen and the fractographs by SEM are shown in Figure 5. It can be seen that the fractographs in Figure 5 (a) and (b) appear ductile fracture features, while they show brittle fracture features in Figure 5(c) and (d), indicating that the stiffness of oxidative stabilized fibers is getting higher with the increasing of temperature. Figure 5 also displays that one single filament is composed of many microfibrils, which is consistent with the observation by other researchers [3, 7]. It demonstrates that with the temperature increasing, the evolution of microstructure undergoes four steps. At initial stage, the fractograph is random with loose and coarse fibrils in the core but tenuous fibrils in the skin as shown in Figure 5 (a). This is probably caused by the radial shrinkage as cyclization of nitrile happens. At the second stage about 255°C, the microfibrils become thinner and distribute uniformly, and the fractograph is more regular as shown in Figure 5 (b). When temperature rises to 270°C, the outer microfibrils combined with each others forming into a dense skin, while the rearrangement in the core is incomplete, as shown in Figure 5 (c). And at last, when temperature is higher than 270°C, the combination between microfibrils becomes denser and it is hard to distinguish single fibril in Figure 5 (d).

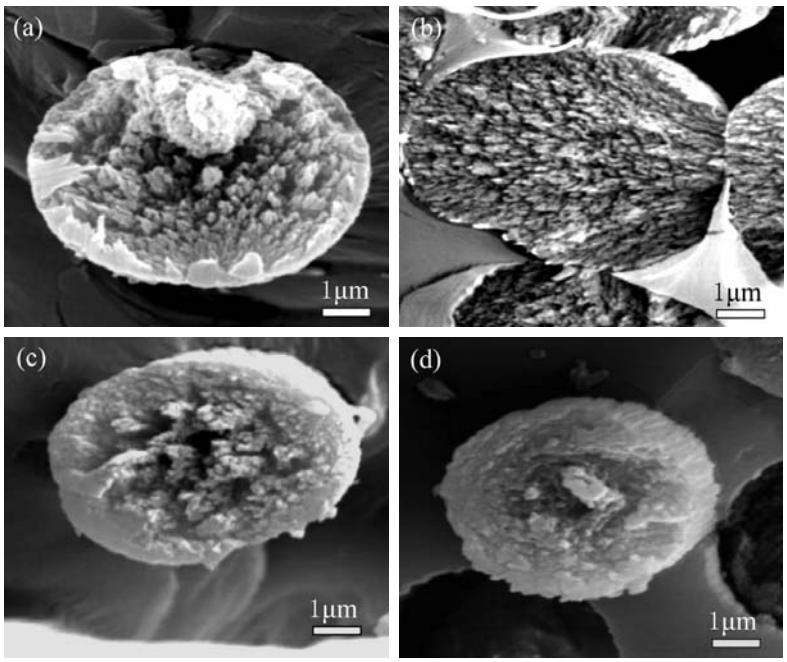

Figure 5. SEM fractograph of oxidative stabilized fibers in experiment I. (a) heated from 195 to 235°C; (b) heated from 195 to 255°C; (c) heated from 195 to 270°C; (d) heated from 195 to 275°C.

SEM microstructure of oxidative stabilized fibers in experiment II

It should be noted that dark centers were found in the light colored core in experiment II when temperature is 250°C, as shown in Figure 2 (c) and Figure 3 (a) and (b), but there is no such evidence at all stages in experiment I. Neither is in experiment II when temperature is 210 and 230°C. In order to clarify whether they are holes or not, the fractograph was analyzed by field emission SEM as shown in Figure 6 (a) and (b). A dark hole can be clearly seen in the center of single filament. From Figure 6 (a) some deformed microfibrils at the rim of the hole indicate ductile fracture feature, while the comparative smooth plane at the skin shows brittle fracture feature, suggesting that the skin and the core is different not in microstructure, but also in mechanical properties. From Figure 6 (b) the radial texture from the hole to outward shows that the hole is the fracture origin. The hole in oxidative stabilized fibers may pass down and even enlarge during the process of carbonization, which will inevitably reduce the tensile strength of the resultant carbon fibers. As shown in Table 2, the same precursor fiber P2 was stabilized in experiment I and II, and carbonized under the same conditions. Stabilized fibers without holes produce carbon fibers with tensile strength of 3.5GPa, while those which have holes in the center of fibers lead to carbon fibers with lower strength. Though the microstructure of as-stabilized fibers is homogeneous in experiment II at 230°C, but the tensile strength of the corresponding carbon fibers is not very high. The result is most likely attributed to the low average oxygen content at that condition.

Previous studies have shown that the oxygen content is higher in the dark-colored skin than in the cream-colored core [17]. So being deficient of oxygen, the chemical structure in the core is not fully stabilized. As a result, it cannot withstand high temperature treatment and fuses into a hole. However, if the PAN precursor fibers are firstly treated at low temperature, oxygen may slowly diffuse into the center of the

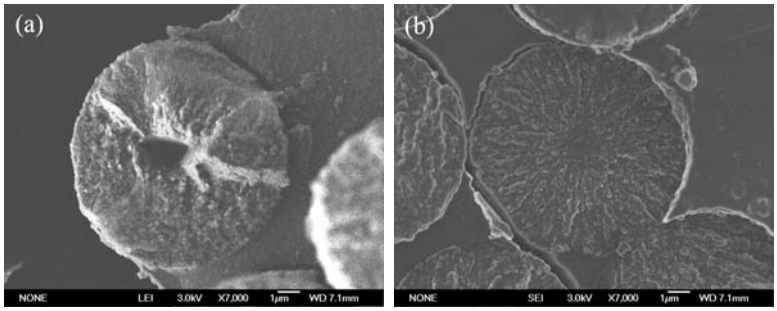

Figure 6. SEM fractograph of oxidative stabilized fibers in experiment II. Fibers in (a) and (b) are both heated at 250°C for 120min.

Table 2. Tensile strength of resulting carbon fibers treated from as-stabilized fibers in experiment I and II

Stabilization conditions	Microstructure of as-stabilized fibers	Tensile strength of resulting carbon fibers (GPa)
Experiment I	Skin-core, without hole	3.5
Experiment II at 230°C	Homogeneous	3.0
Experiment II at 250°C	Skin-core, with hole	2.8

fibers. Then as they subsequently undergo high temperature treatment, the core will be stable enough to avoid fusion. The results show that stepwise increasing temperature in experiment I is helpful improve the properties of the resulting carbon fibers.

Conclusions

By comparing the OM and SEM microstructure of various oxidative stabilized fibers which are treated by two heat treatment modes from three PAN precursor fibers, conclusions can be summarized as follows:
(1) Temperature is the essential reason for the formation of skin-core morphology in oxidative stabilized fibers, while the cross-section shape of precursor fibers is irrelevant to that.
(2) As far as the present experimental condition is concerned, 4μm is the critical diameter for obtaining oxidative stabilized fibers with homogeneous microstructure.
(3) A filament of oxidative stabilized fibers is composed of microfibrils, which changes in size, arrangement and stiffness with the increasing of temperature. The evolution of the microstructure can be divided into four stages: random with loose and coarse fibrils; microfibrils become thinner and rearrange evenly; microfibrils combine to each other; the microstructure compact more densely and rigidly.
(4) Without the low temperature heat treatment, holes will form in the center of fibers at high temperature. Holes are the fracture origin and will reduce the tensile strength of resultant carbon fibers.

Acknowledgements. This work was financially supported by the National Natural Science Foundation of China under grant No. 59783002 and the National High Technology Research and Development Program of China (863 Program) under grant No. 2002AA304130.

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