Effect of Oxygen Uptake and Aromatization on the Skin–Core Morphology During the Oxidative Stabilization of Polyacrylonitrile Fibers

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ABSTRACT: The isothermal oxidative stabilization of polyacrylonitrile fibers has been carried out at 210, 230, and 250°C. The stabilized fibers, treated for different times, have been characterized with elemental analysis, wide-angle X-ray diffraction, optical microscopy, and field emission scanning electron microscopy. A parabola relationship has been established between the oxygen uptake and stabilization time, whereas the aromatization index shows a trend of moderate ascension, retention, and acceleration. With increasing temperature and time, the skin–core morphology of the stabilized fibers becomes more and more distinct, but the skin thickness is almost unchanged for 60 and 120 min at 250°C. The fracture mechanism is ductile fracture in the core but is brittle fracture in the skin. The results indicate that the initial rapid oxygen uptake at a high temperature and the subsequent intense aromatization are responsible for the formation of the skin–core morphology. On the basis of the isothermal stabilization, an onion-like model is proposed for the structure of stabilized fibers that are treated by stepwise increasing temperatures in industrial production. J Appl Polym Sci 107: 1939–1945, 2008

Key words: fibers; morphology; stabilization

INTRODUCTION

The first and most important stage of the preparation of high-property carbon fibers from polyacrylonitrile (PAN) fibers is oxidative stabilization under tension.[1,2] In the process of stabilization, complicated physical and chemical reactions take place in fibers, such as intramolecular cyclization, intermolecular crosslinking, oxidation, and fiber shrinkage, giving rise to the formation of a thermally stable aromatic ladder structure that can withstand high-temperature carbonization.[3–7] The quality of the resulting carbon fibers depends strongly on their microstructure, which is influenced greatly by the morphology of the stabilized fibers. Kulakova et al.[8] found that after rapid carbonization of stabilized fibers possessing a heterogeneous structure, the heterogeneity was even enhanced, and an internal cavity developed. Therefore, it is important to determine what the main factors are that affect the microstructure of stabilized fibers and to analyze the formation mechanism of structural flaws.

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To the best of our knowledge, studies devoted to the microstructure of stabilized PAN fibers are very few, especially since the 1980s. In 1975, Watt and Johnson[1] reported the stabilization of two kinds of PAN fibers in vacuum and air. They showed that in the fiber with an acidic constituent, a two-zone morphology with a dark rim and cream-colored core formed after treatment at 230°C for 4 h in air, but uniform cross sections were seen in the fiber without an acidic constituent under the same conditions. However, when the two kinds of fibers were heat-treated *in vacuo* for 6 h at 230°C and this was followed by heating for 1 h in air, both fibers presented an oxidation zone. In 1979, Warner et al.[9] presented more detailed research on the mechanism of oxidative stabilization related to oxygen uptake. They proposed two limited cases, that is, diffusion-limited and reaction-limited kinetic processes. Under the diffusion-limited condition, the uptake of oxygen varied linearly with the square root of time from the time when a distinct mantle–core boundary was first observed. Under the reaction-limited stabilization condition, the uptake of oxygen was linear with time.

In this study, the influence of the oxygen uptake and aromatization degree on the microstructure of stabilized fibers was analyzed, and a new aspect of

the formation of a skin–core morphology was thereby determined.

EXPERIMENTAL

Precursor fibers

PAN copolymer was polymerized with acrylonitrile and itaconic acid (99/1 wt %) in dimethyl sulfoxide (DMSO) with 2,2′-azobisisobutyronitrile as the initiator under an inert atmosphere of nitrogen. The polymerization solution was wet-spun with a spinneret with 1000 capillaries and was drawn sequentially in a DMSO coagulation bath, boiling water, and water steam. The as-spun PAN fibers had an average titer of 1.05 dtex, a tensile strength of 6.73 cN/dtex, and an elongation at break of 9.9%.

Oxidative stabilization

The oxidative stabilization of PAN fibers was carried out in hot flowing air in self-designed equipment reported in our previous work.[10] Three furnace zones were used and were preset at 210, 230, and 250°C, respectively. The temperature was controlled by a computer program with an error of ±2°C. After the temperature was stable, six tows of the same PAN precursor fibers were quickly passed together through the three zones and were fixed at a constant length. Every other 20 min, from 0 min to 120 min, one tow of stabilized fibers in each temperature zone was cut down for further characterization.

Characterization

Various stabilized fibers were characterized with a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) and D/max-rc diffractometer (Rigaku, Japan) with Ni-filtered Cu Kα radiation. About 2 mg of chopped fiber samples was used for elemental analysis. The scanning rate of wide-angle X-ray diffraction (WAXD) was 4°/min with a scanning step of 0.02°. The crystallite size of the laterally ordered domains (L_c) was estimated with the Scherrer equation:[11]

$$L_c = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where λ is the wavelength of the Cu Kα X-ray, B is the full width at half-maximum (FWHM) intensity of the peak around 2θ = 17°, and K is a constant (0.89). The aromatization index (AI), described by Uchida et al.,[12] was calculated with the following formula:

$$\mathrm{AI} = \frac{I_a}{I_a + I_p} \tag{2}$$

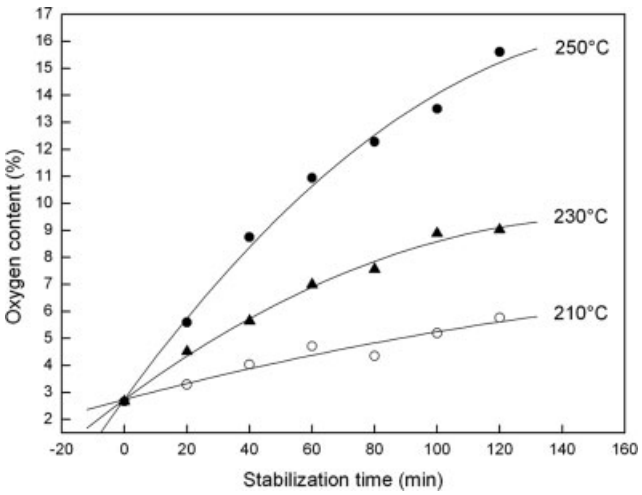

Figure 1 Oxygen content in stabilized fibers as a function of time at different temperatures.

where I_a and I_p are the intensities of the peaks around 2θ = 25.5° and 2θ = 17° in WAXD patterns, respectively.

The tows of various stabilized fibers were mounted vertically in epoxy resin. The polished cross sections of these samples were observed on a Nikon LV100D optical microscope (Nikon, Japan) with a camera. The fracture cross sections prepared in liquid nitrogen were sprayed with carbon and were observed on a JEOL JSM-7600F cold field-emission scanning electron microscope (Japan).

RESULTS AND DISCUSSION

Changes in the oxygen uptake with the stabilization time and temperature

The oxygen contents of stabilized fibers as a function of the heat-treatment time are shown in Figure 1. Although the incremental rates of the oxygen content are different for 210, 230, and 250°C, all three curves show parabolic time dependence. This result is similar to fiber C in Warner et al.'s study,[9] probably because both precursor fibers have an acid comonomer. The corresponding functions deduced from Figure 1 by Origin software are as follows:

$$y_1 = 2.74 + 0.03t - 0.00006t^2 \tag{3}$$

$$y_2 = 2.74 + 0.09t - 0.00027t^2 \tag{4}$$

$$y_3 = 2.74 + 0.16t - 0.00046t^2 \tag{5}$$

where y_1, y_2, and y_3 are the oxygen contents at 210, 230, and 250°C, respectively, for stabilization time t. The rate of oxygen uptake (dy/dt) is illustrated in Figure 2, which shows more intuitively that temperature has a prominent influence on oxygen uptake

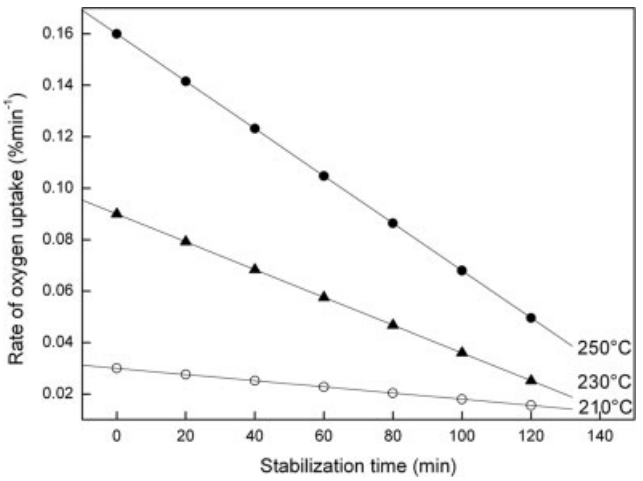

Figure 2 Rate of oxygen uptake as a function of time at different temperatures.

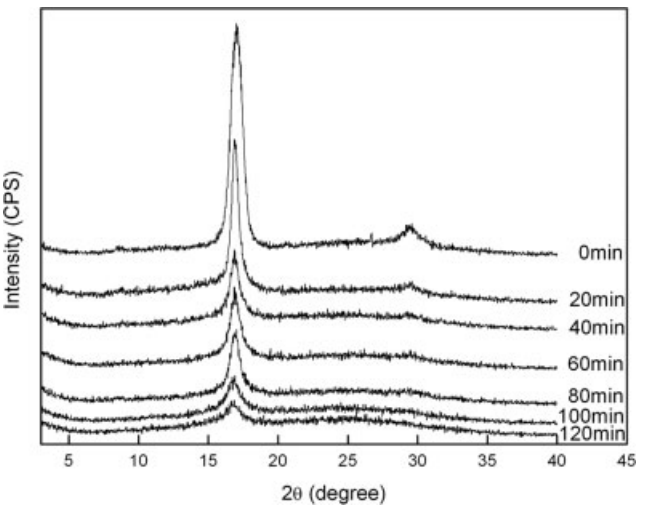

Figure 3 WAXD patterns of stabilized fibers treated for various durations at 230°C.

during oxidative stabilization. With isothermal treatment at 250°C, the rate of oxygen uptake is very high at the beginning of the reaction but decreases quite rapidly with increasing time. By contrast, with isothermal treatment at 210°C, the rate of oxygen uptake is very low at the beginning of the reaction but decreases slowly later. It can be speculated that the rate of oxygen uptake will tend to zero at a certain time that occurs earlier at a high temperature but later at a low temperature. In other words, the oxygen content has a limited value corresponding to one stabilization temperature. The lower the temperature is, the lower the limited value of the oxygen content is. Therefore, to obtain stabilized fibers with an oxygen content of 10–12 wt %, which has been reported to be essential for producing high-quality carbon fibers,[13,14] PAN fibers must undergo high-temperature stabilization rather than just be treated at a low temperature for very long time. This indicates from another point of view that time and temperature are not equivalent during oxidative stabilization. For example, the oxygen content in stabilized fibers that have been heated at 210 or 230°C for 120 min is still much lower than that of fibers heated at 250°C for only 60 min, as shown in Figure 1.

Changes in the aromatization degree with the stabilization time and temperature

PAN fibers are known to be highly atactic, composed of ordered crystalline regions interspersed in a disordered or amorphous phase.[15,16] During oxidative stabilization, the structure of PAN fibers will change remarkably because of physical and chemical reactions, which can be detected by WAXD. Figures 3 and 4 compare the WAXD patterns of PAN and stabilized fibers treated for various durations at 230 and 250°C. Analogously to the research results in the literature,[17] both figures shows similar trends: the intensities of the peaks around $2\theta = 17^\circ$ and $2\theta = 29.5^\circ$ become weaker with prolonged time, and a new diffraction peak appears around $2\theta = 25.5^\circ$ after a long period of treatment. Yet significant differences exist between Figures 3 and 4 because of different temperatures. In Figure 3, the peak around $2\theta = 17^\circ$ first becomes narrower after treatment for 20 min but then becomes broader and broader from 40 to 120 min; this implies that the crystallite size increases first and then decreases. The residual peak can be clearly observed even in the stabilized fibers treated for 120 min. In contrast, the width of the peak around $2\theta = 17^\circ$ in Figure 4 shows no apparent narrowing after treatment for 20 min, and this peak almost disappears after treatment for 100 min. After 120 min, the peak is too weak even to calculate the

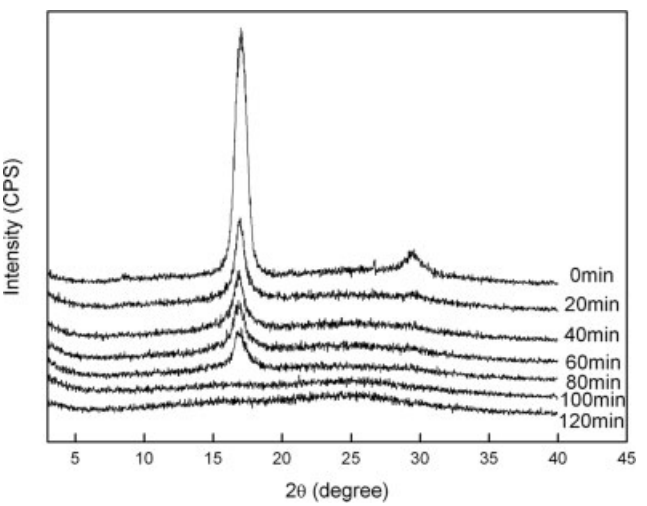

Figure 4 WAXD patterns of stabilized fibers treated for various durations at 250°C.

TABLE I
WAXD Data Based on Figure 3

Stabilization time (min)	Intensity at $2\theta = 17^\circ$ (CPS)	Intensity at $2\theta = 25.5^\circ$ (CPS)	FWHM at $2\theta = 17^\circ$ (°)	Crystallite size (nm)	AI (%)
0	2922	0	0.9802	8.11	0
20	1951	118	0.5766	13.79	6
40	908	164	0.7816	10.17	15.3
60	909	162	0.8861	8.97	15.1
80	858	166	0.8822	9.01	16.2
100	536	170	1.0875	7.31	24.1
120	387	194	1.186	6.70	33.4

FWHM. Therefore, it is indicated that stabilization at a higher temperature can initiate an aromatization reaction earlier and suppress the growth of crystallites.

Detailed data calculated from WAXD patterns, such as the crystallite size and AI, are tabulated in Tables I and II. The changes in AI as a function of the stabilization time at 230 and 250°C are compared in Figure 5. For the two temperatures, the changes in AI display the same increasing trend, including moderate ascension, retention, and acceleration. However, it can be seen that the aromatization reaction is very sensitive to temperature. With heating for 20 min, AI rises to 14.2% at 250°C but to only 6% at 230°C. When the heat-treatment time is longer than 80 min, the increasing rate of AI is much higher at 250°C than that at 230°C. This provides further evidence that stabilization at a higher temperature can enhance the aromatization reaction earlier and lead to more intense reactions subsequently. The changes in the crystallite size in Figure 6 show a trend opposite to that of AI in Figure 5, demonstrating that the aromatization reaction is the direct reason for the transformation from a crystal phase to an amorphous phase in stabilized fibers.

Formation of the skin–core morphology in the stabilized fibers

Three tows of stabilized fibers were used for optical microscopic examination. For the convenience of explanation, the fibers treated at 230°C for 120 min, at 250°C for 60 min, and at 250°C for 120 min are designated A, B1, and B2, respectively. Figure 7 shows the polished cross-section morphologies of these samples. The A fibers exhibit a dark-colored skin and a light-colored core with a blurry interface between them. The skin thickness accounts for about five-sixths of the radius of a single filament, as shown in Figure 7(a). With temperature and time increasing, the skin–core morphology becomes more and more distinct, and a dark hole appears at the center of these fibers, as shown in fibers B1 and B2 in Figure 7(b,c). The thickness of the skin seems unchanged from 1 to 2 h. However, the boundary of the dark hole proceeds outward with increasing stabilization time.

On the basis of the experimental results stated previously, the formation of a skin–core morphology is found to be closely related to the rate of oxygen uptake and to the degree of aromatization. As shown in Figures 1 and 5, the changing trend of AI shows a retention stage followed by an acceleration stage, whereas the oxygen content increases constantly despite the decrease in the rate; this indicates that there is a critical oxygen content that is the prerequisite for further aromatization reaction. This result is different from Warner's model, in which it is proposed that the reactions with oxygen are not involved in the prefatory reactions.[9] In this work, it can be seen that the uptake of oxygen occurs at the beginning of the whole stabilization reactions. Once the oxygen content reaches the critical value, an intense aromatization reaction will spread extensively. A high degree of aromatization leads to the formation of a dense and rigid aromatic structure

TABLE II
WAXD Data Based on Figure 4

Stabilization time (min)	Intensity at $2\theta = 17^\circ$ (CPS)	Intensity at $2\theta = 25.5^\circ$ (CPS)	FWHM at $2\theta = 17^\circ$ (°)	Crystallite size (nm)	AI (%)
0	2922	0	0.9802	8.11	0
20	994	164	0.8120	9.79	14.2
40	713	176	0.9061	8.77	19.8
60	626	175	1.0069	7.89	21.8
80	499	198	1.1417	6.89	28.4
100	90	148	3.3682	2.36	62.2
120	113	191	—	—	62.8

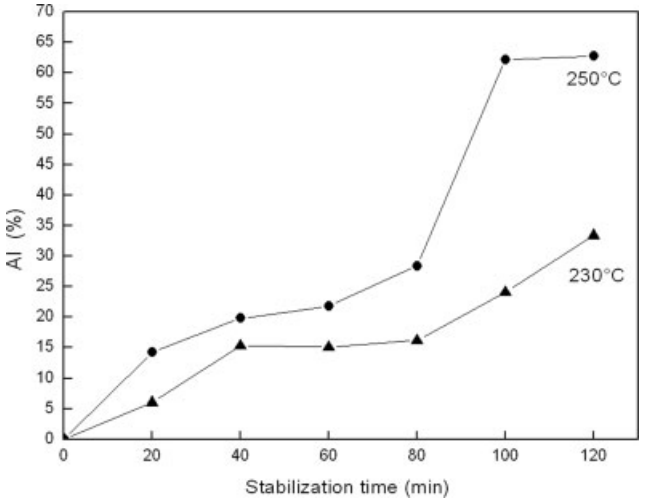

Figure 5 Changes in AI as a function of the stabilization time at different temperatures.

that depresses the inward diffusion of oxygen. Therefore, a skin–core morphology forms with a great difference in the oxygen content and chemical structure between the skin and the core.

As shown in Figure 2, the initial rate of oxygen uptake is very fast at 250°C, so it takes a short stabilization time before the oxygen content reaches the critical value. Subsequently, aromatization reactions are activated rapidly. As a result, a skin–core morphology can be observed clearly in the fibers treated for only 60 min. With time increasing, oxygen accumulates in the skin of the fiber but hardly penetrates to the core, causing the interface to become more and more distinct. At a low temperature such as 210 or 230°C, the rate of oxygen uptake is slow (as shown in Fig. 2), so it takes a long time for the oxygen content to reach the critical value. Thus, a faint skin–core morphology forms in stabilized fibers until they are treated for 120 min.

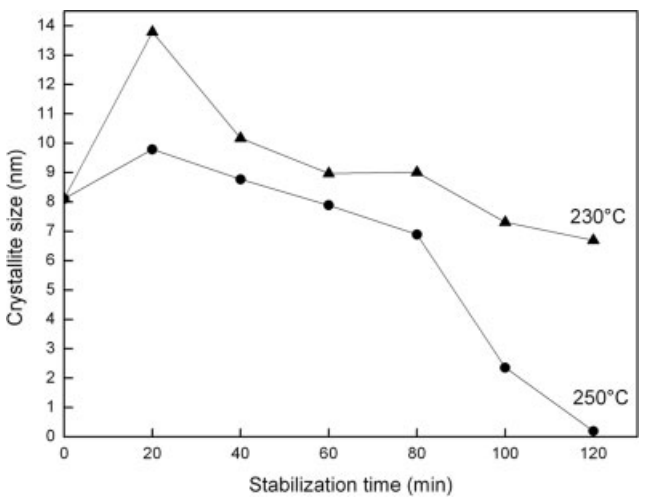

Figure 6 Changes in the crystallite size as a function of the stabilization time at different temperatures.

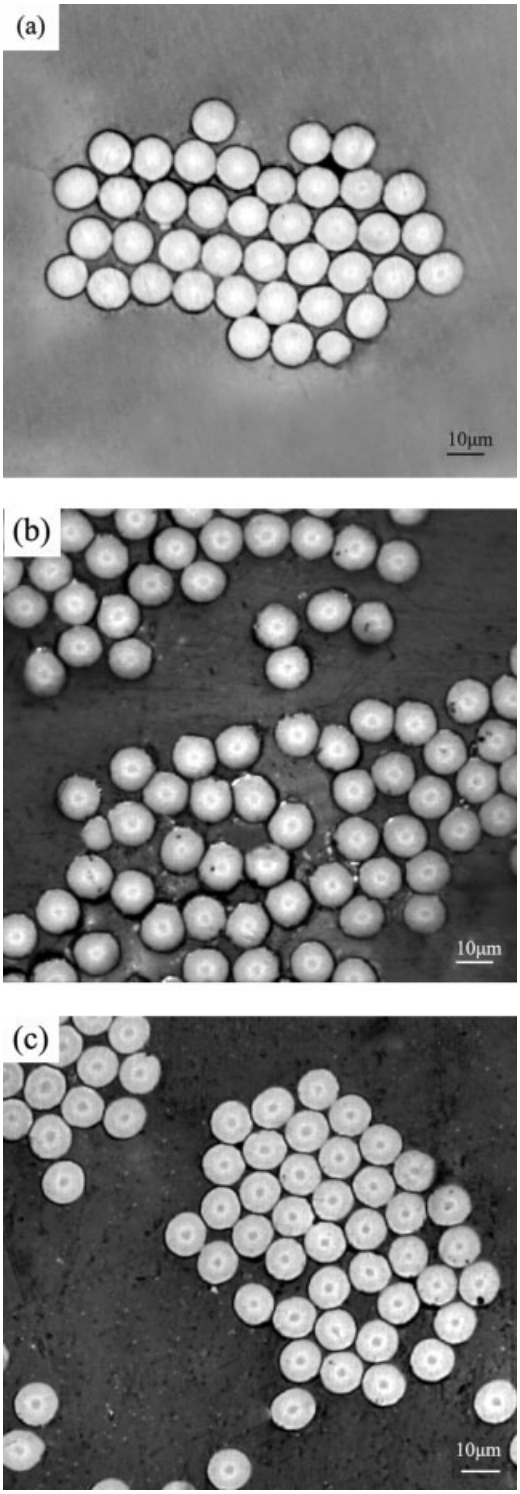

Figure 7 Cross-section morphologies of stabilized fibers treated for various durations at different temperatures. (a) 120 min at 230°C, (b) 60 min at 250°C, and (c) 120 min at 250°C.

Accordingly, the formation of a dark hole in the center of stabilized fibers B1 and B2 is likely due to the absence or low content of oxygen. Without cross-

links with oxygen, the structure of the cream-colored core is unstable and cannot withstand the accumulated heat generated from exothermal reactions, so it fuses into a hole. For confirmation, high-magnification images were obtained by scanning electron microscopy (SEM), as shown in Figure 8(a,b). From the fracture texture of Figure 8(a), some deformed fibrils at the rim of the hole indicate a ductile fracture feature, whereas the comparatively smooth plane at the shell shows a brittle fracture feature. As shown in Figure 8(b), the radially shaped texture from the hole outward shows that the hole is the origin of the fracture. The difference in the fracture mechanisms of the skin and core gives better evidence for the heterogeneous morphology in stabilized fibers.

Onion-like model for stabilized fibers

On the basis of the mechanism of skin–core morphology discussed previously, a rough structural model may be established for the isothermally stabilized fibers, as shown in Figure 9. The dark shade represents the skin with high oxygen content and high AI. The light-colored part represents the core with low oxygen content and low AI. As for the PAN precursor fibers in this article, the skin thickness of isothermally stabilized fibers strongly depends on the temperature. The higher the temperature is, the lower the skin area is. With the temperature increasing, the gradient in the oxygen content and AI between the skin and core will become steeper. Further research will be carried out on the diffusion coefficient of oxygen at a specified temperature and determine the diffusion dynamics.

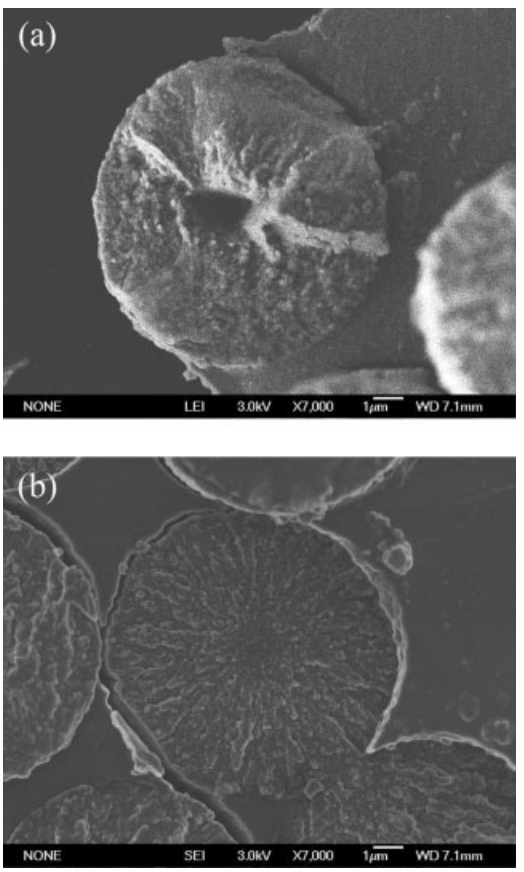

Figure 8 SEM fracture texture of stabilized fibers heat-treated at 250°C for 120 min.

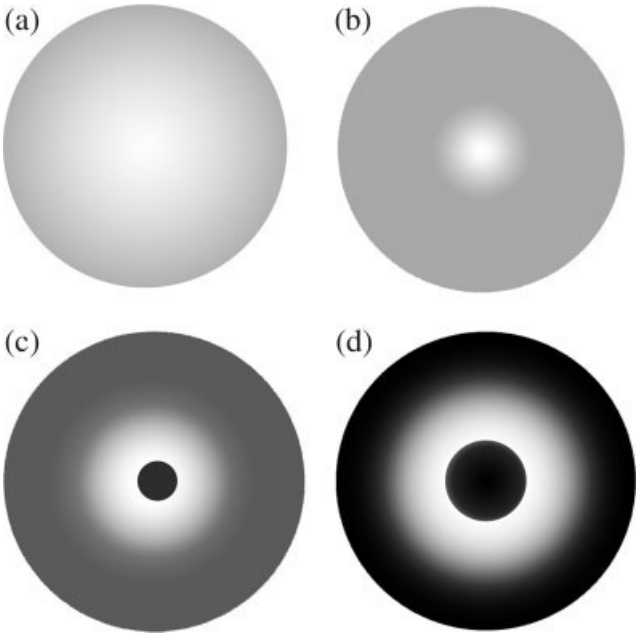

Figure 9 Model for the stabilized fibers treated at various isothermal temperatures: (a) T_1, (b) T_2, (c) T_3, and (d) T_4 ($T_1 < T_2 < T_3 < T_4$).

Compared with the isothermal stabilization method for laboratory research, increasing the temperature stepwise in a continuous stabilization line is more efficient in industrial production.[18,19] If PAN fibers pass sequentially through a series of furnace zones with stepwise increasing temperatures, then the cross-section morphology of the resultant stabilized fibers will resemble an onion, as shown in Figure 10, with a gradient distribution of oxygen and AI. The difference between the outer layer and the inner layer may be varied by the presetting of the stepwise temperatures and the dwell time in each temperature zone. A large difference between adjacent temperatures will lead to a high gradient in the composite and structure in stabilized fibers, whereas a process that prolongs the stabilization time at a low temperature and shortens the time at a high temperature is conducive to obtaining a homogeneous structure. It should be noted that no skin–core morphology has been observed in the stabilized fibers of a small titer in our examination, and this indicates that reducing the titer of PAN precursor fibers may be the best way to eliminate the skin–core morphology in stabilized fibers.

Figure 10 Model for the as-stabilized fibers treated with stepwise increasing temperatures.

CONCLUSIONS

The oxygen uptake, AI, and cross-section morphology of stabilized fibers isothermally treated at various temperatures have been analyzed. The changes in the oxygen content have a parabolic relationship with time. The higher the stabilization temperature is, the higher the rate of oxygen uptake and aromatization is, but the more rapidly the rate of oxygen uptake decreases. Some critical oxygen content is the prerequisite for the intense and extensive aromatization reaction. However, a high aromatization degree will in turn suppress the diffusion of oxygen. As a result, a skin–core morphology may form because of the initially rapid oxygen uptake and the subsequent intense aromatization. A fracture mechanism of ductile fracture in the core but brittle fracture in the skin has been observed by SEM. On the basis of the examination of isothermally stabilized fibers, an onion-like model has been proposed for stabilized fibers treated by stepwise increasing temperatures.

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